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KURITA WATER INDUSTRIES LTD.

4-7, Nishi-Shinjuku 3-chome, Shinjuku-ku, Tokyo 160-8383, Japan

Contributors

- Akeboshi, Takashi
- Ano, Shinji
- Fujita, Saburo
- Fukuda, Mitsugu
- Fukuda, Sadao
- Fuwa, Masaaki
- Hasegawa, Teruichi
- Hashimoto, Akio
- Hashimoto, Masanori
- Hashizume, Jun
- Hayashi, Shiro
- Hirano, Akihide
- Hiroki, Toshiyuki
- Hirota, Miki
- Horiuchi, Masahiro
- Ishida, Toshio
- Ishitsuka, Kaoru
- Iwasaki, Masaji
- Kaneko, Ichiro
- Kataoka,Shunji
- Kawaguchi, Hiromi
- Kawamura, Fumio
- Kiuchi, Kouji
- Kobayashi, Kenji
- Kobayashi, Norimasa
- Kubo, Sotoo
- Kume, Hiroyuki
- Kunihara, Hiroshi
- Majima, Kohei
- Maruoka, Reiji
- Matsui, Hidehiro
- Miyata, Koichi
- Mizuno, Kyousuke
- Mochizuki, Fujiaki
- Morikawa, Ryozo
- Morinaga, Hideo
- Morita, Nobuhiko
- Nakagawa, Jiro
- Nakahara, Toshitsugu
- Nakayama, Haruo
- Nikaido, Kiyoshi
- Nishi, Hidetaka
- Ogasawara, Akiyoshi
- Ooi, Yasuhiro
- Ono, Yuichi
- Ooya, Youichi
- Sakuma, Shigeru
- Sato, Takatoshi
- Sato, Yukinobu
- Sugi, Takumi
- Suzuki, Takashi
- Tawara, Kenji
- Takahashi, Tomoyuki
- Takenaka, Hiroyuki
- Takenobu, Yoshiki
- Tamagawa, Shinya
- Taya, Shiro
- Toki, Tsuyoshi
- Tsuneki, Takao
- Uchida, Takahiko
- Ueda, Fumihiro
- Uehara, Katsunori
- Uozumi, Akihiko
- Watanabe, Minoru
- Watanabe, Takashi
- Wakamatsu, Mineo
- Yajima, Yasuo
- Yamada, Sadao
- Yamamoto, Kazumasa
- Yashiro, Takemoto
- Yazawa, Yukio
- Yoshihara, Katsuji

Preface

In commemoration of our company's 50th Anniversary, it gives us great pleasure to share our accomplishments with our supporters and customers, through the second English edition of our handbook, the "KURITA HANDBOOK OF WATER TREATMENT."

Founded in 1949, KURITA WATER INDUSTRIES LTD., has become a leader in the field of water and environmental management. However, we are not satisfied with simply providing water and sewage treatment facilities, water and process treatment chemicals, and related operational management equipment and maintenance services. We are also expanding our efforts to improve the global environment, through such processes as purification of contaminated soil, detoxification of dioxins, reduction and recycling of excess activated sludge, and immobilization of heavy metals in fly ash produced from waste incineration facilities.

In the area of water treatment and process treatment chemicals, we have made technological improvements to ensure efficient operation and contribute to water and energy conservation in various water systems. We have also addressed critical issues surrounding water system treatment, such as the reduction of environmental impact through the development of non-phosphorus boiler compounds, non-hydrazine oxygen scavengers, and low- or non-phosphorus cooling water treatment chemicals. In addition, we have focused on the important task of ensuring work safety and chemical-handling safety. Our efforts have been rewarded with ISO 9001 and ISO 14001 certifications. We believe that these certifications are proof of our commitment to quality assurance for our products, and to environmental preservation and improvement.

In order to introduce some of our company's innovative technology and accomplishments in the field of water treatment chemicals to a global readership, we published the first English edition of our handbook in 1985. Since then, we have continued working to develop more advanced technology and improved products. In this second edition, we have described our technologies and products in as much detail as possible, to ensure that we provide our readers with useful data.

It is reasonable to assume that tomorrow's technological advancements will proceed at a more dizzying pace than ever. Therefore, intend to continue to update our handbook, which would otherwise quickly become obsolete. This is the primary reason we have turned to electronic publishing and have created this handbook in CD-ROM format. As we plan to revise it once every few years, we are confident that this CD-ROM will provide our readers with the most up-to-date information.

Our company philosophy is, "Study the properties of water and master them, and we will create an environment in which nature and man are in harmony." We are committed to developing advanced technology and products that will contribute to the betterment of our society.

In closing, we would like to express our appreciation and gratitude to the writers and editors responsible for creating this comprehensive handbook. We hope that this handbook will serve as a source of useful information for its readers.

Takahide Santo

President

Takahide Santo

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1. Introduction to Water Treatment

Water has been an important natural resource of the Earth and has been essential for the existence of all living things. The intimate relationship between the human society and water is symbolized by the fact that almost all ancient civilizations originated on the banks of large rivers.

In the present, water is still an essential natural resource for keeping the health and pleasant lives of people, and for making valuable natural and industrial products.

On the other hand, social problems relating to water, such as the shortage of water resources and the occurrence of water pollution, have long been at issue and they are still remaining as important problems to be solved. Those problems have been occurred as the results of the increase in population, the concentration of population in big cities, the development of industries and so on. This fact is advising us to harmonize our life-styles with the natural environment and to realize the sustainable development.

To solve above problems and to harmonize the human society with the natural environment, the scientific understanding of the nature of water and the development of water treatment technologies may play an important role. The research and development in this field require not only the basic knowledge of chemistry, physics, microbiology, metallurgy, etc., but also broad knowledge of applied science, such as chemical engineering, mechanical engineering, electrical engineering and electronics.

The water treatment methods are generally divided into chemical, mechanical and microbiological ones. This handbook describes the chemical treatment methods mainly. This chapter introduces the development and recent trend of water treatment chemicals, the features of water, etc.

1.1 Necessity of Water Treatment

Natural fresh water includes suspended solids, microorganisms, dissolved salts (ions) and dissolved gasses. Those substances in water cause various problems in systems using water.

In the case of drinking water, suspended solids and microorganisms must give a bad influence on the human health.

In cooling water systems and boiler systems, hard soluble matter, such as calcium carbonate, may deposit as a scale on the heat transfer surfaces of heat exchangers and boilers. Then their thermal efficiencies are reduced by the scaling. Dissolved oxygen causes the corrosion of metals composed of those systems and shortens their service lives.

Microorganisms may grow and form slime (biofouling) on heat exchanger tube surfaces, etc. The slime adhesion reduces the thermal efficiencies of heat exchangers and sometimes causes an underdeposit corrosion or microbiologically influenced corrosion (MIC) of metals.

Even when water of same quality is used, the kinds and the degrees of problems caused by water vary depending on the usages of water and the operational conditions of systems.

Therefore, the application of a suitable water treatment program is inevitable to prevent problems caused by water. The selection of the program must be carefully carried out considering the water quality, the usage of water, the operational conditions of an aimed system and so on.

1.2 Development and Recent Trends of Water Treatment Chemicals

The development of water treatment chemicals after 1945 in Japan is divided into four stages.

The first stage is 1945 to 1960, the era of the reconstruction and the preparation for the coming high economic growth. In this stage, Japanese economic was expanded by the growth of primary and light industries mainly. Water treatment chemicals had been developed in the field of boiler water treatment and the chemical cleaning of boilers mainly. The application of corrosion inhibi tors and biocides in cooling water systems, and polymer flocculants was started in this era.

The second stage is 1960 to 1972, the era of the high economic growth. Japanese iron and steel industry, petroleum refining and petrochemical industry, paper and pulp industry, etc., had been remarkably developed in this era. As those industries required a large amount of water for their production processes and utility plants, they were called the water consuming industries. Large scale thermal power plants had been constructed because the rapid growth of industrial and personal electricity consumption. Those plants also consumed a large amount of water.

The growth of those industries had caused a water shortage and had promoted the recycling of water. Therefore, water treatment chemicals had been remarkably developed in their cost performances and contributed to rise the water recycling rate.

On the other hand, the development of industries caused severe water and air pollution problems. Accordingly, in the latter half of this era, the countermeasures for those problems, such as the enforcement of the Water Pollution Control Law in 1970, had been applied. In the field of water treatment chemicals, the conversion of chromate based corrosion inhibitors to non-chromate ones, etc., had been carried out in this era.

A topic for the development of water treatment chemicals in this era was the development and application of polymer based dispersants effective for calcium phosphate scaling in cooling water systems. The polymers realized phosphate based non-chromate cooling water treatments.

The third stage is 1973 to late 1980's. The 1973 was the year of the first oil crisis. After the oil crisis, Japanese industries had paid large efforts to develop technologies for saving energy. In the field of water treatment chemicals, fouling control chemicals and the related technologies had been developed to contribute for the energy saving.

The fourth stage is after late 1980's to the present, it is the era of health and safety. Until the end of the third stage, most of technical targets for the development of water treatment chemicals, such as the maximization of the cost performance, the contribution to the water and energy saving, and the minimization of water pollution, had been realized. In the fourth stage, a new and important concept has been added to the requirements for the function of water treatment chemicals. It is an assurance of health and safety in the all processes of producing, transporting, storing, handling, using and disposing water treatment chemicals. Even until the end of third stage, careful considerations for the health and safety in the application of water treatment chemicals had been taken, however, in the present, more sufficient cares are requested for the health and safety in the field of water treatment chemicals. This kind of trend is symbolized by the popularization of "Responsible Care" and "Environmental Management System" activities.

The requirements for the current water treatment chemicals are summarized as follows:

1.2.1 Reduction of Total Cost Performance

Conventionally, the word, "cost performance", means the chemical cost for obtaining an aimed treatment effect, such as the cost of a corrosion inhibitor for reducing the corrosion rate of carbon steel below 10 $mg/dm^2 \cdot day$ (below 0.05 mm/y).

In the present, the word, "total cost performance", is used to express the comprehensive meaning.

Water treatment chemicals which reduce the total cost performance are required by users. For example, in the case of an open recirculating cooling water system, the total operation cost is composed of following items:

① Chemical cost,
② Water cost,
③ Power (electricity) cost,
④ Personnel expenses,
⑤ Inspection and maintenance cost of the system,
⑥ Depreciation cost of the system,
⑦ Others.

The performance of chemical water treatment program gives a large influence on those costs. Moreover, the efficiencies of production processes may be influenced by the thermal efficiencies of the water cooled heat exchangers.

Therefore, to correctly evaluate "the total cost performance" of the chemical treatment program, all costs relating the operation of the cooling water system and the production processes have to be analyzed. The chemical cost generally occupies a very small part of total cost relating to the cooling water system and the process operation. Therefore, the application of an advanced water treatment program considerably reduces the total operation cost of the factory, even if the chemical cost becomes higher than that of a conventional treatment.

1.2.2 Minimized Influence on the Environment

Most of water treatment chemicals are finally discharged into the environment through or not through wastewater treatment facilities. Therefore, the discharged water quality must satisfy the local regulations for the effluent.

In the present, not only the discharge of toxic substances into the environment is severely regulated, but also the discharge of nontoxic substances, such as phosphates, is regulated for preserving the earth environment.

These trends have promoted the development of safer water treatment chemicals and have realized the use of non-phosphorous boiler compounds, all organic cooling water treatment chemicals and so on.

1.2.3 Assessment of Chemical Safety

The safety of water treatment chemicals must be assured through their life cycles, that is, through their manufacturing, transporting, storing, handling, using and disposing.

Therefore, many kinds of toxicity tests for the raw materials and products have been carried out to assure the safety of water treatment chemicals.

Table 1.1 summarizes the kinds of typical toxicity tests applied for water treatment chemicals.

1.2.4 Contribution to Water Conservation

Economic developments and the concentrations of population into big cities have caused the shortage of water resources in the world. Various measures have applied to save water. Typical water saving methods are as follows:

① The use of cooling tower systems substituting for once through cooling water systems,
② Increase of the cycles of concentration in cooling tower systems,
③ Recycling of boiler condensate and process condensate,
④ Recycling of treated sewage and industrial wastewater,
⑤ Cascading of a discharged water with the better quality to the other processes,
⑥ Utilization of water with a worse quality.

Those water saving methods more or less deteriorate the water quality using in an aimed system or process, and accelerate the occurrence of problems caused by water.

Therefore, the popularization of those water saving operation requires the improvement in the performance of water treatment chemicals to prevent the problems. The combined treatment of chemical and mechanical treatments have often applied for water saving.

1.2.5 Contribution to Energy Conservation

Because Japan is heavily dependent on imported crude oils, the energy conservation has become a highly important subject after the oil crisis in 1973. The chemical water treatment technology has been also developed and improved to contribute the energy conservation.

In boiler systems, the development of polymer based dispersants (scale inhibitors) contributes to minimize the fuel consumption by preventing the scaling on the heating tubes.

In cooling water systems, the development of

Table 1.1 Kinds of toxicity tests for water treatment chemicals

Items of test		Test methods
Contents of toxic substances as impurities		Chemical analysis of As_2O_3, T-Hg, T-Cr, Cd, Pb, CN, etc.
Acute toxicity	Oral	LD_{50} of mouse or rat
	Inhalation	LD_{50} of mouse or rat
Topical irritation	Skin irritation	Draize test
	Eye irritation	Draize test
Biodegradation		MITI method (biodegradation test using activated sludge)
Acute fish toxicity		LD_{50} of fishes
Sensitization		Patch test using guinea pig
Mutation		Ames test
		Mammalian cell gene mutation assay
Subacute toxicity		NOAEL of mouse or rat

fouling control agents, such as scale inhibitors, dispersants and biocides, effectively conserves energies using in cooling water systems and in production plants to be cooled by keeping heat exchangers from the fouling.

In the field of wastewater treatment, the progress of dewatering agents for organic sludges from sewage processing plants remarkably reduces the fuels using in the cake incineration plants by reducing the moisture contents of dewatered cakes.

1.2.6 Realization of Long Time Continuous Operation of Petroleum Refining and Petrochemical Plants

Formerly, petroleum refining and petrochemical plants were generally shut down once a year for the inspection and maintenance. However, the 2 to 5 years continuous operation of those plants has been realized and become popular by the development of corrosion inhibitors and fouling control agents for the both of cooling water side and process fluid side.

The continuous operation increases the production of those plants and reduces the maintenance cost of plants.

1.3 Science of Water

1.3.1 Amount of Water

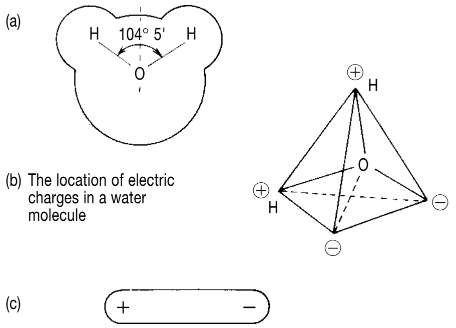
A tremendous amount of water is present on the earth. The total amount is roughly 1.4 billion km^3 as shown in Table 1.2. Around 96.5% of that is seawater and fresh water occupies around 2.5%. Around two-third of fresh water is icebergs and glaciers. Available fresh water for our daily life, industries and so on is only 0.8% of the total amount of water, such as ground water, river water and lake water.

Japanese annual rain fall is around 1,700 mm and 650 billion m^3 on the Japanese land area of around 378 thousand km^2. However, the available amount of water is around 160 billion m^3 (25%) and most of that flows into the sea, permeates into the ground or evaporates into the air.

1.3.2 Molecular Structure of Water

The molecular formula of water is expressed as H_2O. Figure 1.1 (a) shows the molecular structure of water. The atomic distance between the H and O is 0.96 Å, and the angle of H-O-H is 104° 5'. A water molecular has four electrical charges of two positive and two negative ones as shown in Figure 1.1 (b). As the four electrical charges occupy symmetrical positions, a water molecule behaves like a bar magnet as shown in Figure 1.1 (c), that is, it has the dipole moment.

Because of the water molecule structure shown in Figure 1.1 (b), a water molecule has four arms



(b) The location of electric charges in a water molecule

Fig. 1.1 Molecular structure of water

Table 1.2 Amount of water on the earth

Kind of water	Amount (10^6 km^3)	Distribution ratio (%)	
Seawater	1,338	96.53	
Fresh water	35.03	2.53	
(Icebergs and glaciers)	(24.06)	(1.74)	[68.7]
(Groundwater and soil moisture)	(10.85)	(0.78)	[31.0]
(Air moisture)	(0.01)	(0.0007)	[0.03]
(Lake and marshes)	(0.108)	(0.08)	[0.29]
(Rivers)	(0.002)	(0.00015)	[0.006]
Others	12.97	0.94	
Total	1,386	100	

[ ]: Distribution ratio against the total amount of fresh water

making hydrogen bonds. The hydrogen bond is a kind of atomic bond which a hydrogen atom interposes, like O-H··O, O-H··N, N-H··O and so on. Thus a water molecule combines the other water molecules, alcohols, amino acids, etc. Figure 1.2 shows the combination of water molecules by their hydrogen bonding.

These dipole moment and hydrogen bond of water give very unique properties to water comparing with the other organic and inorganic substances.

1.3.3 Properties of Water

Water is a colorless, tasteless and odorless transparent liquid at ambient temperature. Table 1.3 shows the properties of water. Table 1.4 shows the compared thermodynamic properties of water, ethylalcohol and acetone.

Those thermodynamic values generally become larger as the molecular weight becomes larger. However, water with the smallest molecular weight has the largest value among three substances in Table 1.4. This reason is explained by the power of hydrogen bond. Water has the strongest hydrogen bonding power and combines with the other water molecules to increase the apparent molecular weight. Ethylalcohol also has a little stronger hydrogen bonding power than that of acetone.

Water requires much more heat to increase the temperature, to be boiled and to be evaporated comparing with the other substances. In other words, water absorbs much heat and is a good heat transfer medium.

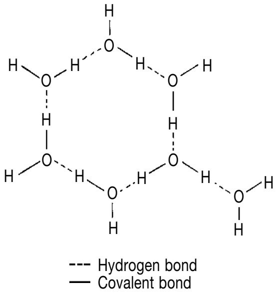


Fig. 1.2 Combination of water molecules by their hydrogen bondings

The latent heat of fusion or vaporization of water is very large. Figure 1.3 shows the sensible heat and latent heat of water for changing the temperature and phase. The heat of fusion at 0° C and the heat of evaporation at 100° C are around 80 kcal/kg and around 540 kcal/kg respectively.

This large latent heat of water is utilized for various industrial and air-conditioning processes, etc. A typical example of such utilization is the recooling of circulation water by the partial evaporation in a cooling tower. The evaporation of the 1% of circulation water reduces the temperature of remaining 99% water by around 5.8° C at an ambient temperature.

As water has the dipole structure, water dissolves most of inorganic substances and some

Table 1.3 Properties of water

Specific gravity (20° C)	0.9982
Melting point (° C)	0.00
Boiling point (° C)	100.00
Vapor pressure (mmHg)	17.535
Temperature giving the maximum density (° C)	4
Dielectric constant (20° C)	82
Refractive index (20° C)	1.33300
Viscosity (20° C) (cp)	1.009
Specific heat (0° C) (cal/g·° C)	1.007
Heat of fusion (kcal/mol)	1.435
Heat of vaporization (100° C) (kcal/mol)	9.719
Ion product (25° C)	1×10^{-14}
Heat of formation (20° C) (kcal/mol)	68.35
Dipole moment (gas) (cgs x 10^{18})	1.84
Density (100° C) (g/ml)	0.958
Surface tension (100° C) (dyne/cm)	58.9

Table 1.4 Thermodynamic properties of water, ethylalcohol and acetone

Substance	Chemical formula	Molecular weight	Boiling point (° C)	Heat of vaporization (cal/g)	Specific heat (0° C) (cal/g·° C)
Water	H_2O	18	100	539.6	1.007
Ethylalcohol	C_2H_5OH	46.07	78.5	204.0	0.536
Aceton	CH_3COCH_3	58.08	56.5	124.5	0.506

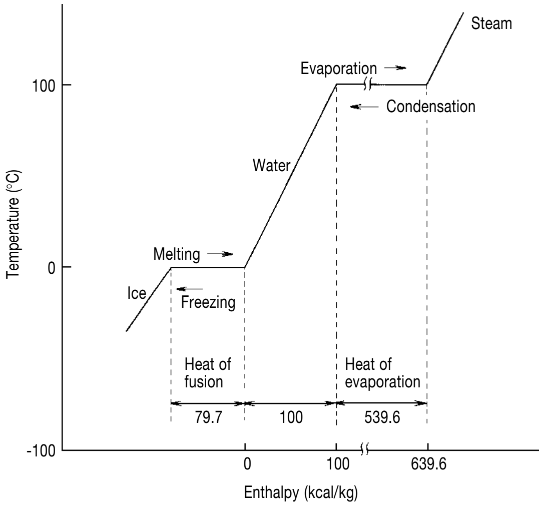


Fig. 1.3 **Sensible heat and latent heat of water for changing the temperature and phase**

organic substances having ionic bonds by dissociating and hydrating them as shown in Figure 1.4. Some organic compounds without ionic bonds, such as sugar, dissolve into water if their molecular sizes fit in the spaces between water molecules.

1.4 Basic Chemistry for Water Treatments

1.4.1 Units Constituting Chemical Substances

(1) Atoms and elements

Atom is the minimum unit of substances and is constituted of an atomic nucleus and electrons. The atomic nucleus is consist of protons and neutrons. Electrons orbit around the atomic nucleus at an extremely high speed. The atomic nucleus has a positive electrical charge and electrons have negative electrical charges. Thus the whole electrical charge of atom becomes neutral.

Atoms show the different properties according to their numbers of protons or electrons. An atom having a specified number of protons is named as an element. At present, the 92 kinds of natural elements and the 11 kinds of artificially produced elements are identified.

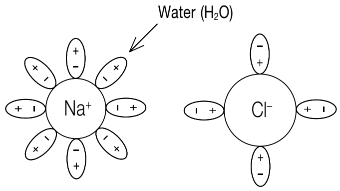


Fig. 1.4 **Dissolution of sodium chloride by water and the hydration**

Figure 1.5 shows a model of a hydrogen atom, the smallest atom. The diameter of the atom is approximately 10^{-8} cm and the diameter of the atomic nucleus is 10^{-12} to 10^{-13} cm.

Electrons regularly move around the atomic nucleus. Since an electron orbit admits a specified number of electrons, the number of orbits increases as the number of electrons increases. Those electron orbits are named as K, L, M and N orbits from near side to the nucleus. Figure 1.6 shows the each electron orbit and the number of acceptable electrons.

Table 1.5 shows a periodical table of elements, which arranges 103 kinds of elements according to their similarities in the properties. The group of elements shown on the right-hand corner of the table, such as helium and neon, are the most chemically stable and are called the inert gasses.

(2) Molecules

A molecule is the smallest unit particle of a substance not losing the characteristics. The mol

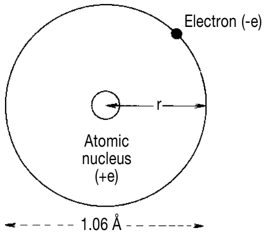


Fig. 1.5 **An atomic model of hydrogen atom**

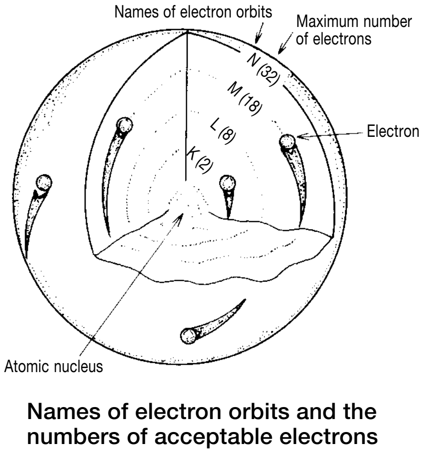


Fig. 1.6 **Names of electron orbits and the numbers of acceptable electrons**

Table 1.5 Periodic table of the elements

Representative Elements *s* block | Transition Elements *d* block | Representative Elements *p* block | Inert gases

Atomic No.
Symbol
Atomic Wt.

Periods	IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIII	VIII	VIII	IB	IIB	IIIA	IVA	VA	VIA	VIIA	0
1	+1 1 H 1.0079																	2 He 4.003
2	+1 3 Li 6.941	+2 4 Be 9.012											+3 5 B 10.81	+4 6 C 12.011	+5 +3 7 N −3 14.007	8 O −2 15.999	9 F −1 18.998	10 Ne 20.18
3	+1 11 Na 22.99	+2 12 Mg 24.30											+3 13 Al 26.98	+4 14 Si 28.08	+5 +3 15 P −3 30.97	+6 +4 16 S −2 32.06	+7 +5 +3 +1 17 Cl −1 35.45	18 Ar 39.95
4	+1 19 K 39.10	+2 20 Ca 40.08	21 Sc 44.96	22 Ti 47.90	23 V 50.94	+6 +3 24 Cr 52.00	+7 +4 +2 25 Mn 54.94	+3 +2 26 Fe 55.85	+3 +2 27 Co 58.93	+3 +2 28 Ni 58.71	+2 +1 29 Cu 63.55	+3 30 Zn 65.38	+3 31 Ga 69.72	+4 +2 32 Ge 72.59	+5 +3 33 As 74.92	+6 +4 34 Se −2 78.96	+7 +5 +3 +1 35 Br −1 79.90	36 Kr 83.80
5	+1 37 Rb 85.47	+2 38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc 98.91	44 Ru 101.07	45 Rh 102.91	46 Pd 106.4	+1 47 Ag 107.87	+2 48 Cd 112.40	+3 49 In 114.82	+4 +2 50 Sn 118.69	+5 +3 51 Sb 121.75	+6 +4 52 Te −2 127.60	+7 +5 +3 +1 53 I −1 126.90	54 Xe 131.30
6	+1 55 Cs 132.91	+2 56 Ba 137.34	57 La 138.91	72 Hf 178.49	73 Ta 180.95	74 W 183.85	75 Re 186.2	76 Os 190.2	77 Ir 192.22	78 Pt 195.09	79 Au 196.97	+2 +1 80 Hg 200.6	+3 +1 81 Tl 204.4	+4 +2 82 Pb 207.2	+5 +3 83 Bi 209.0	+6 +4 84 Po (210)	85 At (210)	86 Rn (222)
7	+1 87 Fr (223)	+2 88 Ra 226.0	89 Ac (227)	104 Ku* 	105 Ha* 													

Inner Transition Elements *f* block

Lanthanum Series	58 Ce 140.12	59 Pr 140.9	60 Nd 144.24	61 Pm (147)	62 Sm 150.4	63 Eu 151.96	64 Gd 157.2	65 Tb 158.93	66 Dy 162.50	67 Ho 164.93	68 Er 167.26	69 Tm 168.93	70 Yb 173.04	71 Lu 174.97
Actinium Series	90 Th 232.0	91 Pa 231.0	92 U 238.0	93 Np 237.0	94 Pu (242)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (247)	99 Es (254)	100 Fm (253)	101 Md (256)	102 No (254)	103 Lr (257)

Mass numbers of the most stable or most abundant isotopes are shown in parentheses.
The elements to the right of the bold lines are called the nonmetals and the elements to the left of the bold line are called the metals.
Common oxidation numbers are given for the representative elements and some transition elements.
* Kurchatovium and Hahnium are tentative names for these elements.

ecule is composed of an aggregate of elements. The concept of molecule was proposed by Avogadro to explain the law of gaseous reaction in 1811. Avogadro predicted that all gases with the same volumes under the same pressure and temperature included the same number of molecules. In the present, the Avogadro's number, that is the number of molecules in one gram-molecule of a gas, is defined at 6.03×10^{23}.

For instance, one gram-molecule of water, the 18 g of water, includes the 6.03×10^{23} of molecules.

1.4.2 Chemical Reactions and Chemical Bonds

A chemical reaction is a phenomenon that a substance changes to another substance by a interaction between its molecules or with the other substances. Most chemical reactions generally proceed to produce more chemically stable substances. Atoms composed of a molecule are bonding each together and this bonding is changed by a chemical reaction. The manners of chemical bonding between atoms largely influences on the chemical stability of each substance.

Table 1.6 shows the electron configurations and the valences of the elements in the first to third periods of the periodic table. The electron configuration and the valence relate to the manner of chemical bonding between atoms.

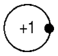
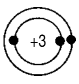
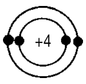
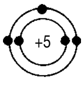
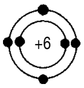
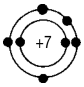
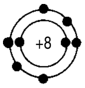
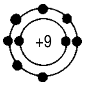
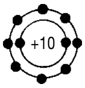
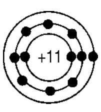
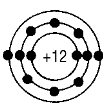
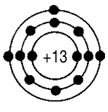
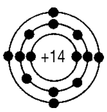
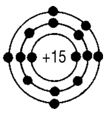
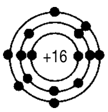
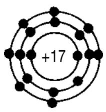
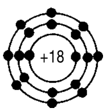
The manners of chemical bonds are classified into the following four categories:

(1) Covalent bond

In the case of a hydrogen molecule, H_2, two hydrogen atoms are combined by owing two electrons jointly on their electron orbits. This type of chemical bond is called the covalent bond. Like inert gasses, atoms that their outer shells are fully occupied by their electrons are chemically stable.

Therefore, the atoms of elements except the inert gasses are tend to own their electrons jointly on their outer shells to chemically stabilize them selves.

Table 1.6 Electron configurations and valences of the principal elements

Group / Period	I	II	III	IV	V	VI	VII	O
First period	 H							 He
Second period	 Li	 Be	 B	 C	 N	 O	 F	 Ne
Third period	 Na	 Mg	 Al	 Si	 P	 S	 Cl	 Ar
Valence	+1	+2	+3	+4 −4	+5 −3	+6 −2	+7 −1	0
Oxide Hydride	R_2O —	RO —	R_2O_3 —	RO_2 RH_4	R_2O_5 RH_3	RO_3 RH_2	R_2O_7 RH	— —

(2) Ionic bond

Sodium has one electron on the outer shell. As the number of acceptable electron of the outer shell is eight, it tends to give one electron to the other element to stabilize itself. As the result, the number of protons exceeds the number of electrons by one and sodium becomes a monovalent cation.

In the case of chlorine, it has seven electrons in the outer shell. Then it tends to accept one electron from the other element and becomes a monovalent anion.

Thus, a sodium and a chlorine combine together by electrostatic force to form a sodium chloride. This type of chemical bond is called the ionic bond. Figure 1.7 shows the ionic bond between a sodium and a chlorine to form the sodium chloride.

(3) Metallic bond

In a metal crystal, one metal atom is surrounded by twelve to fourteen atoms. For example, one valence electron of a sodium atom relates to the bonding with surrounding fourteen sodium atoms. Therefore, the valence electron is not confined in one bonding and shows the property of a free electron. This bond is called the metallic bond.

The high electric conductivities of metals are caused by the presence of not-confined valence electrons.

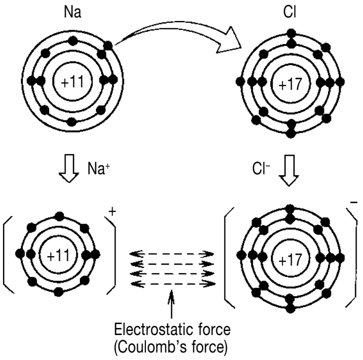


Fig. 1.7 Ionic bond of NaCl

(4) Coordination bond

The coordination bond is the combination of a covalent bond and an ionic bond. This bond between A and B atoms is generally expressed as follows:

$$A^+ - B^- \text{ or } A \rightarrow B$$

For example, in case of trimethylamine oxide, $(CH_3)_3NO$, the N having three valence electrons can not combine with three CH_3 and one O by covalent bonds only. Therefore, the one electron of the N moves to the O and forms one covalent bond. As the result, the N and O have a positive and a negative electrical charges respectively. This bond is expressed as follows:

$(CH_3)_3N^+ - O^-$

1.4.3 Chemistry of Aqueous Solution

(1) Properties of water as a solvent

When a substance dissolves into a liquid, the liquid is called a solvent and the substance is called a solute.

Water easily dissolves many kinds of substances comparing with organic solvents. This property of water is explained by the strong dipole moment. Most of electrolytes dissociate in water and dissolve into water as ions.

Water also dissolves some organic substances, such as sugars and alcohols, because of the special structure of water and its hydrogen bonding force as described in the sections 1.3.2 and 1.3.3.

(2) Dissolution of solutes and the solubilities

The solubility is defined as the maximum amount of a substance (solute) able to dissolve into a given amount of solvent (water) under a specified condition. A solution containing a solute with the same concentration to the solubility is called the saturated solution.

If a solute dissolves into water by exceeding the solubility, it essentially deposits in the water to reduce the concentration up to the solubility.

The solubility of a solute is varied by the change of many factors, such as temperature, pressure and the kinds of substances in the coexistence. As the temperature gives a large influence on the solubility, the solubility is generally expressed with the temperature.

The solubilities of easy-soluble substances in water generally increase as the temperature increases. However, the solubilities of some hard-soluble substances in water reduce as the temperature increases. For example, calcium carbonate deposits as a scale in boiler and cooling water systems because the solubility is reduced by the increase of water temperature.

Table 1.7 shows the solubilities of popular water treatment chemicals at various water temperatures. Figure 1.8 shows the changes in the solubilities of calcium carbonate and calcium sulfates with the change of water temperature.

Gasses also dissolve into water. Table 1.8 shows the solubilities of air, nitrogen, oxygen and carbon dioxide in water at various temperatures.

The dissolving manners of gasses into water are divided into two types. One type is the dissolving as the molecules without chemical reaction, like oxygen and nitrogen. The other type is the dissolving as ions with reactions between water and gasses, like carbon dioxide. Equations (1.1) to (1.3) show the dissolving of carbon dioxide into water.

$$CO_2 + H_2O \leftrightarrows H_2CO_3 \quad\cdots\cdots\cdots \quad (1.1)$$

$$H_2CO_3 \leftrightarrows H^+ + HCO_3^- \quad\cdots\cdots\cdots \quad (1.2)$$

$$HCO_3^- \leftrightarrows H^+ + CO_3^{2-} \quad\cdots\cdots\cdots \quad (1.3)$$

(3) Units of solute concentration

(a) Percentage

When the solute concentration is expressed by percentage, the following three kinds of percentages are generally used:

① weight volume percentage (w/v %),
② weight percentage (w/w %),
③ volume percentage (v/v %).

These three kinds of percentages are calculated from the equations (1.4) to (1.6).

Table 1.7 Solubilities of popular water treatment chemicals

Chemicals	Chemical formula	Temperature (°C)						
		0	10	20	30	40	50	60
Aluminum sulfate	$Al_2(SO_4)_3$	31.2	33.5	36.4	40.5	45.8	52.2	59.2
Sodium chloride	$NaCl$	35.7	35.8	36.0	36.3	36.6	37.0	37.3
Sodium carbonate (soda ash)	Na_2CO_3	7	12.5	21.5	—	48.5	—	46.4
Sodium dihydrogenphosphate	NaH_2PO_4	57.9	69.9	85.2	106.5	—	—	—
Sodium hydrogenphosphate	Na_2HPO_4	1.67	3.6	7.7	20.8	—	80.2	82.9
Sodium phosphate	Na_3PO_4	1.5	4.1	11	20	31	43	55
Sodium hydroxide (caustic soda)	$NaOH$	—	—	109	119	129	146	—
Sodium sulfite	Na_2SO_3	13.9	20	26.9	36	28.0	28.2	28.8

(g/100 g water)

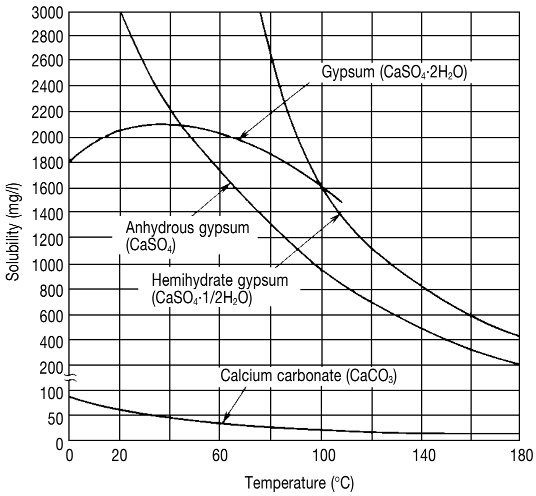


Fig. 1.8 Solubilities of carcium carbonate and calcium sulfates (gypsums)

$$w/v\ (\%) = \frac{W_1}{V_1} \times 100 \quad\cdots\cdots (1.4)$$

$$w/w\ (\%) = \frac{W_1}{W_2} \times 100 \quad\cdots\cdots (1.5)$$

$$v/v\ (\%) = \frac{V_2}{V_1} \times 100 \quad\cdots\cdots (1.6)$$

where

W_1 = weight of solute in the solution (g)
V_1 = volume of the solution (ml)
W_2 = weight of the solution (g)
V_2 = volume of liquid solute in the solution (ml)

In the field of water treatment, the weight volume percentage is most frequently used and the weight percentage follows.

(b) ppm, ppb and ppt

The ppm, ppb and ppt mean parts per million, parts per billion and parts per trillion respectively. These units are correctly expressed as weight/weight or volume/volume based unit.

However, in the field of water treatment, those units are conventionally expressed as weight/volume base units, such as mg/*l* and g/m^3, for dilute aqueous solutions.

(c) Molar concentration (mole/*l*)

The molar concentration is expressed by the number of moles of a solute dissolved in a solution. The molar concentration is calculated from the equations (1.7) and (1.8).

$$NM = \frac{w}{MW} \quad\cdots\cdots (1.7)$$

$$MC = \frac{NM}{V_3} \quad\cdots\cdots (1.8)$$

where

NM = number of mole
w = weight of solute in one liter solution (g)
MW = molecular weight of solute
MC = molar concentration (mole/*l*)
V_3 = volume of solution (*l*)

(d) Normality (equivalent concentration)

The normality (N) is the expressed by the gram equivalent of a solute to be dissolved in one liter

Table 1.8 Solubilities* of air, nitrogen, oxygen and carbon dioxide

Temperature (°C)	Air	N_2	O_2	CO_2
0	2.86	2.31	4.89	17.13
10	2.24	1.83	3.80	11.94
20	1.83	1.52	3.10	8.78
30	1.54	1.32	2.61	6.65
40	1.32	1.16	2.31	5.30
50	1.14	1.07	2.09	4.36
60	0.98	1.02	1.95	3.65
70	—	0.98	1.83	3.19
80	0.60	0.96	1.76	—
90	—	0.95	1.72	—
100	0.00	0.95	1.70	—

* Volume of gas dissolving into water at 0°C and 760 mmHg (ml/100 ml water) converted from the solubility of gas at t°C and 760 mmHg of the partial pressure.

of the solution. The normality is calculated from the equation (1.9).

$$N = \frac{W_3}{E_q} \quad \text{...} \quad (1.9)$$

where

W_3 = amount of solute in one liter solution (g)

E_q = gram equivalent of solute

For example, as the gram equivalents of hydrochloric acid and sodium hydroxide are 36.5 g and 40 g respectively, the normalities of hydrochloric acid solution of 36.5 g/*l* and sodium hydroxide solution of 40 g/*l* are the same at 1 N.

Since the normality is based on the gram equivalent of solute, this unit is a very convenient for volumetric analyses, such as neutralization titration and redox titration.

(e) Calcium carbonate equivalent concentration

The calcium carbonate equivalent concentration is obtained from the equation (1.10).

$$C_{cal} = C \times \frac{E_{cal}}{E_s} \quad \text{..} \quad (1.10)$$

where

C_{cal} = calcium carbonate equivalent concentration of solute (mg $CaCO_3$/*l*)

C = concentration of solute (mg/*l*)

E_{cal} = gram equivalent of calcium carbonate (50)

E_s = gram equivalent of solute

This concentration is usually used for ion exchange treatment to calculate the total cation and total anion concentrations of a water to be treated. For example, the both of sodium ion of 23 mg/*l* and chloride ion of 35.5 mg/*l* are converted to 50 mg $CaCO_3$/*l* from the equation (1.10).

(4) Electrical conductivity of aqueous solution

When electrolytes dissolve into water, they increase the electrical conductivity of aqueous solution. Therefore, the electrical conductivity gives an approximate total concentration of salts in the solution. As the unit of electrical conductivity, μS/cm is generally used.

Since the conductivity changes with the change of the solution temperature, the conductivity measured at an environmental temperature is converted to the value at a specified temperature, such as 25°C in the case of Japanese Industrial Standard.

When an electrolyte dissolves into water, the electrical conductivity of solution is calculated from the equation (1.11).

$$EC = (C^+ \times \lambda o^+ + C^- \times \lambda o^-) \times 10^3 \quad \text{.................} \quad (1.11)$$

where

EC = electrical conductivity (μS/cm)

C^+, C^- = equivalent concentration of the cation and anion dissociated from an electrolite (mol/*l*)

λo^+, λo^- = equivalent electrical conductivities of the cation and the anion at an infinite dilution (S·cm²/mol)

The equivalent electrical conductivities of typical ions are shown in Table 1.9.

For example, the electrical conductivity of 100 mg/*l* sodium chloride solution at 25°C is calculated as follows:

$$C^+ = 100 \times \frac{23}{58.5} \times \frac{1}{23} \times \frac{1}{1{,}000}$$

$$= 1.71 \times 10^{-3} \quad \text{..} \quad (1.12)$$

$$C^- = C^+ = 1.71 \times 10^{-3} \quad \text{..................................} \quad (1.13)$$

$$EC = (1.71 \times 10^{-3} \times 50.1 + 1.71 \times 10^{-3} \times 76.4) \times 10^3$$

$$= 216.3 \ (\mu S/cm) \quad \text{..................................} \quad (1.14)$$

The electrical conductivity of a solution containing more than two electrolytes is calculated as the sum of the electrical conductivities calculating for each substance by the above method.

Since the equivalent electrical conductivities of ions considerably increase with the temperature increase as shown in the Table 1.9, the conductivity of solution increases as the temperature increases.

The relationship between the concentration of an electrolyte and the electrical conductivity of the solution is varied depending on the kind of the electrolyte. Therefore, the solute concentration of solution including unknown solutes is hardly calculated from the electrical conductivity. However, the solute concentration of natural fresh water, such as river water, is calculated by using the following empirical equation (1.15) because the kinds of solutes are generally limited.

$$TDS = EC \times (0.70 \text{ to } 0.75) \quad \text{.........................} \quad (1.15)$$

where

TDS = total dissolved solids (mg/*l*)

EC = electrical conductivity of water at 25°C (μS/cm)

Table 1.9 The equivalent electrical conductivities of ions at the infinite dilution

($S\cdot cm^2/mol$)

Cation	0°C	18°C	25°C	100°C	Anion	0°C	18°C	25°C	100°C
H^+	225	315	350	630	OH^-	105	171	198	450
Li^+	19.4	32.8	38.7	115	F^-	—	47.3	55.4	—
Na^+	26.5	42.8	50.1	145	Cl^-	41.0	66.0	76.4	212
K^+	40.7	63.9	73.5	195	$1/2\ SO_4^{2-}$	41	68.4	80.0	260
NH_4^+	40.2	63.9	73.6	180	SCN^-	41.7	56.6	66.5	—
$1/2\ Mg^{2+}$	28.9	44.9	53.1	165	NO_2^-	44	59	72	—
$1/2\ Ca^{2+}$	31.2	50.7	59.5	180	NO_3^-	40.0	62.3	71.5	195
$1/3\ Al^{3+}$	29	—	63	—	$H_2PO_4^-$	—	—	57	—
$1/2\ Fe^{2+}$	28	44.5	53.5	—	HCO_3^-	—	—	44.5	—
$1/3\ Fe^{3+}$	—	—	68	—	$1/2\ CO_3^{2-}$	36	60.5	72	—
$1/2\ Cu^{2+}$	28	45.3	56	—	CN^-	—	—	78	—
$1/2\ Zn^{2+}$	28	45.0	53.5	—	CH_3COO^-	20.1	35	40.9	—

The electrical conductivity of theoretically pure water is calculated by using the equation (1.11).

The both of equivalent concentrations of H^+ and OH^- ions of pure water are 10^{-7} at 25°C. The equivalent electrical conductivities of them are shown in Table 1.9. Thus the electrical conductivity is obtained as follows:

$$\begin{aligned} EC &= (10^{-7} \times 350 + 10^{-7} \times 198) \times 10^3 \\ &= 5.48 \times 10^{-2}\ (\mu S/cm) \ \ldots\ldots\ldots\ldots\ldots (1.16) \end{aligned}$$

As this conductivity is a very small, the electrical conductivity of water itself can be ignored when the solute concentration is estimated from the electrical conductivity of the aqueous solution.

In case of water demineralization, the water purity is often expressed by the specific electrical resistance. The specific electrical resistance (ER) of theoretical pure water is calculated from the above electrical conductivity.

$$ER = \frac{1}{5.48 \times 10^{-2}} = 18.2\ (M\Omega) \ \ldots\ldots\ldots\ldots (1.17)$$

(5) pH of aqueous solution

The pH indicates the concentration of hydrogen ion in an aqueous solution and is used as an index showing the acidity or alkalinity of water.

Water only slightly dissociates into hydrogen ion (H^+) and hydroxide ion (OH^-).

$$H_2O \leftrightarrows H^+ + OH^- \ \ldots\ldots\ldots\ldots\ldots\ldots (1.18)$$

This ion product of water is a constant and it is 1×10^{-14} at 25°C.

$$[H^+]\ [OH^-] = 1 \times 10^{-14} \ \ldots\ldots\ldots\ldots\ldots (1.19)$$

where

$[H^+]$, $[OH^-]$ = molar concentration of H^+ and OH^- at 25°C

The pH is calculated from the H^+ concentration by using the equation (1.20).

$$pH = \log \frac{1}{[H^+]} = -\log[H^+] \ \ldots\ldots\ldots\ldots\ldots (1.20)$$

In case of pH 7, $[H^+]$ and $[OH^-]$ are equal at 1×10^{-7} and this water is said to be neutral. Water with pH of lower than 7 is acidic and higher than 7 is alkaline. Figure 1.9 shows the relationship between pH and the concentrations of H^+ and OH^- at 25°C.

However, the dissociation degree of water changes with temperature as shown in Figure 1.10. Therefore, the pH of pure water changes from 7.00 at 25°C to 6.13 at 100°C or 5.65 at 200°C as the temperature increases. Since this pH reduction is caused by the increase in the dissociation of water, the increase of H^+ ions corresponds to the increase of OH^- ions and the relationship of the "$[H^+] = [OH^-]$" is always kept. That is, the $[H^+]$ of neutral aqueous solutions changes with temperature.

In case of chemical treatment for cold water,

	Acidic							Neutral							Alkaline
pH	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14
$[H^+]$	1	10^{-1}	10^{-2}	10^{-3}	10^{-4}	10^{-5}	10^{-6}	10^{-7}	10^{-8}	10^{-9}	10^{-10}	10^{-11}	10^{-12}	10^{-13}	10^{-14}
$[OH^-]$	10^{-14}	10^{-13}	10^{-12}	10^{-11}	10^{-10}	10^{-9}	10^{-8}	10^{-7}	10^{-6}	10^{-5}	10^{-4}	10^{-3}	10^{-2}	10^{-1}	1

Fig. 1.9 Relationship between pH and the concentrations of H^+ and OH^- ions at 25°C

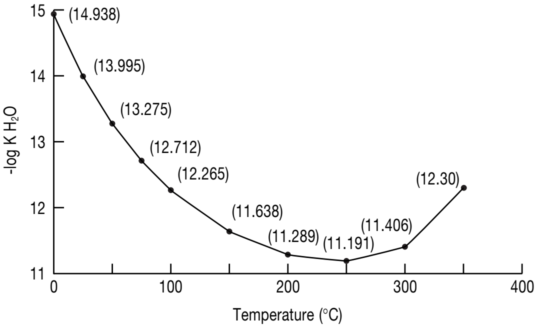


Fig. 1.10 Change in the dissociation degree of water with temperature

such as cooling water, the pH at 25° C, "cold pH", represents the water property. However, in case of hot water like boiler condensate, the pH at that temperature, "hot pH", has to be discussed.

The measurement of the "hot pH" is difficult in the field. The "hot pH" is generally calculated from the kinds, concentrations, dissociation degrees of solutes and so on by using a computer.

(6) Acids, bases and neutralization

Acids are substances which dissociate hydrogen ions, H^+, exactly oxonium ion, H_3O^+, in the aqueous solutions. Equations (1.21) to (1.23) show the dissociation of typical acids.

$$HCl \rightleftarrows H^+ + Cl^- \quad (1.21)$$
$$CH_3COOH \rightleftarrows H^+ + CH_3COO^- \quad (1.22)$$
$$H_2SO_4 \rightleftarrows 2H^+ + SO_4^{2-} \quad (1.23)$$

Substances which dissociate hydroxide ions, OH^-, in aqueous solutions are called bases.

$$NaOH \rightleftarrows Na^+ + OH^- \quad (1.24)$$
$$Ca(OH)^2 \rightleftarrows Ca^{2+} + 2OH^- \quad (1.25)$$

The strength of an acid or a base depends on the dissociation degree in water. The degree of dissociation is expressed by the equation (1.26).

$$\alpha = \frac{[So^+]}{[So]} \text{ or } \frac{[So^-]}{[So]} \quad (1.26)$$

where

α = degree of dissociation
$[So]$ = molar concentration of solute (mol/*l*)
$[So^+]$, $[So^-]$ = molar concentration of dissociated solute (mol/*l*)

An acid or a base with the higher dissociation degree is the stronger acid or base. Table 1.10 shows the dissociation degrees of typical acids and bases.

The reaction between an acid and a base is called neutralization. A salt and water are produced by the neutralization. The neutralization reactions are divided into following four types depending on the strengths of acids and bases:

① Formation of neutral salts from strong acids and bases,

$$HCl + NaOH \rightleftarrows NaCl + H_2O \quad (1.27)$$

② Formation of acidic salts from strong acids and weak bases,

$$HCl + NH_4OH \rightleftarrows NH_4Cl + H_2O \quad (1.28)$$

③ Formation of alkaline salts from weak acids and strong bases,

$$H_2CO_3 + 2NaOH \rightleftarrows Na_2CO_3 + 2H_2O \quad (1.29)$$

④ Formation of neutral salts from weak acids and bases,

$$H_2CO_3 + 2NH_4OH \rightleftarrows (NH_4)_2CO_3 + 2H_2O \quad (1.30)$$

The neutralization is a very important for treating supply water, wastewater, etc., and preventing metallic corrosion in various industrial processes.

In case of a neutralization for a high temperature process, the concept of "hot pH" described in the section 1.4.3 (5) has to be considered for realizing sufficient neutralizing effect. Figure 1.11

Table 1.10 Dissociation degrees of various acids and bases for their 0.1 N solutions at 25°C

Substance	Formula of dissociation	Degree of dissociation
Nitric acid	$HNO_3 \rightleftarrows H^+ + NO_3^-$	0.92
Hydrochloric acid	$HCl \rightleftarrows H^+ + Cl^-$	0.91
Hydroiodic acid	$HI \rightleftarrows H^+ + I^-$	0.91
Sulfuric acid	$H_2SO_4 \rightleftarrows H^+ + HSO_4^-$	0.61
Phosphoric acid	$H_3PO_4 \rightleftarrows H^+ + H_2PO_4^-$	0.27
Acetic acid	$CH_3COOH \rightleftarrows H^+ + CH_3COO^-$	0.013
Carbonic acid	$H_2CO_3 \rightleftarrows H^+ + HCO_3^-$	0.0017
Hydrogen sulfide	$H_2S \rightleftarrows H^+ + HS^-$	0.0007
Boric acid	$H_3BO_3 \rightleftarrows H^+ + H_2BO_3^-$	0.0001
Potassium hydroxide	$KOH \rightleftarrows K^+ + OH^-$	0.89
Sodium hydroxide	$NaOH \rightleftarrows Na^+ + OH^-$	0.84
Barium hydroxide	$Ba(OH)_2 \rightleftarrows Ba^{2+} + 2OH^-$	0.80
Aqueous ammonia	$NH_3 + H_2O \rightleftarrows NH_4^+ + OH^-$	0.013

shows the difference of pH at 25°C and 100°C when an acidic solution containing 200 mg/*l* of hydrochloric acid and 1,000 mg/*l* of acetic acid is neutralized by using various bases.

The change in the pH is caused by the changes in the dissociation degrees of water, acids and bases. Generally, the pH at a higher temperature becomes smaller than that at a lower temperature. Even in a neutral pH, higher hydrogen ion concentration at higher temperature often accelerates the metallic corrosion in the system.

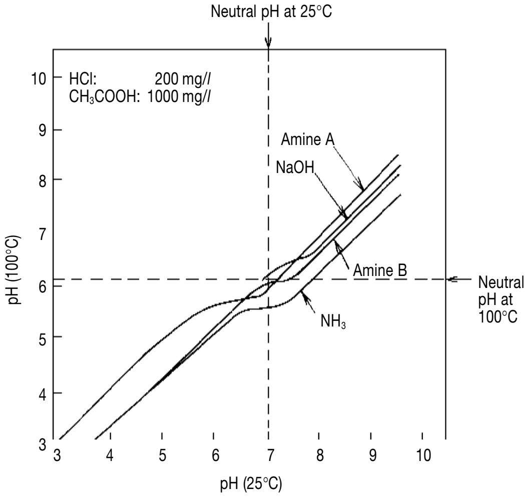


Fig. 1.11 Relationship between the pH of an acid solution at 25°C and 100°C under various neutralization conditions

(7) Oxidation and reduction

Typical oxidation and reduction reactions are summarized in Table 1.11. The oxidation and reduction reactions proceed at the same time as shown in the equation (1.31).

$$2H_2 + O_2 \rightleftarrows 2H_2O \quad\text{.......................................}\quad (1.31)$$

In this reaction, the hydrogen is oxidized by combining with the oxygen, and the oxygen is reduced by combining with the hydrogen.

In the field of water treatment, some oxidation and reduction reactions should be prevented and some ones are utilized. For example, the oxidation (corrosion) of iron has to be prevented to extend the service lives of equipments made of iron.

$$4Fe + 6H_2O + 3O_2 \rightarrow 4Fe(OH)_3 \quad\text{.................}\quad (1.32)$$

The reaction between oxygen and sodium sulfite is utilized to remove the oxygen from a boiler water for preventing the boiler corrosion.

$$O_2 + 2Na_2SO_3 \rightarrow 2Na_2SO_4 \quad\text{..........................}\quad (1.33)$$

(8) Ionization series of metals

The ionization series expresses to the orderly arrangement of ionization tendencies for metals in an aqueous solution. Table 1.12 shows an ionization series for popular metals. A metal in the lefter side more easily yields the metallic ion or corrodes in an aqueous solution.

For example, when iron and copper are im-

Table 1.11 Typical oxidation and reduction reactions

Oxidation	Reduction
① Combining with oxygen $2\underline{\underline{H_2}} + O_2 \rightarrow 2\underline{\underline{H_2O}}$	① Losing oxygen $\underline{\underline{CuO}} + H_2 \rightarrow \underline{\underline{Cu}} + H_2O$
② Losing hydrogen $\underline{\underline{N_2H_4}} + O_2 \rightarrow \underline{\underline{N_2}} + 2H_2O$	② Combining with hydrogen $2H_2 + \underline{\underline{O_2}} \rightarrow 2\underline{\underline{H_2O}}$
③ Losing electron $\underline{\underline{Fe}}^0 \rightarrow \underline{\underline{Fe}}^{2+} + 2e^-$	③ Getting electron $2\underline{\underline{H}}^+ + 2e^- \rightarrow \underline{\underline{H_2}}$
④ Increasing of oxidation number $4\underline{\underline{Fe}}(OH)_2 + 2H_2O + O_2 \rightarrow 4\underline{\underline{Fe}}(OH)_3$ Fe(II) Fe(III)	④ Decreasing of oxidation number $2\underline{\underline{Cu}}O + H_2 \rightarrow \underline{\underline{Cu_2}}O + H_2O$ Cu(II) Cu(I)

mersed into a diluted sulfuric acid solution and they are connected with a lead wire, the iron corrodes (yields ferrous ion) and hydrogen is generated on the copper surface.

$$Fe \rightarrow Fe^{2+} + 2e^- \quad \text{(1.34)}$$
$$2H^+ + 2e^- \rightarrow H_2 \text{ (on copper surface)} \quad \text{(1.35)}$$

When iron is immersed in a cupric sulfate solution, the iron is corroded and copper is deposited on the iron surface.

$$Fe \rightarrow Fe^{2+} + 2e^- \quad \text{(1.36)}$$
$$2e^- + Cu^{2+} \rightarrow Cu \text{ (on iron surface)} \quad \text{(1.37)}$$

As mentioned above, when two kinds of metals are coexistence in an aqueous solution, the metal which is more easily ionized is said to have larger ionization tendency. A metal with the larger ionization tendency is easily corroded (oxidized). That is, the reactivities of metals in various environment are estimated from the ionization series.

The metals in the righter side of ionization series are very stable in various aqueous solutions under ambient temperature and are called noble metals.

Table 1.12 Ionization series of metals and their reactivities

Ionization series	K, Ca, Na, Mg, Al, Zn, Cr, Fe, Ni, Mo, Sn, Pb, (H_2), Cu, Hg, Ag, Pt, Au
Oxidation by oxygen in air	Rapidly Gradually Scarcely
Reaction with water	React with cold water React with hot water Scarcely react
Reaction with acids	React with non-oxidizing acids React with oxidizing acids React with aqua regia

2. Water Treatment and Chemicals for Boiler Water Systems

2.1 General

2.1.1 Types of Boilers

A boiler is used to heat water and generate required steam or hot water. There are various types of boilers according to their uses. Boilers are classified according to their structures, the methods of water circulation, the types of fuels, and the kinds of the materials used. In general, they are roughly classified into cylindrical boilers and water-tube boilers.

(1) Cylindrical boilers

The types of cylindrical boilers are vertical boilers, flue-tube boilers, fire-tube boilers, and fire and flue-tube boilers.

The recent fire and flue-tube boilers have progressed in the evaporation rate and efficiency in Japan. The evaporation rate per unit heating surface area was 30 to 65 kg/m^2·h$^{1)}$ about 25 years ago. However, it has increased to 60 to 100 kg/m^2·h as shown in Figure 2.1, and boiler efficiency has also increased to about 80 to 90% in the present.

The fire and flue-tube boilers generally have the evaporation capacities of below 1 t/h to 20 t/h with the operation pressures of up to 10 kgf/cm^2.

Figure 2.2$^{2)}$ shows the typical examples of the combustion gas flow in the fire and flue-tube boilers.

(2) Water-tube boilers

A water-tube boiler evaporates water on the inside heating surfaces of the tubes. The heating surface area of this boiler can be made large by increasing the number of water tube bundles, and the high pressure operation is easily achieved.

Therefore, boilers of this type are broadly used, ranging from the small or medium size boilers for general industries to the large size boilers for electricity generation. In the case of small to medium size boilers with the evaporation capacity of 50 t/h or less, the evaporation rate per unit heating surface area is 60 to 100 kg/m^2·h as shown in Figure 2.3.

Sufficient attention should be paid to the treatment of feedwater and boiler water since the water tube boiler generates great amounts of steam at the inside of tubes. The higher in the pressure, the higher level of treatment is required.

According to the water circulation methods, the water-tube boilers are classified into natural circulation boilers, forced circulation boilers and once-through boilers. In the natural circulation boilers, the circulation of boiler water is caused by the difference between the density of water and that of the steam and water mixture. About 80% of the water-tube boilers use this circulation method which is broadly employed for small to large capacity boilers. Figure 2.4 shows an example of the structure applied for small to medium size water-tube boilers.

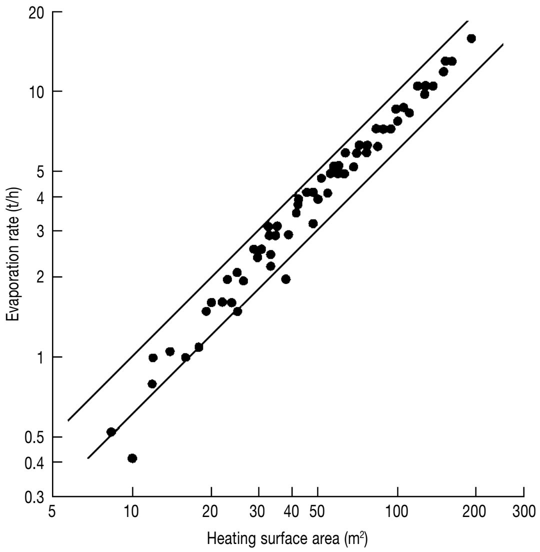


Fig. 2.1 Relationship between the heating surface area and the evaporation rate of fire and flue-tube boilers

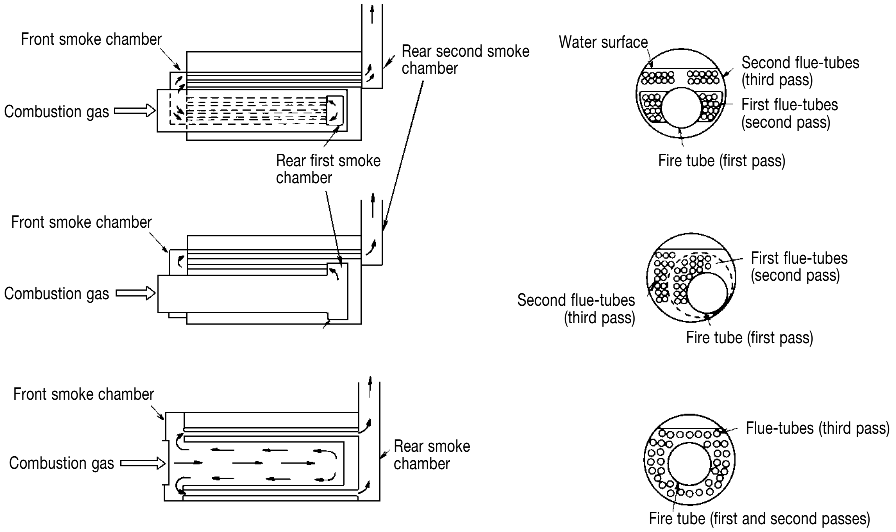


Fig. 2.2 Combustion gas flows in fire and flue-tube boilers

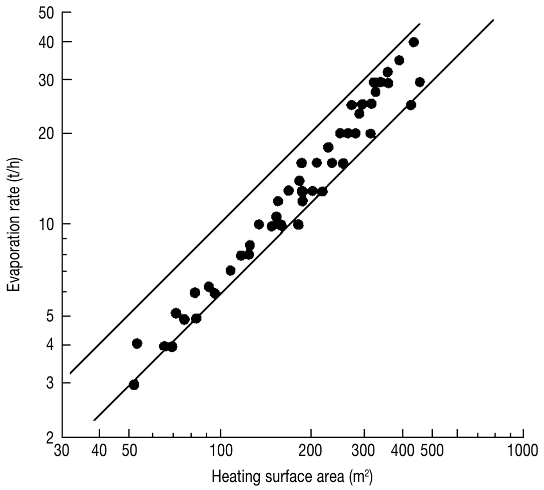


Fig. 2.3 Relationship between the heating surface area and the evaporation rate of water-tube boilers

In the forced circulation boilers, the boiler water is circulated by using circulation pumps. This method is suitable for high pressure boilers where the natural circulation becomes difficult due to the small difference between the densities of saturated water and saturated steam.

In the once-through boilers, water is fed at one end of a long heating tube. It is heated and evaporated through the tube, and finally it leaves as superheated steam at the other end of the tube. It is especially suitable for high pressure steam gen-

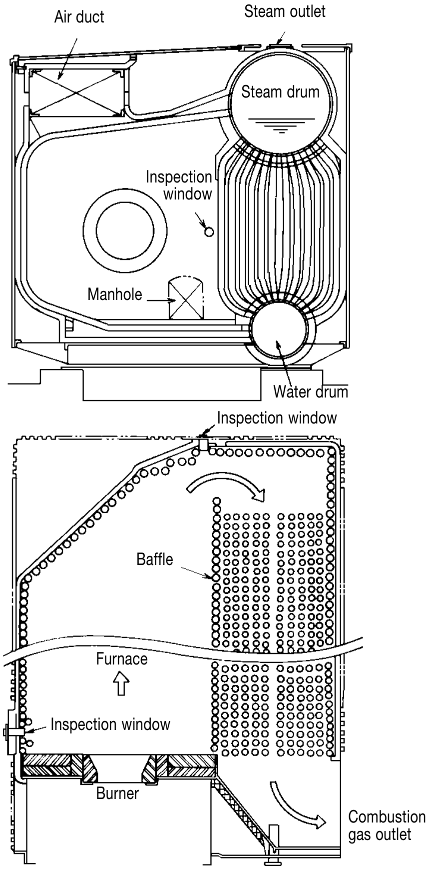


Fig. 2.4 Typical structure of small to medium size water-tube boilers

eration because it is constructed of only water-tube bundles, which is different from the natural circulation and forced circulation boilers. Once-through boilers are often employed for thermal power plants.

Mini-circulation boiler consists of water-tubes and has the steam and water separator which returns the separated hot water to the heating tubes. Normally, the ratio of the amount of circulation water to that of maximum feedwater is 2 or less. There are the single tube type and the multiple tube type, however, the multiple tube type is widely used. The structure of a typical mini-circulation boiler is shown in Figure 2.5.

Since the mini-circulation boiler has the higher boiler efficiency of 80 to 90%, and is easy to operate, it is widely used in small or medium size factories, buildings, hospitals, etc. Recently it is increase to install the mini-circulation boiler in place of the cylindrical boiler with small capacity.

2.1.2 Necessity of Water Treatment for Boilers

Waters used as boiler feedwater, such as tap water, industrial water, underground water and river water, usually contain various substances such as suspended solids, dissolved solids and gases. The amounts of these substances vary largely depending on the sources of raw waters, as shown in Table 2.1.

The use of such raw water without the pretreatment may result in problems, such as scale, corrosion and carryover, in boilers and the auxiliary

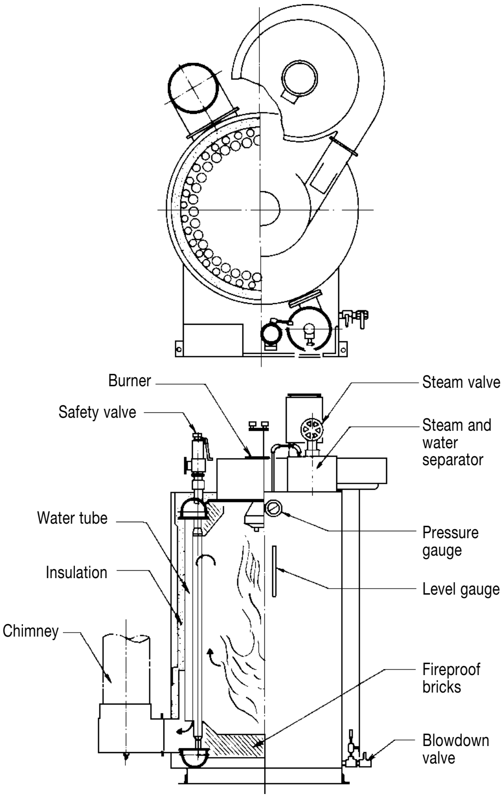


Fig. 2.5 Structure of a typical mini-circulation boiler

Table 2.1 Examples of raw water qualities

Water source	River				Lake		Well	
Location	Osaka, Japan	Seria, Burunei	Shanghai, China	Bratislava, Slovakia	Perth, Australia	Kaohsiung, Taiwan	Milano, Italy	Jakarta, Indonesia
pH	7.0	5.3	8.1	8.1	6.8	8.0	7.6	8.4
Electrical conductivity (μS/cm)	175	28	490	361	453	299	260	529
M-alkalinity (mg $CaCO_3$/l)	52	1	92	161	31	120	142	296
Total hardness (mg $CaCO_3$/l)	44	8	16	230	76	150	190	24
Ca-hardness (mg $CaCO_3$/l)	34	1	100	172	43	100	130	5
Chloride ion (mg/l)	23	1	81	22	124	2	17	5
Sulfate ion (mg/l)	33	7	41	39	23	45	—	—
Silica (mg SiO_2/l)	20	6	7	9	9	7	25	13
Total iron (mg Fe/l)	< 0.2	4.0	3.7	0.47	< 0.1	0.25	0.1	—

Table 2.2 Troubles in the operation of boiler systems and their causes

Classification of problems	Troubles in operation of boiler system	Causes of troubles
Scaling	Reduction of boiler efficiency by adhesion of hardness or silica scale	Leakage of hardness and/or silica from softener or demineralizer
	Expansion or bursting of evaporation tubes by heavy scale adhesion	Inadequate quality control of feedwater or boiler water
		Application of inadequate chemical treatment
Corrosion	Corrosion damage of pipings of feedwater and condensate, evaporation tube, etc., by dissolved oxygen and/or carbon dioxide	Insufficient deaeration of feedwater Reduction of boiler water or condensate pH
	Corrosion damage of evaporation tube under deposition of metal oxides	Iron contamination of feedwater from condensate line
		Oxygen incoming to boiler during the idle time
Carryover	Reduction of steam purity	Rapid fluctuation of boiler operation load
	Reduction of turbine efficiency by silica scale	Excess concentration of boiler water
	Deterioration of product quality treated with the steam	Boiler water contamination with organic matters

equipments.

Table 2.2[3)] shows the troubles in boiler operation caused by water.

Most of low pressure boilers* use raw water or softened water as the feedwater and usually no deaerator is employed. Therefore, those boilers are subjected to troubles such as hardness and silica scale adhesion, corrosion due to dissolved oxygen and corrosion by carbon dioxide in the condensate line.

Medium or high pressure boilers* are generally supplied deaerated and demineralized water as the feedwater. However, since they are operated at the high temperature and high pressure, the presence of a small amount of impurities causes problems, such as metal oxide deposits on the heating surface of the boiler, the corrosion of the auxiliary equipments, and scale adhesion in the superheaters or on turbine blades.

In order to prevent these problems and to operate the boilers safely and efficiently, the application of suitable water treatment is required for each boiler. The water treatment for boilers is divided into the external (mechanical) and internal (chemical) treatment. The mechanical treatment is to remove the impurities in water by applying coagulation, sedimentation, filtration, ion exchange, deaeration treatments, etc.

The chemical treatment is divided into the treatment for the feedwater and condensate lines, and for the boiler itself.

The chemical treatment for the feedwater and condensate lines aims to control corrosion by adding oxygen scavengers and corrosion inhibitors to the lines, and to supply water containing as little impurities as possible into the boiler. Boiler compounds, oxygen scavengers, sludge dispersants and so on are used for the chemical treatment of boilers. Those chemicals prevent corrosion and make the scale forming components the water insoluble and dispersed particles to discharge them from the boiler with the blowdown water.

Those water treatments are indispensable for operating boilers safely and efficiently.

2.1.3 History of Boiler Water Treatment in Japan

(1) Water treatment for low pressure boilers

The importance of boiler water treatment was recognized among the users of large size water-tube boilers before 1945, and boiler compounds were used. However, most of the low pressure boilers were operated without the internal (chemical) water treatment. Natural organic compounds, such as sodium lignin sulfonate and starch, sodium carbonate and sodium phosphates were used as

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* The pressures of the boilers are usually divided into low pressure, medium pressure and high pressure. In this chapter, the pressure of boilers are defined as follows:

Low pressure:	below 20 kgf/cm^2
Medium pressure:	20–75 kgf/cm^2
High pressure:	above 75 kgf/cm^2

boiler compounds.

In 1946, the production of ion exchange resins (cation exchange resins) was started on a commercial basis in Japan. In the 1950's, water softening equipment using ion exchange resins was applied to treat boiler feedwater. From 1955, the use of softeners became popular for low pressure boilers.

As the performance of low pressure boilers was much progressed, the purpose of boiler water treatment changed from the scale prevention to the total treatment including corrosion control. The boiler compounds were required not only the function of scale control but also to control the pH, and alkalinity of boiler water for the corrosion prevention. Therefore, phosphate based boiler compounds having the excellent effects were widely used.

Sodium sulfite was widely used as the oxygen scavenger from the old time, but hydrazine was applied for high pressure boilers in thermal power plants from 1952. The use of hydrazine for low pressure boilers was also started afterward.

During this period, neutralizing amines, such as morpholine and cyclohexyl amine, came to be used for controlling the corrosion of the pipings and equipments in the feedwater and the condensate lines.

After 1955, the boiler water treatment changed drastically from the internal treatment for boiler itself to the total treatment for whole boiler system including the feedwater and condensate lines.

Since 1965, boilers have become more efficient and more compact. Therefore, the importance of boiler water treatment has increased.

On the other hand, the problem of water pollution, such as "red tide" problem due to nutrification in closed sea areas like Setonaikai in Japan, became a big social issue. As the increase of phosphate concentration in closed water areas was suspected to accelerate the occurrence of "red tide", the development of non-phosphorous boiler compound was required. At first, the natural high molecular weight compounds were applied for the non-phosphorous boiler compounds, but the synthetic polymer treatment which showed the excellent scale prevention was established from the middle of 1970's.

After the oil crisis in 1973, the saving of energy and man-power became to be highly concerned. To save energy and reduce man-power in the boiler operation, the reduction of blowdown, the increase of the condensate recovery, the use of multifunctional chemicals with easy handing and so on were employed.

In the 1980's, the safety of chemicals became a big issue. The chemicals based on food additive grade, and Food and Drug Administration of U.S.A.(FDA) approved grade products were applied for the boilers especially in food factories and hospitals. Saccharide based chemicals and so on, which are safer, were also applied as the oxygen scavengers besides sodium sulfite.

(2) Water treatment for medium or high pressure boilers

In 1945, the pressure of boilers for thermal power plants was only up to 40 kgf/cm^2. The operational pressure increased to 60 kgf/cm^2 in 1950's, and to 100 kgf/cm^2 in 1960's. During this period, the caustic treatment was the major boiler water treatment method, in which the boiler water pH and phosphate ion concentration were controlled in the ranges of 10.5 to 11.0 and 10 to 20 mg PO_4/l respectively.

However, the corrosion problems of boiler evaporation tubes often happened after the boiler pressure exceeded 100 kgf/cm^2. The results of investigations in those days identified the cause of corrosion as the concentration of alkali on the heat transfer surface. Then, the treatment by using sodium phosphate (Na_3PO_4), which scarcely yielded free hydroxide alkali in boiler water, was employed. However, as the phosphate concentration in boiler water was controlled in the higher range of 5 to 15 mg PO_4/l than that of present phosphate program, the hide-out of sodium phosphate [refer to the section 2.2.2, (2), (b), (iv)] happened. Finally, the coordinated phosphate treatment which controls the phosphate ion in lower range in boiler water was applied to prevent the alkaline corrosion and the hide-out of sodium phosphate.

In the late 1960's, the boiler pressure became 170 to 180 kgf/cm^2, and the once-through boiler was used. In the case of once-through boiler, chemicals which remain the evaporation residue in boiler water, like phosphate, cannot be applied. Therefore, the volatile treatment using volatile products, such as hydrazine, ammonia and volatile amines, was necessary for the once-through boiler.

In large size thermal power stations, the operation of supercritical pressure boilers with the pressure of more than 246 kgf/cm^2 started from the second half of the 1960's, using volatile treatment.

2.2 Boiler Problems Caused by Water

2.2.1 Scaling

(1) Scaling in low pressure boilers

Since most low pressure boilers use fresh water or softened water as the feedwater, the substances which cause the scaling in boilers are mainly hardness components and silica. When a water including hardness components and silica is fed to a boiler, these substances yield insoluble matters and they deposit in the internal feedwater pipe and its surroundings.

The dissolved solid concentration in boiler water becomes higher on the heating surface than that at the other parts as shown in Figure 2.6. Therefore, the substances with low solubilities deposit and form the scale on the heating surface when their concentrations exceed their solubilities.

Since these scale components have the small thermal conductivities as shown in Table 2.3[4)–6)], the scale adhesion on the heating surface remarkably reduces the thermal efficiency of boiler. When the part covered with the scale is locally superheated, the mechanical strength of the tube material is reduced and the bursting may occur eventually.

Most scales formed on the heating surface are generally composed of several mixed substances. The thermal conductivity of such mixed scale is approximately 1 to 2 kcal/m·h·°C.

Figure 2.7[7)] shows a model of heating surface covered with scale and the inner skin temperature of the tube under the scale, obtained from the following equation:

$$t_2 = t_4 + \left(\frac{1}{\alpha} + \frac{D}{k_2} \right) \times Q \quad \text{.......................... (2.1)}$$

where

t_2 = inner skin temperature of tube (°C)

t_4 = boiler water temperature (bulk) (°C)

α = heat transfer coefficient of boiling surface (kcal/m^2·h·°C)

D = scale thickness (m)

k_2 = thermal conductivity of scale (kcal/m·h·°C)

Q = heat flux (kcal/m^2·h)

Figure 2.8 shows the relationship between the scale thickness and the inner skin temperature of tube at each heat flux when a scale with thermal conductivity of 2 kcal/m·h·°C adheres on the boiler tube inside with the pressure of 10 kgf/cm^2.

Figure 2.9[8)] shows the relationship between the

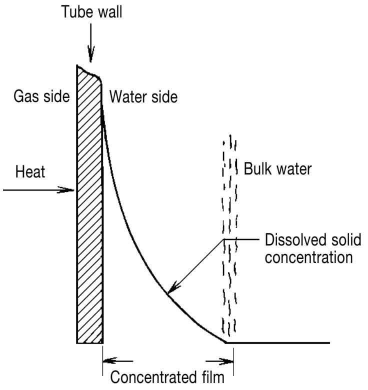
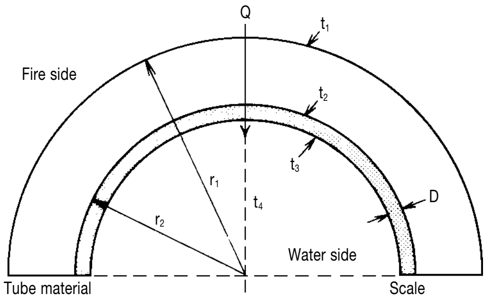


Fig. 2.6 Schematic model of dissolved solid concentration on a heating surface

Table 2.3 Thermal conductivities of scale components and metals

Substance	Thermal conductivity (kcal/m·h·°C)
Silica scale	0.2–0.4
Calcium carbonate scale	0.4–0.6
Calcium sulfate scale	0.5–2.0
Calcium phosphate scale	0.5–0.7
Iron oxide (hematite) scale	3–5
Iron oxide (magnetite) scale	1
Carbon steel	40–60
Copper	320–360



Q : Heat flux (kcal/m^2·h)
t_1 : Outer skin temperature of tube (°C)
t_2 : Inner skin temperature of tube (°C)
t_3 : Surface temperature of scale (°C)
t_4 : Boiler water temperature (bulk) (°C)
D : Scale thickness (m)
r_1 : Outer radius of tube (m)
r_2 : Inner radius of tube (m)

Fig. 2.7 Model of heating surface covered with scale temperature and the allowable tensile stresses of carbon steels using as boiler tubes. When the temperature exceeds 350° C, the allowable stress starts to decrease and reaches the 50 to 60% of the original value at 450° C. Therefore, the tube wall temperature should be kept below 450° C for the safe boiler operation and the scale thickness on the tube has to be controlled thinner than 1 to 2 mm as shown in Figure 2.8.

Photograph 2.1 (p. 2-66) shows a typical expansion trouble of an evaporation tube caused by the scale adhesion. The scale thickness was around 2.0 mm and the composition is shown as the sample A in Table 2.4. The main component of the scale was calcium silicate ($CaSiO_3$) and the cause of scaling was the hardness leakage from the softener for the feedwater treatment.

Photograph 2.2 (p. 2-66) is an expansion trouble of a boiler tube by the silica scale adhesion. The scale thickness was about 1.5 mm and the scale analysis is shown as the sample B in Table 2.4. This trouble was caused by the shortage of boiler

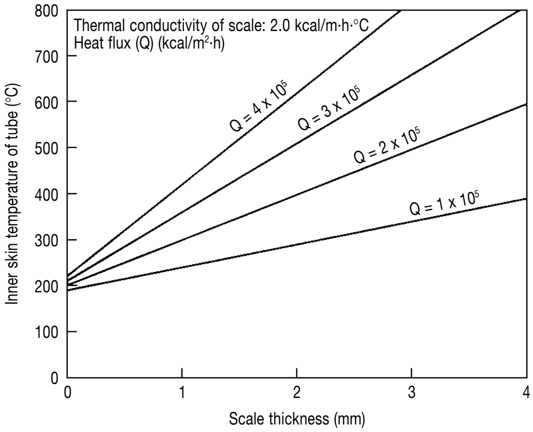


Fig. 2.8 Relationship between the scale thickness and inner skin temperature of a boiler tube

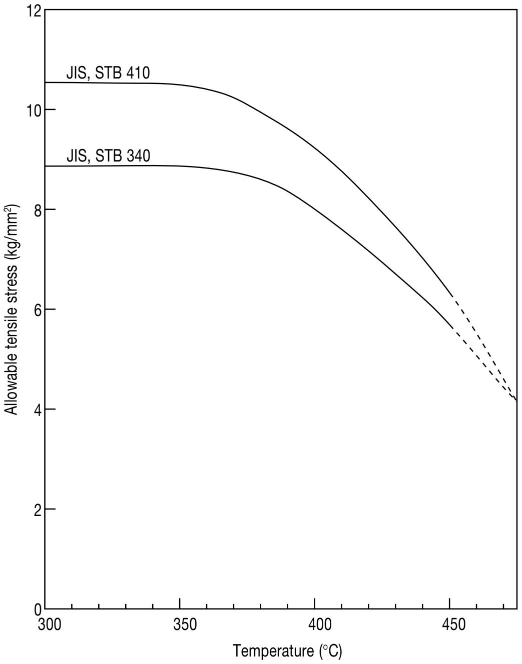


Fig. 2.9 Relationship between temperature and the allowable tensile stress of carbon steel tubes

Table 2.4 Scale analyses of low pressure boilers

(Weight %)

Sample	A	B	C
Calcium oxide (CaO)	32.9	7.0	7.4
Magnesium oxide (MgO)	1.7	0.7	1.3
Iron oxide (Fe_2O_3)	3.9	2.8	27.3
Copper oxide (CuO)	Trace	Trace	Trace
Acid insoluble matter*	40.3	83.9	15.2
Sulfuric acid anhydride (SO_3)	7.3	Trace	Trace
Carbonic acid anhydride (CO_2)	Trace	Trace	Trace
Phosphoric acid anhydride (P_2O_5)	4.7	5.9	4.7
Ignition loss	1.1	2.1	5.7
Zinc oxide (ZnO)	Trace	Trace	31.7
Aluminum oxide (Al_2O_3)	Trace	Trace	Trace
Sodium oxide (Na_2O)	1.0	—	Trace

* The main component of acid insoluble matter is generally silica (SiO_2).

water P-alkalinity keeping silica as the water soluble silicate ion.

Recently, comparatively higher concentration of zinc is sometimes detected in the scales and sludges collected from the boilers. In a boiler where galvanized steel pipes are used for the feedwater and condensate lines, zinc ions deposit and form the scale in the boiler, which are dissoluted from the pipings and enter the boiler together with the feedwater and recovered condensate. The sample C of Table 2.4 shows a typical example of such scale.

Since the electrical potential of the zinc becomes higher than that of steel[9] in high temperature water (over 60° C) containing oxygen and zinc does not work as a sacrificial anode, the steel of the galvanized tube is attacked by the pitting corrosion. Therefore, it is recommended to avoid the use of galvanized steel pipe for the feedwater and condensate lines.

The following measures are applied to prevent scale troubles caused by hardness components, silica and so on in low pressure boilers;

① Removal of hardness by using softener,
② Use of boiler compounds and sludge dispersants,
③ Control of the boiler water concentration.

(2) Scaling in medium or high pressure boilers

In general, a boiler of the higher pressure has the higher capacity and the higher heat flux. Since the bad influences of the impurities in feedwater on a boiler operation increase as the pressure becomes higher, demineralized water is used as the feedwater of medium or high pressure boiler. In that case, the substances causing scale problems are mainly the corrosion products which are formed in the boiler or came into the boiler from the feedwater and condensate lines. Table 2.5 shows the typical scale analyses of medium or high pressure boilers. The scale components are usually iron oxides. In the case where copper and copper alloys are used for the auxiliary equipments in the feedwater and condensate lines, the scale contains copper, nickel, zinc and so on as the corrosion products of the copper and copper alloys.

These corrosion products coming into the boiler with the feedwater tend to adhere more on the tube surface of the fire side with a higher heat flux. The scale adhesion condition in an actual boiler tube is illustrated in Figure 2.10[10]. The scale amounts at the position A and C are 2.37 and 0.3 times respectively against the mean value at the position B. This fact shows that the scale amount increases at the fire side of tube with the higher heat flux.

In general, the relationship between the scaling rate of iron oxide and the heat flux is shown in the following equation:

$$A = K \times C \times Q^n \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (2.2)$$

where

A = scaling rate of iron oxide ($mg/cm^2 \cdot h$)
C = concentration of iron oxide in boiler water (mg/l)
Q = heat flux ($kcal/m^2 \cdot h$)
K = constant
n = multiplier

Mankina, et al.[11], reported that the K and n in the equation (2.2) were 5.7×10^{-14} to 8.3×10^{-14}

Table 2.5 Scale analyses of medium or high pressure boilers

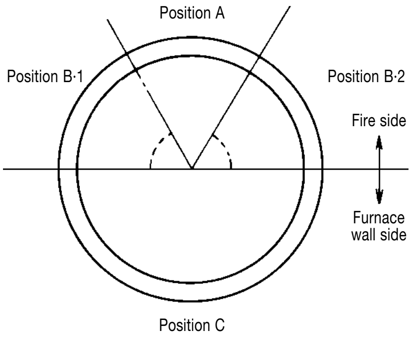
(Weight %)

Sample	A	B	C	D
Pressure of boiler (kgf/cm^2)	113	92	69	103
Calcium oxide (CaO)	Trace	Trace	2.0	0.5
Magnesium oxide (MgO)	Trace	Trace	Trace	Trace
Iron oxide (Fe_2O_3)	99.7	88.9	91.2	90.1
Copper oxide (CuO)	Trace	Trace	Trace	Trace
Acid insoluble matter	0.2	4.9	0.5	2.6
Sulfuric acid anhydride (SO_3)	Trace	Trace	Trace	Trace
Carbonic acid anhydride (CO_2)	Trace	Trace	Trace	Trace
Phosphoric acid anhydride (P_2O_5)	Trace	3.7	3.3	2.1
Ignition loss	3.3	2.5	2.2	0.4
Zinc oxide (ZnO)	—	Trace	—	—
Aluminum oxide (Al_2O_3)	Trace	Trace	Trace	Trace

and 2 respectively, namely the scaling rate increased in proportion to the square of the heat flux. Sakae, et al.[10)], reported that the n value was 1.3.

During the annual boiler operation period of approximately 8,000 hours, the scale of 8 to 10 mg/cm^2 generally adheres on the evaporation tube even an appropriate boiler water treatment is applied. Therefore, sufficient attention must be paid to the water treatment for the feedwater and recovered condensate of high pressure boilers for minimizing the scaling rate.

Since the thermal conductivity of scale composed of iron oxide mainly is a low and about 1 kcal/m·h·°C, the scale adhesion on the tubes disturbs the heat transfer and raises the tube skin temperature. The rise of the tube wall temperature due to the scale adhesion is calculated by using the equation (2.1) and the result is shown in Figure 2.11.



Position of evaporation tube against fire

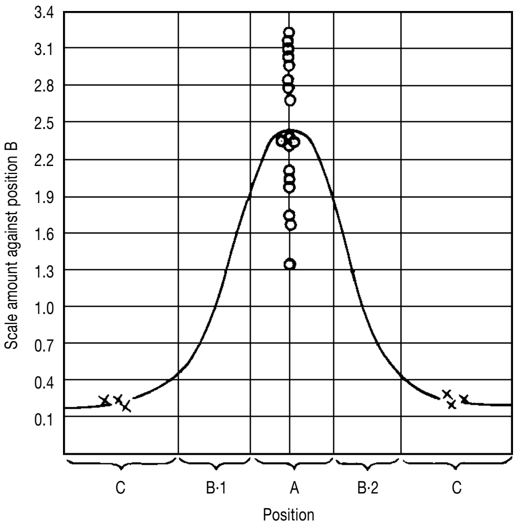


Fig. 2.10 Relationship between the scale amount and position of a boiler tube against fire

When the allowable tube wall temperature is set at 450° C, the allowable scale thickness of a boiler with a heat flux of 4 X 10^5 kcal/m^2·h becomes around 0.25 mm. Since the density of iron oxide scale is around 3 g/cm^3[3, 6)], the allowable scale amount becomes around 75 mg/cm^2.

In order to prevent the scale problems caused by the impurities in the feedwater, the following measures must be taken:

① Reduction of the impurities coming into the boiler by employing the pH control, iron removal, demineralization and so on of the feedwater and recovered condensate,

② Determination of the time for the chemical cleaning and the application of the cleaning by periodically inspecting the scale adhesion condition of evaporation tubes sampled from the high heat load part of the boiler.

When organic substances, such as humic acid and fulvic acid, are including in the raw water, most of them are removed by the pretreatment, such as coagulation-sedimentation, filtration and demineralization, however, still some traces of the organic substances come into the boiler. These organic substances in the boiler are partly decomposed to organic acids which reduces the pH of the boiler water and are partly carbonized on the heating surface to form carbon scale. This carbon remarkably disturbs the heat transfer and increases the skin temperature of tube[12)].

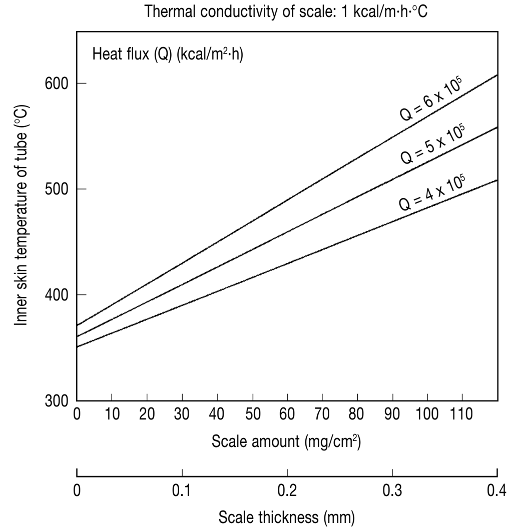


Fig. 2.11 Relationship between the iron oxide scale thickness and inner skin temperature of a boiler tube

When the carbon scale layer and iron oxide scale layer are separately adhere on the heating surface as shown in Figure 2.12, the skin temperature of tube under the scale is calculated from the following equation:

$$t_1 = t_2 + \left(\frac{1}{\alpha} + \frac{D_c}{k_c} + \frac{D_s}{k_s}\right) \times Q \quad \ldots\ldots\ldots\ldots\ldots (2.3)$$

where

t_1 = skin temperature of tube under scale (°C)
t_2 = bulk water temperature (°C)
α = heat transfer coefficient of boiling surface (kcal/m^2·h·°C)
k_c = thermal conductivity of carbon scale (kcal/m·h·°C)
k_s = thermal conductivity of iron oxide scale (kal/m·h·°C)
D_c = thickness of carbon scale (m)
D_s = thickness of iron oxide scale (m)
Q = heat flux (kcal/m^2·h)

The thicknesses of carbon and iron oxide scales are calculated from the following equations:

$$D_c = \frac{S \times C \times 10^{-4}}{d_c} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2.4)$$

$$D_s = \frac{S \times (100 - C) \times 10^{-7}}{d_s} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (2.5)$$

where

S = total scale amount (mg/cm^2)
C = carbon content of scale (%)
d_c = density of carbon scale (g/cm^3)
d_s = density of iron oxide scale (g/cm^3)

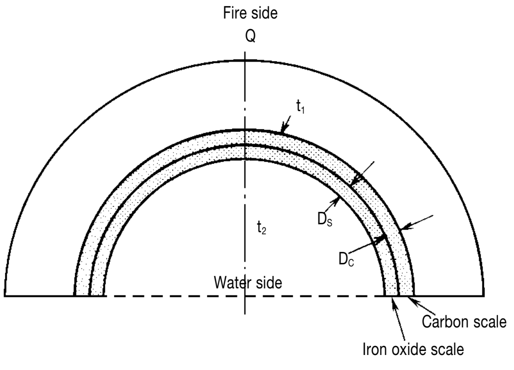


Fig. 2.12 Model of heating surface covered with a scale composed of double layers

Thus, the equation (2.6) is derived from the equations (2.3), (2.4) and (2.5).

$$S = \frac{\left(\frac{t_1 - t_2}{Q} - \frac{1}{\alpha}\right) \times 10^7}{\frac{C}{k_c \times d_c} + \frac{1 - C}{k_s \times d_s}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (2.6)$$

In the case of boiler with the pressure of 100 kgf/cm^2 and the allowable tube wall temperature of 450°C, the relationship between the carbon content of scale and the allowable scale amount is shown in Figure 2.13. When the carbon content of scale becomes higher, the allowable scale amount becomes smaller.

Therefore, when organic substances, such as humic acid, are including in the raw water, the following measures should be taken:

① Removal of organic substances from raw water by applying coagulation, filtration, oxidation and adsorption treatments, etc,
② Strict control of boiler water pH,
③ Periodical scale sampling and the carbon content analysis for determining the time of chemical cleaning.

2.2.2 Corrosion

(1) Corrosion of low pressure boilers

Various factors, such as pH, dissolved gases (oxygen, carbon dioxide, etc.), the kinds and concentrations of dissolved matters, temperature, and

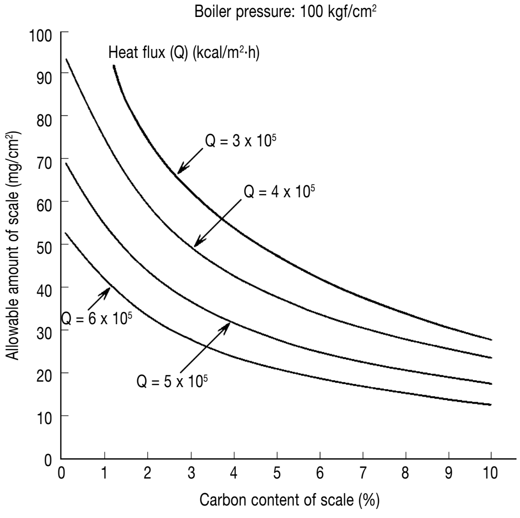


Fig. 2.13 Relationship between the carbon content of scale and the allowable scale amount

water flow rate, influence the corrosion reactions of metals. In the case of low pressure boilers, the most important factors are the dissolved gases and pH.

(a) Corrosion of feedwater line

The corrosion reactions take place electrochemically in water. As the feedwater is usually neutral and includes dissolved oxygen, iron is attacked by the following reactions:

At anode; $Fe \rightarrow Fe^{2+} + 2e^-$ .... (2.7)

At cathode; $H_2O + 1/2O_2 + 2e^- \rightarrow 2OH^-$ .... (2.8)

In water; $Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2$ .... (2.9)

Ferrous hydroxide [$Fe(OH)_2$] further reacts with dissolved oxygen and water to produce ferric hydroxide [$Fe(OH)_3$] as shown below:

$4Fe(OH)_2 + O_2 + 2H_2O \rightarrow 4Fe(OH)_3$ ... (2.10)

The corrosion problem in the feedwater line of low pressure boilers is not so serious because of the relatively low water temperature and the no installation of important auxiliary equipment. Recently, the installation of economizer or feedwater preheater utilizing the heat of blowdown water and recovering of condensate as feedwater are actively employed for saving energy. Because these measures increase the feed-water temperature, the corrosion of such equipments and feedwater lines including the tanks becomes serious.

Figure 2.14[13] shows the influence of temperature on carbon steel corrosion. In an open system like the feedwater tank, the corrosion rate increases as the temperature increases up to about 80°C. In closed systems like the feedwater preheater and the economizer, the corrosion rate increases in proportion to the water temperature increase. Photograph 2.3 (p. 2-66) shows the corrosion of an economizer tube.

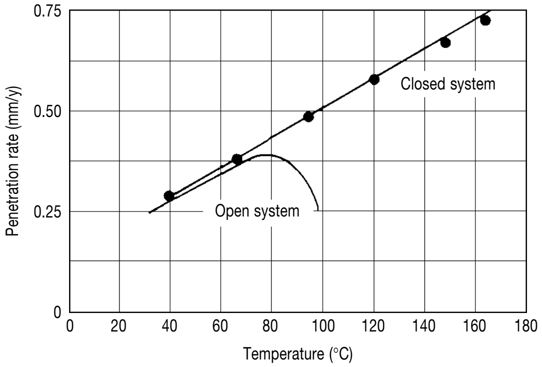


Fig. 2.14 Influence of temperature on carbon steel corrosion in water including dissolved oxygen

In order to prevent the corrosion of the feedwater preheater and economizer, the only pH control of feedwater is insufficient. Thus the use of corrosion resistant materials like stainless steels or the removal of dissolved oxygen from feedwater is employed.

At first, carbon steel tubes were used for the feedwater preheater utilizing the heat of blowdown water. However, since the corrosion problems occurred in a comparatively short period, stainless steel tubes are now widely employed. As the economizer tubes are generally carbon steel, the dissolved oxygen concentration at the inlet has to be kept as low as possible to prevent the corrosion.

For preventing the corrosion of feedwater tanks, the use of corrosion-resistant materials or, the application of coatings or linings is employed.

(b) Corrosion of boiler

The corrosion of low pressure boilers is caused by dissolved oxygen, the precipitation of corrosion products, the concentration of alkalis, etc.

(i) Corrosion due to dissolved oxygen

When the protective film of iron oxide in a boiler is partly destroyed due to the poor boiler water quality, thermal stress, etc., a local cell is formed between the exposed carbon steel surface and the iron oxide film surface contacting with water as shown in Figure 2.15. Ferrous ion yields from the local anode. The ferrous ion (Fe^{2+}) becomes ferric hydroxide [$Fe(OH)_3$] through the reactions of equations (2.9) and (2.10) in the presence of the dissolved oxygen. The corrosion products deposit on the anode as shown in Figure 2.16. Under this condition, an oxygen concentration cell is formed between the steel surface under the deposit and the clean iron oxide film surface because the deposit disturbs the oxygen diffusion through itself. Thus ferrous ions yield moreover from the anode and the local corrosion (pitting) proceeds.

Corrosive anions, such as chloride ion (Cl^-) and sulfate ion (SO_4^{2-}), in boiler water accelerate the corrosion in the presence of the dissolved oxygen as shown in Figure 2.17. Therefore, when the concentration of sulfate ions and chloride ions is high in boiler water, the sufficient oxygen removal is required.

Photographs 2.4 and 2.5 (p. 2-67) show the corrosion caused by the dissolved oxygen in a fire and flue-tube boiler, and a water tube boiler respectively. The both corrosions were caused by the insufficient oxygen removal.

(ii) Corrosion due to the precipitation of corrosion products

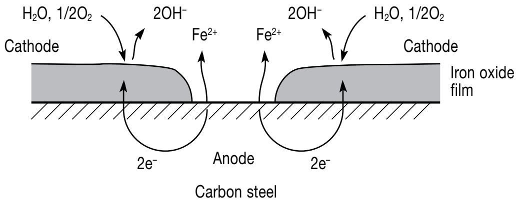


Fig. 2.15 Formation of a local cell due to the partial destruction of oxide film on carbon steel

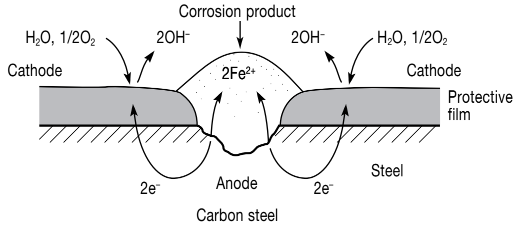


Fig. 2.16 Formation of an oxygen concentation cell due to the deposition of corrosion product

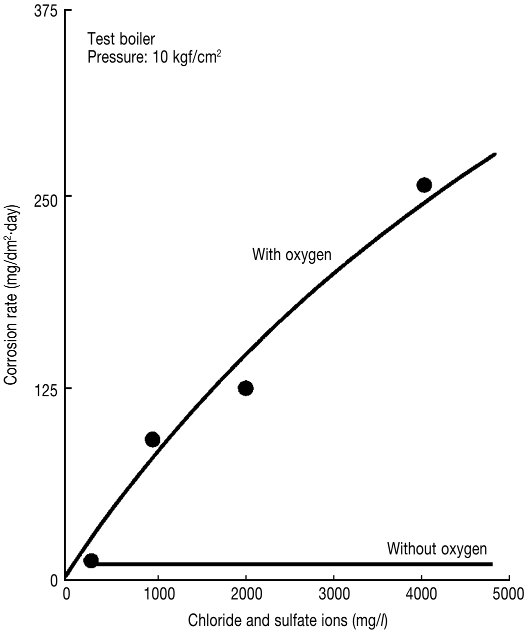


Fig. 2.17 Influence of chloride and sulfate ions on carbon steel corrosion

When corrosion products, such as iron oxide and copper oxide, come into the boiler from the feedwater and condensate lines, they precipitate at the places with the low water circulation, like the drum bottom, or deposit on the evaporation tube surface with higher heat flux. Then the oxygen concentration cells are formed under the precipitation or the deposition of corrosion products, and the corrosion proceeds there if oxygen is present.

(iii) Corrosion due to alkali concentration

When evaporation tubes with the higher heat flux are locally superheated, the boiler water becomes extremely concentrated at that part and the steel is corroded by the concentrated alkali.

However, this type of corrosion is seldom found in low pressure boilers.

Corrosion inhibition methods for low pressure boilers are summarized as follows:

① Removal of dissolved oxygen from the feedwater,
② Control of pH and alkalinity of boiler water,
③ Prevention of boiler water contamination with corrosion products by feedwater and the deposition of corrosion products.

(c) Corrosion of condensate line

Bicarbonate and carbonate ions in feedwater thermally decompose to carbon dioxide gas (CO_2) in a boiler.

$$2HCO_3^- \rightarrow CO_3^{2-} + CO_2 + H_2O \quad \text{..............} \quad (2.11)$$

$$CO_3^{2-} + H_2O \rightarrow 2OH^- + CO_2 \quad \text{..................} \quad (2.12)$$

This carbon dioxide gas transfers to the steam and condensate line along with steam, and dissolves into the condensate as carbonic acid (H_2CO_3) when the steam is condensed.

$$CO_2 + H_2O \rightleftarrows H_2CO_3 \quad \text{..............................} \quad (2.13)$$

$$H_2CO_3 \rightleftarrows H^+ + HCO_3^- \quad \text{............................} \quad (2.14)$$

$$HCO_3^- \rightleftarrows H^+ + CO_3^{2-} \quad \text{..............................} \quad (2.15)$$

In the case of water containing a little dissolved matters, like the condensate, the pH is readily reduced by the presence of a weak acid like carbonic acid because of the weak pH buffering action.

Figure 2.18 shows the relationship between the pH and the concentration of carbon dioxide in water.

The carbonic acid produced by the reaction (2.13) corrodes the carbon steel by the following reaction;

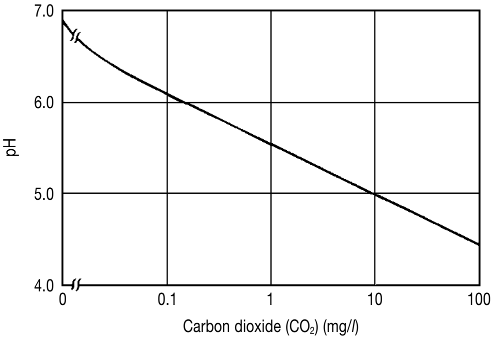


Fig. 2.18 Relationship between the pH and carbon dioxide concentration in water

$$\mathrm{Fe + 2H_2CO_3 \rightarrow Fe(HCO_3)_2 + H_2} \quad \text{..........} \ (2.16)$$

Moreover, the corrosion is promoted by the reproduction of carbon dioxide gas under the presence of dissolved oxygen:

$$\mathrm{2Fe(HCO_3)_2 + 1/2O_2 \rightarrow Fe_2O_3 + 4CO_2 + 2H_2O} \quad \text{....................................} \ (2.17)$$

Figure 2.19[14)] shows the relationship between the corrosion rate of carbon steel and pH under the presence of oxygen and carbon dioxide gas. Figure 2.20 shows the influence of dissolved oxygen (DO) on the carbon steel corrosion in a condensate line. Photograph 2.6 (p. 2-67) shows the corrosion of a condensate piping.

The following measures are required to prevent the corrosion of the condensate line:

① Removal or decrease of carbonate in feedwater (the application of dealkalization softening treatment, etc.),

② The pH control of condensate (the use of volatile amines),

③ Use of corrosion inhibitors (filming amines, etc.),

④ Removal of dissolved oxygen from feedwater (use of oxygen scavengers and deaerators).

(2) Corrosion of medium or high pressure boilers

(a) Corrosion of feedwater and condensate lines

Since demineralized water is used as the feedwater for medium or high pressure boilers, the corrosion of feedwater line before the inlet of the deaerator is not serious because of the comparatively lower feedwater temperature. However, the carbon steel and copper materials of the piping and auxiliary equipments after the deaerator are corroded when the operation of the deaerator or the water treatment is improper because of the higher water temperature.

Figure 2.21 shows the relationship between the pH and total iron of feedwater in a high-pressure

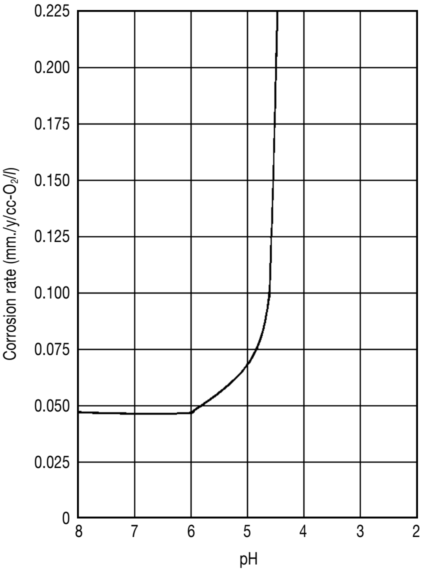


Fig. 2.19 Relationship between the corrosion rate of carbon steel and pH under the presence of oxygen and carbon dioxide gas

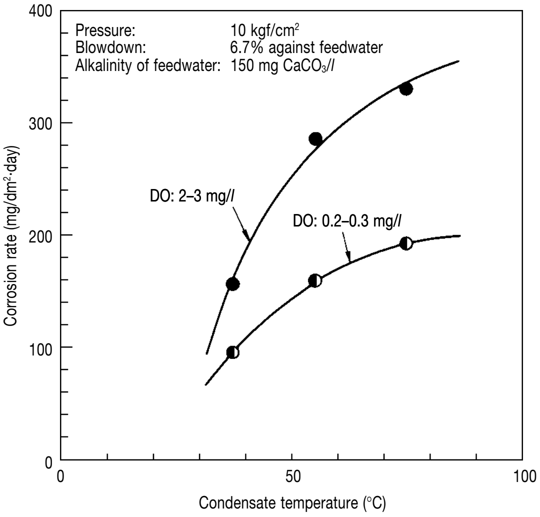


Fig. 2.20 Influence of dissolved oxygen on the corrosion of carbon steel in a condensate line

boiler of 105 kgf/cm². The total iron is reduced by controlling the pH at around 9.

Corrosion problems of deaerators are often found at the nozzles, tray mounting sections and the inner wall in the deaerator chamber. The corrosion of the inner wall contacting with the spray water is due to the dissolved oxygen and the erosion-corrosion caused by a mechanical impact. The use of corrosion resistance materials like stainless steels is the best measure for preventing the deaerator corrosion, however, it is possible to reduce the corrosion by injecting oxygen scavengers at the inlet of the deaerator and by controlling the feedwater pH.

Table 2.6 shows the reduction of total iron in feedwater at the deaerator outlet when the injection point of an oxygen scavenger was changed from the outlet to the inlet of the deaerator.

The materials of heating tubes employed in high pressure feedwater heaters are cupro-nickels, carbon steels, stainless steels and so on. If the oxygen concentration of feedwater becomes higher than the specified concentration by the reduction of deaerator performance, etc., the cupro-nickel and carbon steel tubes may be corroded. Especially in the case of cupro-nickel tubes, the tube cracking sometimes happens.

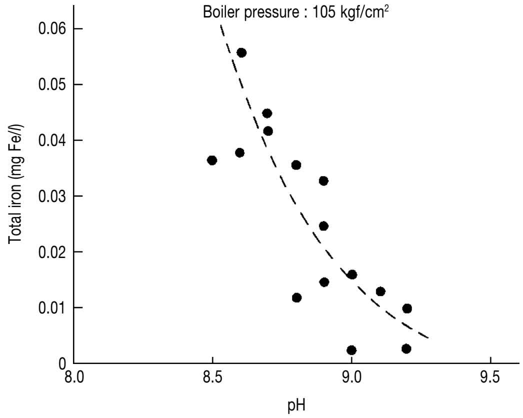


Fig. 2.21 Relationship between the pH and total iron of feedwater

Table 2.6 Relationship between the injection points of an oxygen scavenger and the total iron of feedwater

Injection point of oxygen scavenger	Outlet of deaerator	Inlet of deaerator
Feedwater pH	6.7	8.0
Total iron of feedwater (mg Fe/*l*)	0.43	0.13

Dosage of oxygen scavenger: 0.13 mg/*l* as active ingredient

The carbon steels using as the heating tubes of the economizers are scarcely subjected to corrosion problems under the proper feedwater quality. However, the serious corrosion sometimes happens at the part within approximately 50 cm from the header of water inlet. This type of corrosion is called “inlet attack”, which is a kind of erosion-corrosion due to the turbulent water flow generated at the inlet of the economizer. Photographs 2.7 and 2.8 (p. 2-68) show a typical inlet attack of an economizer.

Basically, the structure should be improved in order to prevent such erosion-corrosion. However, the feedwater treatment is very important to minimize the erosion-corrosion, because a poor feedwater quality, such as a low pH, and a higher concentration of dissolved oxygen and suspended solids accelerates the corrosion. Figure 2.22[15] shows the influence of pH on the erosion-corrosion of carbon steel. The erosion-corrosion is minimized by controlling the pH higher.

Copper and copper alloys are usually employed for the condenser tubes. The corrosion at the steam side of condenser is caused by ammonia

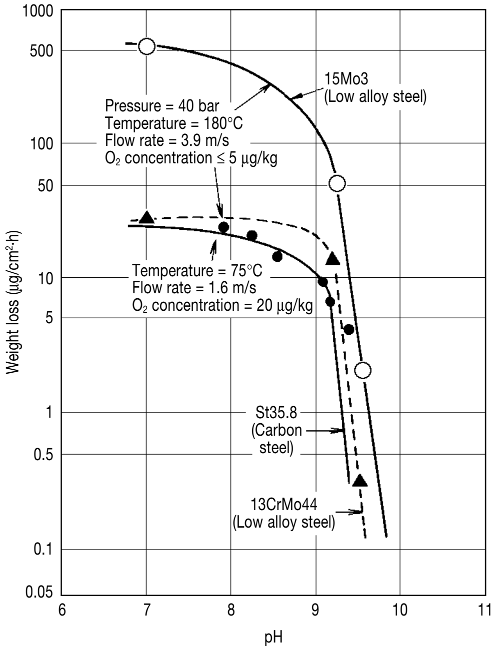


Fig. 2.22 Influence of pH on the erosion-corrosion of carbon steel

and oxygen including in the steam or by the impingement with steam and the mechanical vibration[16)].

When non-condensed gases, such as ammonia and oxygen, are contained in the steam, they are highly concentrated near the air ejector and copper is attacked by the following reactions:

$$Cu + 1/2O_2 + H_2O \rightarrow Cu(OH)_2 \quad \text{.............} \quad (2.18)$$

$$Cu(OH)_2 + 4NH_3 \rightarrow [Cu(NH_3)_4](OH)_2 \quad \text{.....................................} \quad (2.19)$$

$$[Cu(NH_3)_4](OH)_2 \rightleftarrows Cu(NH_3)_4^{2+} + 2OH^- \quad \text{.....................................} \quad (2.20)$$

The parts contacting with condensate including ammonia and oxygen over a long time, like the surroundings of the baffle plates, are also severely attacked as shown in Photograph 2.9 (p. 2-68).

Therefore, a sufficient care is required to avoid an excess dosing of ammonia or hydrazine using for the pH control and oxygen removal. Recently, titanium is sometimes used for the condenser tubes at the near part from the air ejector which tends to be subjected to the influence of ammonia and oxygen.

The erosion-corrosion due to the impingement with steam occurs at the most upper part of the condenser tube bundle where is hit by the steam including the condensate at the high velocity. The mechanical damage of tubes by the vibration occurs when the spacing of baffle plates is an inappropriate or the space between the baffle plate and the tube bundle is large.

(b) Corrosion of boiler

The occurrence of corrosion problems caused by dissolved oxygen is seldom in the case of medium or high pressure boilers because deaerated demineralized water is used as the feedwater. However, a sufficient attention is required for preventing the corrosion caused by alkali and impurities including in the feedwater because of the high thermal load of the evaporation tubes.

(i) Corrosion due to dissolved oxygen

As described above, the corrosion problem caused by dissolved oxygen is not serious under the normal operation of medium or high pressure boilers. However, the corrosion of evaporation tubes by dissolved oxygen sometimes happens during the start-up or the lower loading operation because the performance of deaerator is lowered and the feedwater including dissolved oxygen is supplied into the boiler at that time.

Figure 2.23[17)] shows the influence of pH on the oxygen corrosion of carbon steel in a high pressure and a high temperature water. The weight loss is reduced by increasing the pH. When a relatively higher concentration of oxygen is dissolved in the feedwater, it is required for the corrosion prevention to control the pH of boiler water at the upper level of the control range as well as to increase the dosage of the oxygen scavenger.

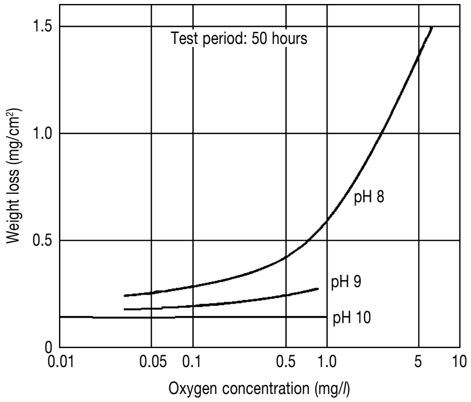


Fig. 2.23 Influence of pH and oxygen on the corrosion of carbon steel in a high pressure and high temperature water

(ii) Corrosion due to alkali

If a evaporation tube with the high heat flux is locally superheated, the boiler water is extremely concentrated at that point. Then hard soluble substances deposit and easy soluble ones, such as sodium hydroxide, form a concentrated film there.

Figure 2.24[18)] shows the relationship between the degree of superheating* and the highest concentration of sodium hydroxide in the concentrated film. When the concentration of sodium hydroxide exceeds approximately 20%, the corrosion of carbon steel rapidly proceeds as shown in Figure 2.25[18)].

The reaction of iron and sodium hydroxide is shown by the following equation:

$$Fe + 2NaOH \rightarrow Na_2FeO_2 + H_2 \quad \text{..............} \quad (2.21)$$

The Na_2FeO_2 produced by the equation (2.21) is stable in the concentrated alkali, but it is decomposed and produces free-alkali when it contacts with boiler water as shown below. Then the corrosion proceeds again.

---

* Difference between the superheated temperature and saturation temperature at a specified pressure.

$$3Na_2FeO_2 + 4H_2O \rightarrow 6NaOH + Fe_3O_4 + H_2 \quad \text{.....................................} \ (2.22)$$

$$3Na_2FeO_2 + 3H_2O + 1/2O_2 \rightarrow 6NaOH + Fe_3O_4 \quad \text{.....................................} \ (2.23)$$

Trisodium phosphate, potassium hydroxide, tripotassium phosphate and so on also cause the alkaline corrosion.

In order to prevent such alkaline corrosion, coordinated phosphate or volatile treatments are generally applied, which yield no free-alkali.

(iii) Corrosion due to impurities in feedwater

When the corrosion products of feedwater and condensate lines come into a boiler, they cause the under deposit corrosion and the alkaline corrosion because their adhesion on the heating surface causes the superheating. The feedwater contamination with seawater from the steam condenser causes the carbon steel corrosion because magnesium chloride in seawater is hydrolyzed and yields hydrochloric acid on the heating surface by the following reactions:

$$MgCl_2 + 2H_2O \rightarrow Mg(OH)_2 + 2HCl \quad \text{.....................................} \ (2.24)$$

$$Fe + 2HCl \rightarrow FeCl_2 + H_2 \quad \text{........................} \ (2.25)$$

The magnesium hydroxide in the reaction (2.24) and the ferrous chloride in the reaction (2.25) react together as shown in the reaction (2.26) and produce magnesium chloride again. Then carbon steel is corroded again.

$$Mg(OH)_2 + FeCl_2 \rightarrow MgCl_2 + Fe(OH)_2 \quad \text{.....................................} \ (2.26)$$

If a sufficient amount of alkali is maintained in the boiler water, it immediately neutralizes the hydrochloric acid produced by the reaction (2.24) and no corrosion happens. When the detection of the seawater leakage to the condensate from the condenser is delayed, the pH of the boiler water is reduced.

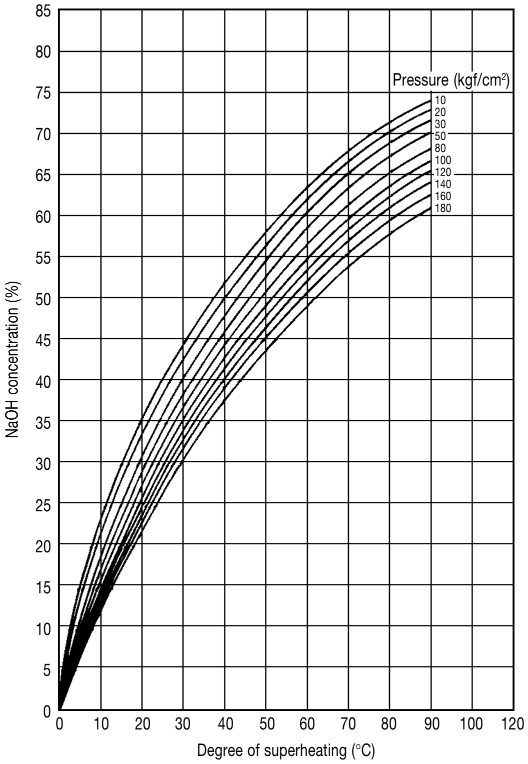


Fig. 2.24 Relationship between the degree of superheating at the inner surface of boiler tube and the highest concentration of NaOH in the concentrated film

(iv) Hide-out

Some substances among the dissolved salts in the boiler water deposit on the heating surface when the boiler load is increased and their concentration is increased in the concentrated film. Then they dissolve again when the load is decreased.

This phenomenon of which a specific salt concentration in the boiler water decreases at the high load because of the deposition and returns to the original concentration at the low load, is called "Hide-out." Sodium phosphate (Na_3PO_4) and so-

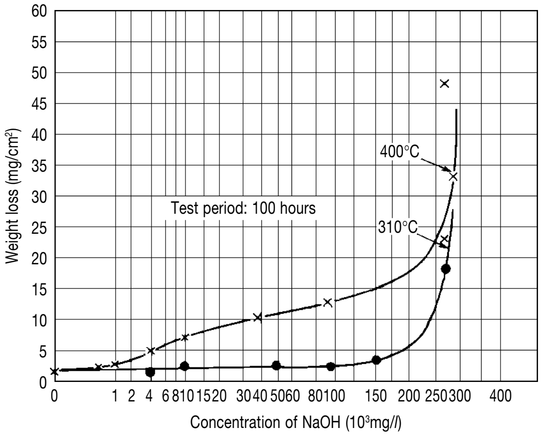


Fig. 2.25 Relationship between alkali concentration and the corrosion of carbon steel

dium sulfate (Na_2SO_4) are typical substances causing the hide-out. Since the solubility of sodium phosphate using as a boiler compound becomes remarkably small at the temperature over 250° C as shown in Figure 2.26[19)], the hide-out is experienced in high pressure boilers with the high heat fluxes.

The influence of the hide-out of sodium phosphate on the tube materials is insignificant in comparison with the alkaline corrosion, but it makes the water quality control difficult. In that case, the application of a volatile or coordinated phosphate treatment is recommended.

2.2.3 Carryover

(1) Carryover in low pressure boiler

Steam generated in boilers essentially includes no dissolved solids, however, the dissolved solids in boiler water sometimes transfer to the steam due to various causes.

This phenomenon is called "Carryover." The following factors are the main causes of carryover, and if the "Priming" or "Foaming" occurs, it accelerates the carryover.

① Factors related to the boiler water quality control:
Excess concentration of the boiler water, the contamination of boiler water with oils and fats, the dissolution of silica to steam, etc.

② Factors related to the operating control of boiler:
Operation at the high water level, the rapid fluctuation of heat load, etc.

③ Factors related to the mechanical structure of boiler:
Poor condition of the water and steam separator, etc.

The priming is an occurrence of abnormal violent evaporation caused by a rapid increase of the heat load and so on. In the result, a large amount of boiler water droplets and foams from the boiler water transfer to the steam line together with the steam.

The foaming is a phenomenon which a large amount of foams are produced on the boiler water surface by the water contamination with fats and oils or by an excess concentration of dissolved solids in the boiler water. In that case, the bubbles containing the dissolved solids transfer to the steam line.

As most of low pressure boilers have no superheater and steam turbine, the problem due to carryover is not serious. However, the carryover leads to a deterioration of the product quality when the steam directly contacts with the products.

Photograph 2.10 (p. 2-69) shows a bursting of the superheater tubes of a boiler with a pressure of 10 kgf/cm^2, caused by the accumulation of dissolved solids in the tubes due to a poor operation condition of the steam and water separator.

Table 2.7 shows a typical analysis of scale accumulated in a superheater by the carryover problem. In case of such scale, the main component is often sodium sulfate. Since the solubility of sodium sulfate in superheated steam is lower[20)] than that of the other salts, such as sodium chloride

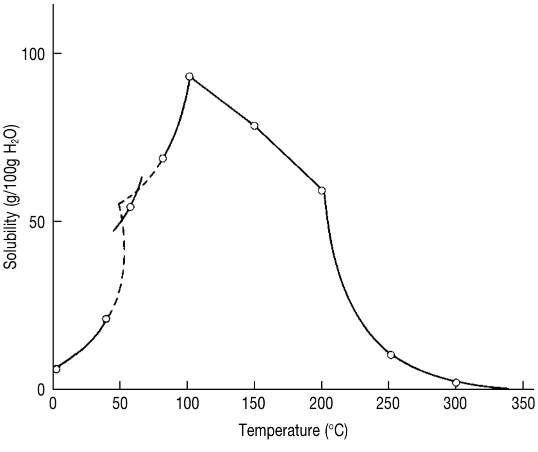


Fig. 2.26 Relationship between the solubility of trisodium phosphate and water temperature

Table 2.7 Analysis of a scale accumulated in a superheater by the carryover problem

(Weight %)

Calcium oxide (CaO)	Trace
Magnesium oxide (MgO)	Trace
Iron oxide (Fe_2O_3)	Trace
Copper oxide (CuO)	Trace
Acid insoluble matter	11.1
Sulfuric acid anhydride (SO_3)	32.5
Carbonic acid anhydride (CO_2)	5.1
Phosphoric acid anhydride (P_2O_5)	1.4
Ignition loss	4.8
Zinc oxide (ZnO)	Trace
Aluminum oxide (Al_2O_3)	Trace
Sodium oxide (Na_2O)	38.2

and sodium hydroxide, it easily deposits and accumulates in superheater tubes.

In order to prevent carryover in a low pressure boiler, the boiler has to be operated with a constant load and appropriate water level along with a suitable control for boiler water quality and blowdown.

(2) Carryover in medium or high pressure boilers

Since the medium or high pressure boilers are equipped with the superheaters and steam turbines in many cases, the sufficient attention must be paid to prevent the carryover. The main cause of carryover in the medium or high pressure boilers is the dissolution of dissolved salts and metal oxides in the boiler water into the steam[21]. The carryover due to the transfer of the boiler water to the steam line scarcely occurs.

The solubility of salts and metal oxides in steam becomes higher as the steam pressure and temperature increase. The carryover of silica is a primary problem especially in the case of subcritical pressure boilers because the solubility of silica in steam is higher than those of the other salts and metal oxides. Figure 2.27[22] shows the solubility of silica in superheated steam.

When steam containing silica and other salts is supplied to a steam turbine, these salts deposit and adhere on the turbine blades and nozzles. Thus the turbine efficiency is reduced. Figure 2.28[23] shows a typical relationship between scale composition and the stage of turbine blades. Sodium salts deposit at the high-pressure stages and silica mainly deposits at after the medium-pressure stages.

The silica concentration in steam must be kept below 0.02 mg SiO_2/l for preventing the silica deposition on turbine blades.

The silica concentration in steam is calculated from the boiler pressure and the silica concentration in boiler water by using the following equation[24]:

$$\log A = 0.0135 \times P + \log B - 3.6 \quad \ldots\ldots\ldots\ldots\ldots \quad (2.27)$$

where

A = silica concentration in steam (mg SiO_2/l)
B = silica concentration in boiler water (mg SiO_2/l)
P = boiler pressure (kgf/cm^2)

Figure 2.29 shows the relationship between boiler pressure and the maximum allowable concentration of silica in boiler water in the case that the allowable silica concentration in steam is set

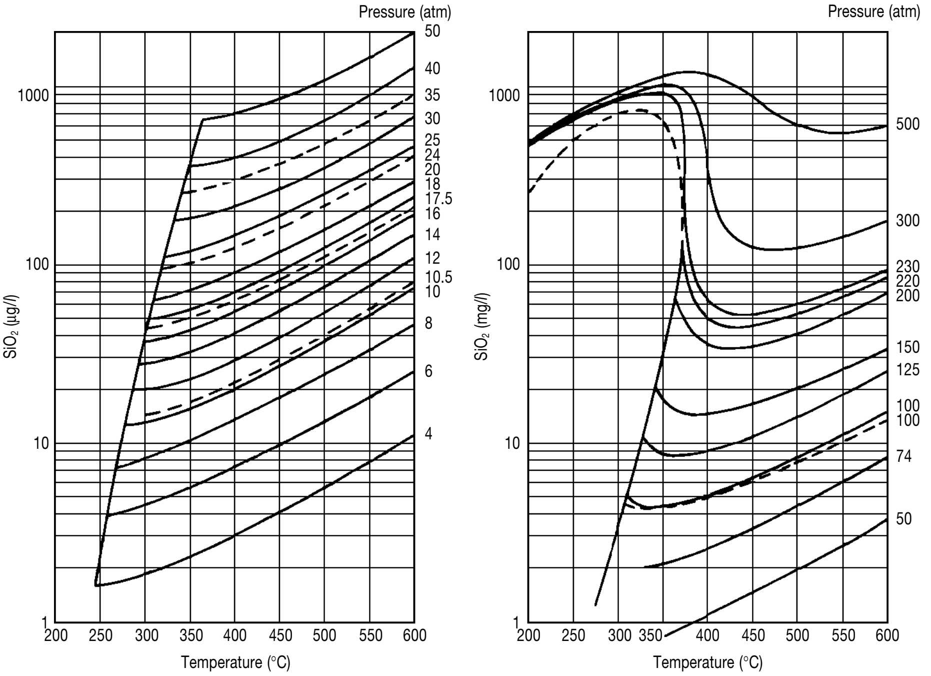


Fig. 2.27 Solubility of silica in superheated steam

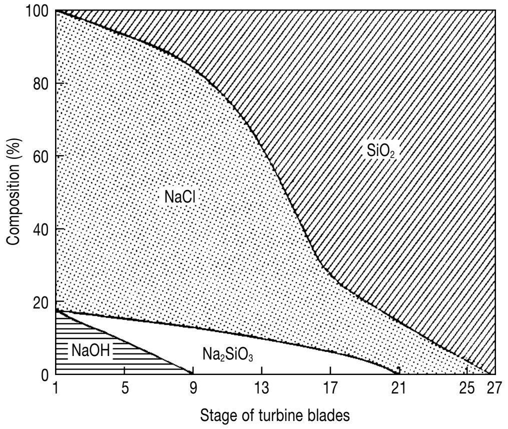


Fig. 2.28 **Relationship between scale compositions and the stage of turbine blade**

at 0.02 mg SiO_2/l. Figure 2.30[25)] shows the distribution ratio of silica in the boiler water to the steam. When the silica concentration in boiler water increases, the silica concentration in steam increases. Therefore, it is required to control the silica concentration in the boiler water below an allowable concentration so as to keep the silica concentration in steam below 0.02 mg/l.

When the silica concentration in boiler water increases due to a poor operation condition of demineralizer or the presence of colloidal silica in the feedwater, the pH of boiler water must be controlled at the upper limit of the control range and the blowdown rate is increased.

2.3 External Boiler Water Treatment

Since various substances exist in raw water, the use of the raw water for boilers causes various problems in the boilers and their auxiliary equipments as described in the section 2.2. In order to prevent these problems, a proper water treatment should be applied for each boiler system. Boiler water treatments are classified into the chemical treatment (internal) and the mechanical (external) treatment.

The external boiler water treatment is discussed in this section.

2.3.1 Raw Water and Feedwater Treatments

For the raw water and feedwater treatments, coagulation, sedimentation, filtration, ion exchange, deaeration treatments and so on are applied alone or in the combination according to the quality of

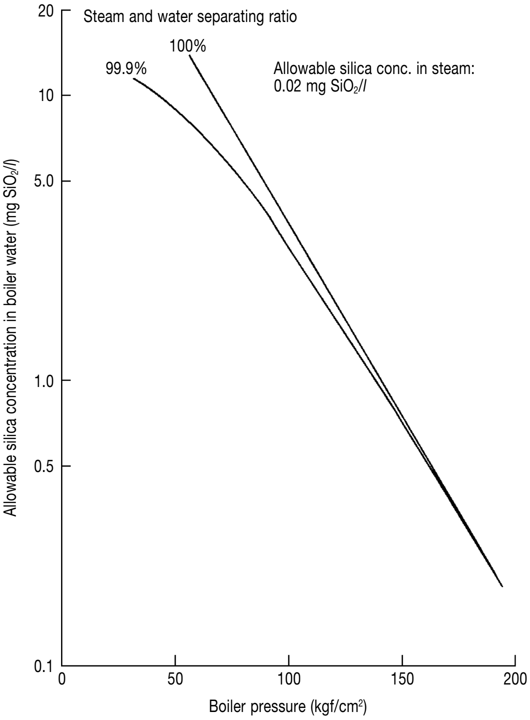


Fig. 2.29 **Relationship between boiler pressure and the allowable silica concentration in boiler water**

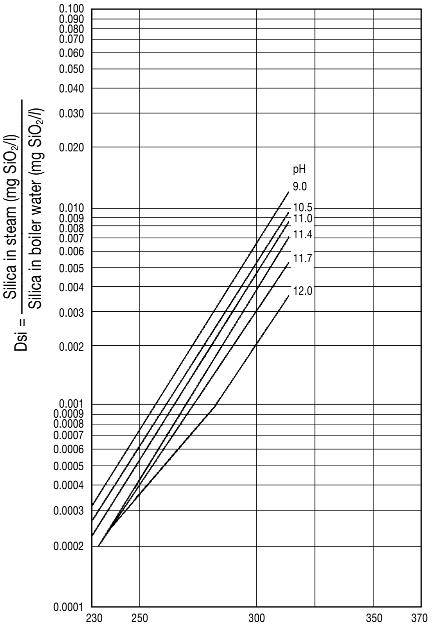


Fig. 2.30 **Distribution ratio (Dsi) of silica between boiler water and steam**

the raw water and the purpose of the treatment.

In this section, the ion exchange and the deaeration treatments are mainly discussed.

(1) Ion exchange treatment

In ion exchange treatment, dissolved ions in raw water are removed or exchanged by using ion exchange resins to obtain the appropriate quality of treated water for each boiler system. The removal of all dissolved ions is called the demineralization. The exchange of calcium and magnesium ions with sodium ions is called the softening.

(a) Softening

The hardness component (Ca^{2+} and Mg^{2+}) causing scale problems in low pressure boilers are exchanged with sodium ion (Na^+) by using cation exchange resins.

The ion exchange resins used for the softening are the Na-form of the strongly acidic cation exchange resins. When raw water is passed through the bed containing this resin, the hardness components (Ca^{2+} and Mg^{2+}) in the raw water are exchanged with Na^+ ions of the ion exchange resin and the softened water is obtained as shown in the reactions (2.28), (2.29) and the Figure 2.31.

(Softening reactions)

$$R(\text{-}SO_3Na)_2 + Ca^{2+} \rightarrow R(\text{-}SO_3)_2Ca + 2Na^+ \quad \text{......} \quad (2.28)$$

$$R(\text{-}SO_3Na)_2 + Mg^{2+} \rightarrow R(\text{-}SO_3)_2Mg + 2Na^+ \quad \text{......} \quad (2.29)$$

The ion exchange resin losing its exchange capability is regenerated by using about 10 percent sodium chloride solution and reused. The following reactions show the regeneration reactions of the resin.

$$R(\text{-}SO_3)_2Ca + 2Na^+ \rightarrow R(\text{-}SO_3Na)_2 + Ca^{2+} \quad \text{......} \quad (2.30)$$

$$R(\text{-}SO_3)_2Mg + 2Na^+ \rightarrow R(\text{-}SO_3Na)_2 + Mg^{2+} \quad \text{......} \quad (2.31)$$

Scale problems with hardness components are prevented by feeding the softened water to boilers. But actually, scale problems still occur because the hardness leakage from softeners often happens by the result of the insufficient operational control. Table 2.8 shows the causes of troubles and the countermeasures in the operation of softener.

(b) Demineralization

Most popular demineralizer is a two-beds and one-degasifier type. This demineralizer is composed of a cation column filled with the H-form of strongly acidic cation exchange resin (H-bed), a degasifier and an anion column filled with the OH-form of strongly basic anion exchange resin (OH-bed).

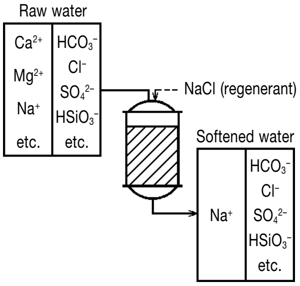


Fig. 2.31 Softening treatment

Table 2.8 Causes and their countermeasures of hardness leakage from softeners

Trouble	Cause	Countermeasure
Sudden increase in hardness of treated water	Intake of softened water over the capacity of softener	Regeneration of resin
Fluctuation in softened water production for one cycle	Fluctuation in hardness of raw water	Periodical analysis of hardness in raw and product water
Gradual reduction of water production	Deterioration of exchange capacity of resin	Supplement of resin Removal of contaminants from resin and raw water
Leakage of resin	Break of valves, water collecting plate, etc.	Repair of softener
Swelling of resin	Oxidation of resin by chlorine, etc.	Supplement of resin Removal of oxidizing substances from raw water
Continuous leakage of hardness	Break of valves Poor regeneration and insufficient backwashing of resin	Repair of softener Application of appropreate regeneration and backwashing of resin

As shown in Figure 2.32, the cations in raw water are exchanged with hydrogen ions (H^+) in the H-bed and the carbon dioxide generated by the pH reduction is removed in the decarbonator. Then, the anions are exchanged with hydroxide ions (OH^-) in the OH-bed. Converting the decarbonator into a vacuum deaerator system makes it possible to remove dissolved oxygen and carbon dioxide simultaneously.

The electrical conductivity and silica content of demineralized water are 5 to 10 μS/cm and 0.05 to 0.3 mg SiO_2/l respectively. In the case that the treated water is used as the feedwater for a high pressure boiler, the water is additionally treated by a mixed bed type demineralizer (polisher).

The typical reactions of demineralization are as follows:

H-bed;

$$R(\text{-}SO_3H)_2 + Ca^{2+} \rightarrow R(\text{-}SO_3)_2Ca + 2H^+ \quad \cdots\cdots \ (2.32)$$

$$R(\text{-}SO_3H)_2 + Mg^{2+} \rightarrow R(\text{-}SO_3)_2Mg + 2H^+ \quad \cdots\cdots \ (2.33)$$

$$R\text{-}SO_3H + Na^+ \rightarrow R\text{-}SO_3Na + H^+ \quad \cdots\cdots \ (2.34)$$

OH-bed;

$$R{\equiv}NOH + HCO_3^- \rightarrow R{\equiv}NHCO_3 + OH^- \quad \cdots\cdots \ (2.35)$$

$$R({\equiv}NOH)_2 + SO_4^{2-} \rightarrow R({\equiv}N)_2SO_4 + 2OH^- \quad \cdots\cdots \ (2.36)$$

$$R{\equiv}NOH + Cl^- \rightarrow R{\equiv}NCl + OH^- \quad \cdots\cdots \ (2.37)$$

$$R{\equiv}NOH + HSiO_3^- \rightarrow R{\equiv}NHSiO_3 + OH^- \quad \cdots\cdots \ (2.38)$$

The reactions of the regeneration of resin are as follows:

H-bed;

$$R(\text{-}SO_3)_2Ca + 2H^+ \rightarrow R(\text{-}SO_3H)_2 + Ca^{2+} \quad \cdots\cdots \ (2.39)$$

$$R(\text{-}SO_3)_2Mg + 2H^+ \rightarrow R(\text{-}SO_3H)_2 + Mg^{2+} \quad \cdots\cdots \ (2.40)$$

$$R\text{-}SO_3Na + H^+ \rightarrow R\text{-}SO_3H + Na^+ \quad \cdots\cdots \ (2.41)$$

OH-bed;

$$R{\equiv}NHCO_3 + OH^- \rightarrow R{\equiv}NOH + HCO_3^- \quad \cdots\cdots \ (2.42)$$

$$R({\equiv}N)_2SO_4 + 2OH^- \rightarrow R({\equiv}NOH)_2 + SO_4^{2-} \quad \cdots\cdots \ (2.43)$$

$$R{\equiv}NCl + OH^- \rightarrow R{\equiv}NOH + Cl^- \quad \cdots\cdots \ (2.44)$$

$$R{\equiv}NHSiO_3 + OH^- \rightarrow R{\equiv}NOH + HSiO_3^- \quad \cdots\cdots \ (2.45)$$

When the quality of demineralized water is deteriorated, the cause should be surveyed and the countermeasures must be applied to improve the water quality. Typical causes of the water quality deterioration are as follows:

① Deterioration of raw water quality,
② Excess water intake over the capacity of demineralizer,
③ Insufficient regeneration of ion exchange resin,
④ Deterioration or contamination of resin,
⑤ Mechanical troubles of demineralizer.

(2) Deaeration

The deaeration of boiler feedwater is carried out to remove the corrosive dissolved gasses (oxygen and carbon dioxide) for preventing corrosion problems in boiler systems.

The deaeration utilizes the fundamental principle that the solubility of dissolved gasses in water becomes zero at the boiling point of water. Thus deaeration methods are divided into vacuum and heating deaerations.

(a) Heating deaeration

In the case of heating deaeration, the dissolved gasses in boiler feedwater are removed by heating the feedwater up to the saturation tempera

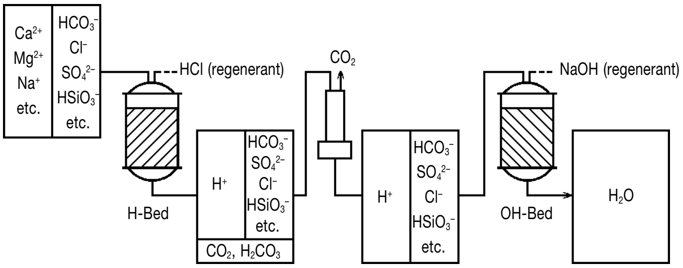


Fig. 2.32 Demineralization treatment (2-beds and 1-degasifier type)

ture (boiling point) under the inner pressure of a deaerator.

This system is widely used for medium or high pressure boilers because the dissolved oxygen in feedwater is deaerated to less than 0.007 mg/*l*. Figure 2.33[26)] shows the typical structure of a spray-tray type deaerator.

Recently, boilers equipped with the internal deaerators become popular in Japan. The internal deaerator is a kind of heating deaerator and utilizes the steam generated from the boiler for heating the feedwater to remove the dissolved gasses in the steam drum. The dissolved oxygen in the feedwater is removed to about 0.5 mg/*l*. Figure 2.34 shows the structure of an internal deaerator.

In the case of internal deaerator, the performance of deaeration becomes insufficient when the boiler is restarted after the stoppage. Therefore, it is necessary to increase the dosage of oxygen scavenger at the start-up time.

(b) Vacuum deaeration

Vacuum deaerators remove the dissolved gasses in water by reducing the pressure in the inside to the vapor pressure of the water corresponding to the water temperature. The dissolved oxygen in the deaerated water becomes around 0.1 to 0.3 mg/*l*. This system is mainly used for low pressure boilers.

2.3.2 Condensate Treatment

When steam condensate is recovered as boiler feedwater, the suspended solids consisting of corrosion products mainly and the dissolved solids in the condensate must be removed in accordance with the required feedwater quality.

The condensate treatment for low pressure boilers is mainly chemical treatment. However, medium or high pressure boilers require the chemical treatments together with the mechanical treatments because they require the high purity of feedwater.

Filtration and ion exchange treatment are used either alone or in the combination according to the substances and their concentration to be removed from condensate, and the required feedwater quality.

The relationship between the boiler pressure and the condensate treatment equipments applied is shown in Table 2.9.

(1) Filtration

The suspended solids contained in condensate are mainly corrosion products such as iron oxides. The amount of corrosion products in condensate is minimized by chemical treatment, but some corrosion products may be present in condensate depending on the operating conditions of boiler and the structure of condensate line.

Filters of various types are used for removing those corrosion products from condensate. The filtration units are divided into the cartridge type and the precoat type. The cartridge type filter removes corrosion products of 1 to 5 μm or more in the particle size.

The precoat type filter removes the suspended solids of more than 0.5 μm in the particle size from condensate.

The precoat filters are divided into the tubular type and the leaf type. Their structures are shown in Figures 2.35[27)] and 2.36[28)] respectively.

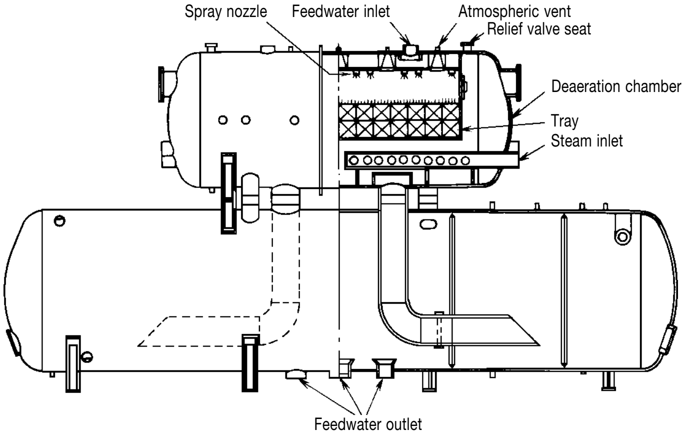


Fig. 2.33 Structure of a spray-tray type deaerator

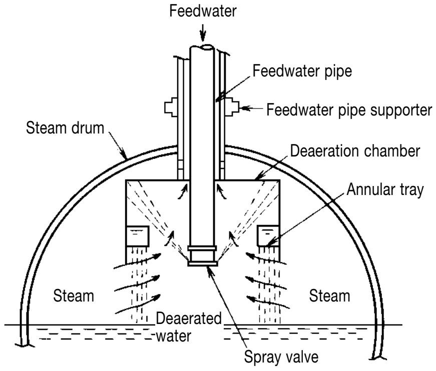


Fig. 2.34 Structure of an internal deaerator

Table 2.9 Relationship between boiler pressure and the condensate treatment equipments

Boiler pressure / Equipment	Low	Medium	High
Cartridge filter	○	×	×
Precoat filter	×	○	○
Demineralizer	×	△	○
Precoat filter with powder type ion exchange resin	×	×	○
Electro-magnetic filter	×	×	○

Note: ○ applied, △ sometimes applied, × not applied

In general, the iron oxide concentration in the filtrate from precoat filters becomes 0.01 to 0.03 mg Fe/*l* or less.

(2) Demineralization

Demineralization treatment removes the small amounts of dissolved solids in condensate by using mixed bed demineralizers (condensate polishers) which contain the strongly acidic cation exchange resin of H-form and the strongly basic anion exchange resin of OH-form.

In the case of medium or high pressure boilers in manufacturing plants, the polisher of main demineralizer often utilizes for polishing the condensate recovered.

The temperature of condensate fed to the demineralizer should be reduced less than 40°C to prevent the deterioration in the ion exchange capacity of the anion resin.

2.4 Internal Boiler Water Treatment

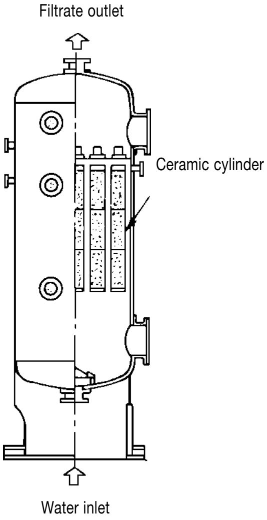


Fig. 2.35 Tubular type precoat filter

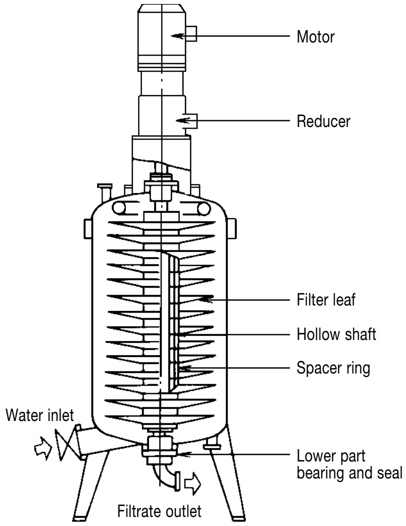


Fig. 2.36 Leaf type precoat filter

Even if the external boiler water treatment is employed, it is difficult to perfectly prevent the boiler water contamination with substances which cause the corrosion and scale problems. Boiler water treatment chemicals are used for protecting whole boiler systems including the feedwater and the steam condensate line from those problems.

2.4.1 Kinds of Boiler Treatment Chemicals and Their Functions

The kinds, functions and typical chemical names of boiler treatment chemicals are summarized in Table 2.10.

The main purposes of these chemical application are as follows:

① The scaling components are converted to the suspended fine sludge so as to be easily discharged from boiler with blowdown water to prevent the scale formation on the heating surface of boilers.

② The pH of boiler water is maintained in an adequate alkaline range to prevent the corrosion and silica scale formation by keeping silica in the water soluble form.

③ Dissolved oxygen is removed from feedwater and boiler water to prevent the corrosion.

④ The pH of condensate is kept in an appropriate range to prevent the corrosion of condensate line by oxygen and carbon dioxide.

⑤ Prevention of carryover problems.

The quality control criteria of boiler water have been established to attain these purposes. These chemicals show the insufficient effects if the application conditions are inadequate. Therefore, the sufficient attention must be paid for the chemical injection control and the quality control of feedwater and boiler water.

2.4.2 Boiler Compounds

Boiler compounds have two functions, that is, preventing scale formation and adjusting the pH of boiler water to inhibit corrosion. The boiler compounds are classified into two groups of phosphate and non-phosphate bases according to their main components as shown in Figure 2.37.

(1) Phosphate based boiler compounds

Phosphates formulated in the phosphate based boiler compounds are listed in Table 2.11. These phosphates must be used selectively based on the boiler pressure, the quality of feedwater, etc.

(a) Boiler compounds for low pressure boilers

Phosphate based boiler compounds for low pressure boiler contain phosphates and alkalis. Both phosphates and alkalis prevent scale formation on the heating surfaces of boilers by the following functions:

Table 2.10 Kinds, functions and typical chemical names of boiler treatment chemicals

Kind	Function	Chemical name
Alkalinity and pH control agents	Control of the pH and alkalinity of feedwater and boiler water to prevent corrosion and scaling	Sodium hydroxide Sodium carbonate Sodium phosphates Sodium polyphosphates Phosphoric acid
Scale inhibitors	Scale control by converting the hardness components in boiler water to insoluble precipitates to discharge from system with blowdown water	Sodium hydroxide Sodium phosphates Sodium polyphosphates Potassium phosphates
Sludge dispersants	Dispersion of suspended solids in boiler water so as to be easily discharged by blowdown to prevent the scaling	Synthetic polymers Tannins Sodium lignin sulfonates Starches
Oxygen scavengers	Removal of dissolved oxygen from feedwater and boiler water to prevent corrosion	Sodium sulfite Hydrazine Saccharides Tannins Amines Polyphenols
Antifoaming agents	Prevention of foaming of boiler water for preventing carryover problems	Surfactants
Corrosion inhibitors for condensate line	pH control of condensate and protective film formation to prevent corrosion	Ammonia Morpholine Cyclohexylamine Alkylamines Hydroxyl amines

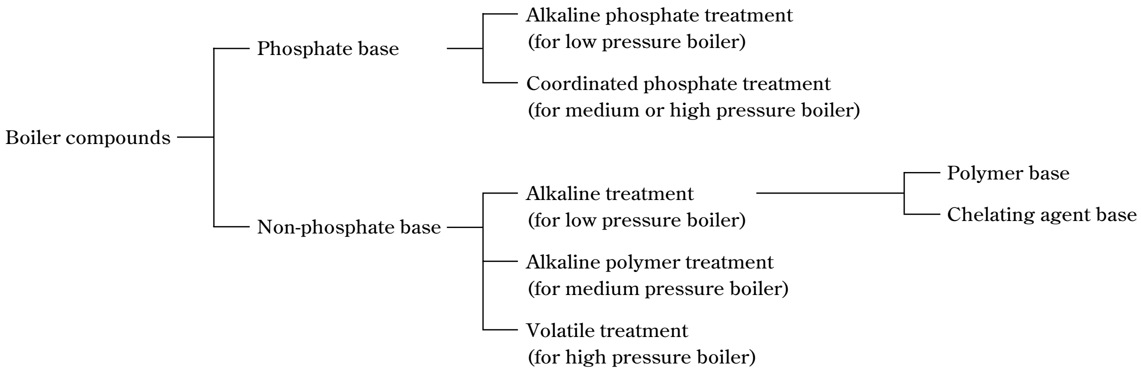


Fig. 2.37 Classification of boiler compounds

Table 2.11 Phosphates used for boiler compounds

Chemical name	Appearance	pH (1% sol.)	PO_4 (%)	P_2O_5 (%)	Remarks
Trisodium phosphate	$12H_2O$ salt: White crystal	12.0	24.9	18.9	Commonly used
	Anhydride: White powder		57.6	43.2	
Disodium hydrogen phosphate	$12H_2O$ salt: White crystal	8.2	26.5	19.9	
	Anhydride: White powder		66.8	50.1	
Sodium dihydrogen phosphate	$2H_2O$ salt: White crystal	4.3	60.8	45.6	
	Anhydride: White powder		79.1	59.3	
Sodium hexametaphosphate	White powder or flake	6.0–7.2	93.1	69.9	Hydrolyzed in boiler water to produce NaH_2PO_4
Sodium tripolyphosphate	White powder	9.0–9.5	77.5	58.1	Hydrolyzed in boiler water to produce $2Na_2HPO_4$ and NaH_2PO_4

① By reacting with hardness components (Ca^{2+}, Mg^{2+}) in water and converting them into the suspended solids to be easily discharged from boiler with blowdown water,

② By keeping silica in the water soluble form.

Among the hardness components in water, calcium ion forms calcium carbonate ($CaCO_3$) and calcium silicate ($CaSiO_3$), and deposits as the scale without boiler compounds. Under the coexistence of phosphates, calcium ions form the suspended fine particles of hydroxyapatite $\{[Ca_3(PO_4)_2]_3Ca(OH)_2\}$ which scarcely form the scale. That reaction is expressed in the equation (2.46). In this case, the required amount of phosphate against 1 mg $CaCO_3$/l of calcium hardness is 0.57 mg PO_4^{3-}/l.

$$10Ca^{2+} + 6PO_4^{3-} + 2OH^- \rightarrow [Ca_3(PO_4)_2]_3 \cdot Ca(OH)_2 \quad \text{......} \quad (2.46)$$

Magnesium ions never react with phosphates but react with alkalis to form suspended magnesium hydroxide [$Mg(OH)_2$] and magnesium silicate ($MgSiO_3$).

$$Mg^{2+} + 2OH^- \rightarrow Mg(OH)_2 \quad \text{......} \quad (2.47)$$

$$Mg^{2+} + HSiO_3^- + OH^- \rightarrow MgSiO_3 + H_2O \quad \text{......} \quad (2.48)$$

The magnesium silicate tends to form the scale if the pH of boiler water is low. The analyses of typical scales in a boiler are shown in Table 2.12. The larger amounts of acid insoluble matter (silica) and magnesium oxide (MgO) are found in the scale of the internal feedwater pipe comparing with the other scales. The lower water pH near the feedwater pipe may cause such silica scale formation. Therefore, the control of the pH and P-alkalinity of boiler water is important for preventing magnesium scales.

Silica is stabilized in the form of water soluble sodium metasilicate (Na_2SiO_3) by reacting with alkalis.

Table 2.12 Typical analyses of scales in a boiler

(Weight %)

Sample	Scale of upper drum	Scale of internal feedwater pipe	Scale in evaporation tube
Color	Light brown	Beige	Light brown
Calcium oxide (CaO)	15.1	6.7	25.9
Magnesium oxide (MgO)	2.9	18.2	6.7
Iron oxide (Fe_2O_3)	41.8	1.4	5.2
Copper oxide and copper (CuO)	Trace	Trace	Trace
Acid insoluble matter	17.4	46.6	29.5
Sulfuric acid anhydride (SO_3)	Trace	Trace	Trace
Carbonic acid anhydride (CO_2)	Trace	Trace	Trace
Phosphoric acid anhydride (P_2O_5)	12.3	7.2	15.5
Ignition loss (600 ± 25° C)	3.5	7.3	4.3

Remarks: Main component of acid insoluble matter is usually silica.

$$H_2SiO_3 + 2NaOH \rightarrow Na_2SiO_3 + 2H_2O \quad \text{.....} (2.49)$$

The reaction (2.49) shows that the required amount of alkali as P-alkalinity to keep silica in the soluble form in boiler water is 1.7 times of silica concentration in mg SiO_2/l. Accordingly, the pH and phosphate concentration of boiler water must be maintained in the appropriate ranges for preventing the scale problems of boilers.

Another function of boiler compounds is the adjustment of pH and P-alkalinity of boiler water. In general, the M-alkalinity components in raw water mainly exist in the form of bicarbonates. Those bicarbonates are converted to sodium bicarbonate by treating with softener. The sodium bicarbonate is thermally decomposed to sodium carbonate and carbon dioxide in boiler water. Then, the sodium carbonate, further decomposes into sodium hydroxide and carbon dioxide.

$$2NaHCO_3 \xrightarrow{Heat} Na_2CO_3 + CO_2 + H_2O \quad \text{.....} (2.50)$$

$$Na_2CO_3 + H_2O \xrightarrow{Heat} 2NaOH + CO_2 \quad \text{.....} (2.51)$$

Thus carbonate alkali changes to caustic alkali (P-alkalinity) in boilers. This decomposition of bicarbonate is essentially affected by temperature, pH, heating period, etc. For obtaining the thermal decomposition rate in boilers, Figures 2.38 and 2.39 are generally used.

When the P-alkalinity to be maintained in the boiler water is higher than the P-alkalinity given by the feedwater, the difference must be supplied by a boiler compound. In this case, an alkaline boiler compound is used. While, if the P-alkalinity given by the feedwater is in an excess, the P-alkalinity of boiler water must be lowered to the desired level by using an acidic boiler compound. When the acidic boiler compound is used, the corrosion of the chemical injection line and the feedwater line may be sometimes promoted due to the acidity of the compound. Therefore, the dealkalization softening of feedwater is sometimes employed to avoid the use of acidic boiler compounds.

The following measures should be carried out for obtaining the sufficient effects provided by boiler compounds:

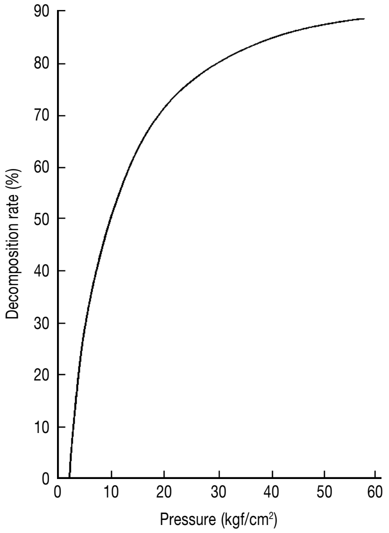


Fig. 2.38 **Relationship between the decomposition rate of carbonate alkali to caustic alkali and boiler pressure**

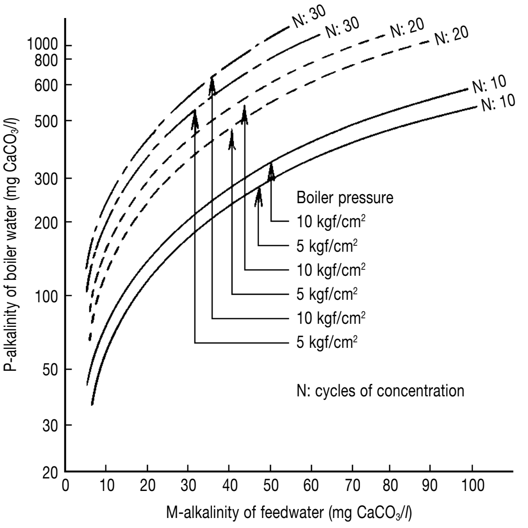


Fig. 2.39 Relationship between the M-alkalinity of feedwater and P-alkalinity of boiler water under various boiler pressure and cycles of concentration

(i) Initial dosing

When boiler operation starts up after a scheduled inspection, the initial dosing of a boiler compound is done to keep the pH and the phosphate ion concentration of the boiler water within their control limits for preventing the scale and corrosion problems. However, when an acidic boiler compound is applied, the initial dosing is prohibited to avoid the acid corrosion.

(ii) Chemical dissolution

Boiler compounds should be dissolved with softened water, demineralized water, or feedwater. If raw water is used, the hardness components will precipitate with the boiler compounds in the dissolving tank, which causes the clogging of chemical feed line.

(iii) Chemical dosing

As the boiler compounds are usually alkaline, they attack copper and copper alloys. Therefore, a sufficient attention should be paid for selecting the materials of chemical dosing system and the dosing point.

(iv) Measure for hardness leakage from softener

When a hardness leakage from a softener is detected or the white turbidity of boiler water is observed, boiler compounds must be additionally dosed to keep the specified concentration of phosphate in boiler water.

(v) Analysis of phosphate ion concentration

When the phosphate ion concentration is analyzed, the sample water must be filtered. If not, the suspended hydroxyapatite will be dissolved by the analytical reagent and will give a positive error.

(b) Boiler compounds for medium or high pressure boilers

Generally, alkaline or coordinated phosphate treatments are applied for medium pressure boilers. For high pressure boilers with the high heat flux, coordinated phosphate treatments are employed in order to prevent the alkali corrosion of the heating surfaces.

That is, the boiler compounds for the coordinated phosphate treatment of medium or high pressure boilers must be designed so as to yield no free alkali in boiler water and to have the optimum Na/PO_4 mole ratio suitable for the water quality control standard of each boiler. The relationship among pH, phosphate ion concentration and the Na/PO_4 mole ratio of boiler compound is shown in Figure 2.40. Phosphate based boiler compounds of the mole ratio 2.6 to 3.0 are generally employed for medium or high pressure boilers.

The pH of boiler water sometimes decreases due to the contamination with organic matters, such as humic and fulvic acids, which are hardly removed by the external water treatments. In that

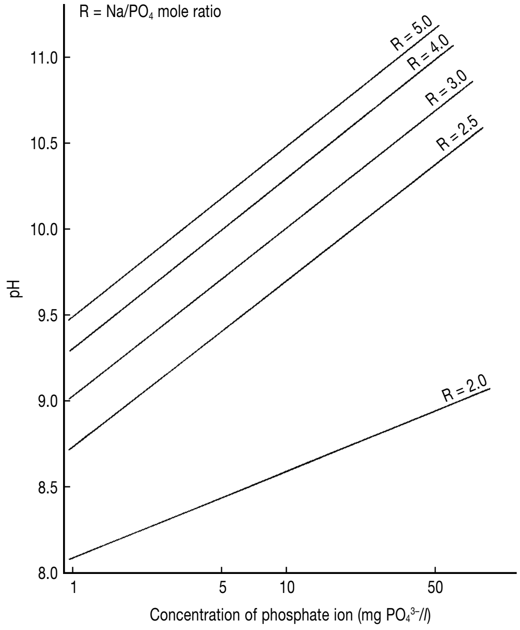


Fig. 2.40 Relationship among pH, phosphate ion concentration and the Na/PO_4 mole ratio of boiler compound

case, the boiler compounds of the Na/PO_4 mole ratio of more than 3.0 may be applied to prevent the pH drop of boiler water.

(2) Non-phosphate based boiler compounds

During these twenty years, the occurrence of “red tide” caused by nutrification in Japanese closed water areas, such as the Biwa Lake and the Setonaikai, has become one of serious water pollution problems. Since many local governments have enforced the regulations to prevent the discharge of effluent including phosphorous for preventing the nutrification, non-phosphorous boiler compounds have been developed. The non-phosphorous boiler compounds for low or medium pressure boilers are classified into polymer based and chelating agent based ones.

(a) Polymer based boiler compounds

Natural polymers and synthetic polymers shown in Table 2.13 have been employed as sludge dispersants in combination with phosphate based boiler compounds. Among them, some kinds of synthetic polymers have been found to show the excellent scale inhibitions without phosphate in the boiler water of high pH and high temperature, and have been utilized as non-phosphorous boiler compounds. Their mechanisms for scale prevention are as follows:

① Reduction of the crystal growth rate of scale by changing the crystal structure (crystal distortion),

② Dispersion of micro-crystals of scale by giving the negative electrical charges against the crystals with the polymer adsorption.

(i) Inhibition of calcium carbonate scale

Figure 2.41 shows the inhibition effects of various chemicals against calcium carbonate scaling on heat transfer surface. Among those chemicals, an acrylic acid homopolymer (polymer A) shows the best performance.

The polymer A reduces the crystal growth rate of calcium carbonate (calcite) by the crystal distortion effect mainly. Photographs 2.11 to 2.13 show the crystal distortion effect of polymer A. Photograph 2.11 shows the normal crystals of calcium carbonate formed in the absence of polymer A. Photograph 2.12 shows the calcium carbonate crystals formed in the presence of an insufficient concentration of polymer A. Photograph 2.13 shows the crystals perfectly distorted by dosing the sufficient amount polymer A.

Table 2.13 Polymers using as bolier sludge dispersants

Type of polymer	Kind of polymers
Synthetic polymers	Acrylic acid homopolymers Methacrylic acid homopolymers Acrylic acid based copolymers Maleic acid based copolymers
Natural polymers	Sodium lignin sulfonates Tannins Starches

The reduction of crystal growth rate with the crystal distortion effect is caused by the polymer adsorption on crystal surfaces. As this polymer adsorption is not stoichiometric, but it must be quantitatively identified for the successful application of polymer A to boilers. The adsorption of

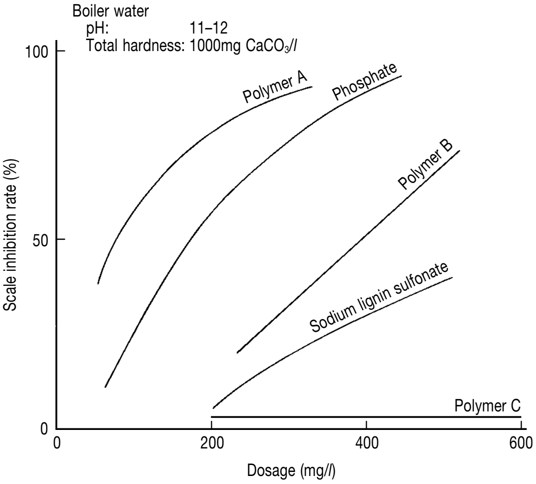
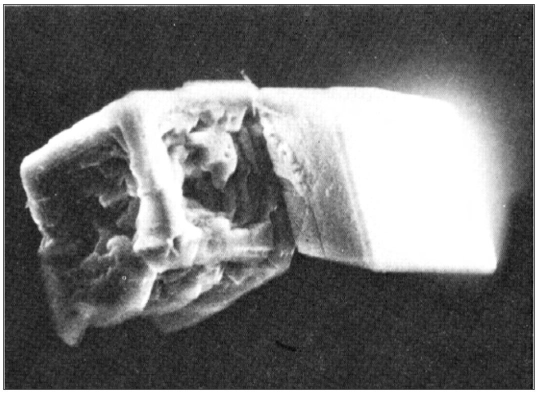
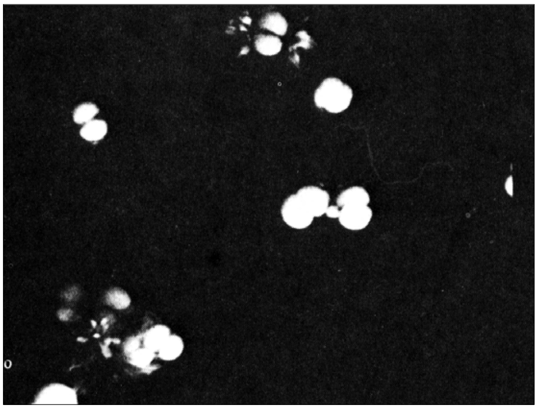


Fig. 2.41 Inhibition effects of various chemicals against calcium carbonate scale



(x 3,000, electron microscopic photograph)
Photo 2.11 Normal crystal shape of calcium carbonate (calcite)

(x 3,000, electron microscopic photograph)
Photo 2.12 Calcium carbonate crystals insufficiently distorted by adding a low concentration of polymer A



(x 3,000, electron microscopic photograph)
Photo 2.13 Perfectly distorted calcium carbonate crystals by adding a sufficient amount of polymer A

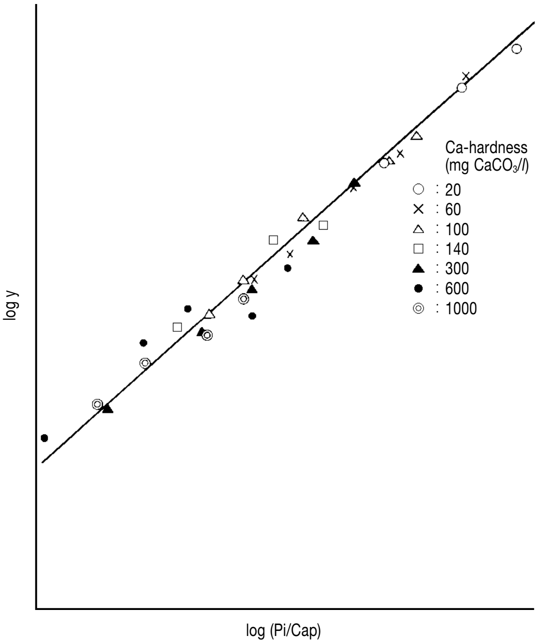
polymer A does not follow Langumuir's chemical adsorption isotherm nor Freuntrich's physical adsorption isotherm, but it is represented by the relationship as shown in Figure 2.42. The relationship is given by the equation (2.52).

$$P_{ad} = K \times (Pi)^{n} \times (C_{ap})^{1-n} \quad \text{......................} \quad (2.52)$$

where

P_{ad} = polymer concentration adsorbed on scale crystal (mg/l)
Pi = polymer concentration added (mg/l)
C_{ap} = concentration of calcium carbonate deposited (mg $CaCO_3$/l)
K, n = constants

The relationship among the amount of polymer A adsorbed on the crystals of calcium carbonate (the adsorption ratio, $y = P_{ad}/C_{ap}$), the scale inhibition effect and the crystal shape are typically illustrated in Figure 2.43.



Pi = Polymer concentration added (mg/l)
Pad = Polymer concentration adsorbed on the crystal of scale (mg/l)
Cap = Concentration of crystalized calcium carbonate (mg $CaCO_3$/l)
y = Pad/Cap

Fig. 2.42 Relationship between calcium carbonate deposition and the adsorption of polymer A

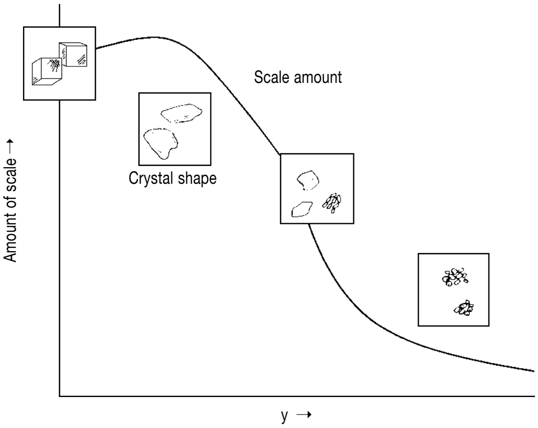
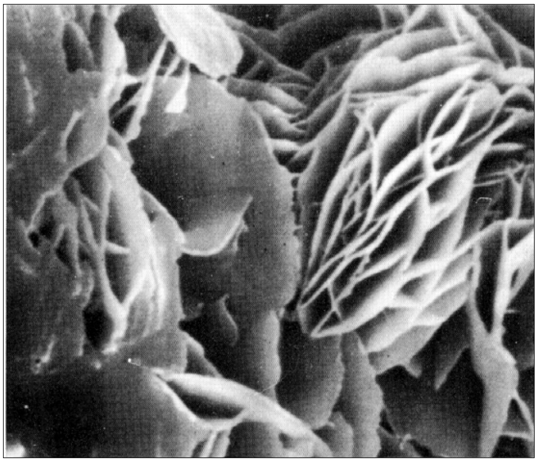


Fig. 2.43 Relationship between the adsorption ratio (y) of polymer A and the scale inhibition effect

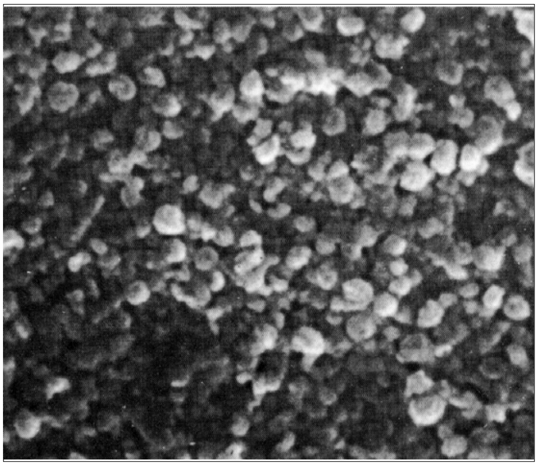
When the adsorption ratio (y) is kept at a specified value or more, the polymer A inhibits the crystal growth and provides the sufficient scale inhibition.

(ii) Inhibition of calcium silicate scale

The scale inhibition mechanism of polymers on calcium silicate is the same as that on calcium carbonate. However, the kinds of effective polymers are different from the case of calcium carbonate. Polymer D shows the excellent effect against calcium silicate. Polymer D controls the crystal growth of calcium silicate by changing the crystal shape as shown in Photographs 2.14 and 2.15.



(x 5,000, electron microscopic photograph)
Photo 2.14 Normal crystal shape of calcium silicate



(x 5,000, electron microscopic photograph)
Photo 2.15 Distorted calcium silicate crystals by adding polymer D

Recently, the control range of silica in boiler water is increased more than 500 mg SiO_2/l by using polymer D.

(iii) Typical laboratory test results

The flow diagram of a test boiler is illustrated in Figure 2.44.

The comparison of the scale amounts deposited on the heating surface when treated with an alkaline, a phosphate based or a polymer based boiler compound is shown in Figure 2.45.

The appearances of the heating surfaces under those treatments are shown in Photograph 2.16 (p. 2-69).

As shown in those data and photograph, the polymer treatment provides the same or better scale inhibition comparing with that of phosphate treatment.

(iv) Field test results

A polymer based boiler compound including an alkaline agent for pH control had been applied in place of a phosphate base boiler compound during 1 year for a boiler operating at the boiler pressure of 7 kgf/cm^2.

The conditions of the inner surface of a boiler during the phosphate based treatment and the polymer based treatment are shown in Photographs 2.17 and 2.18 (p. 2-70). The polymer based treatment had been successfully applied, as no white scaling was observed in the boiler inside.

As some kinds of polymers will thermally decomposed even at about 5 kgf/cm^2, a sufficient attention should be paid to select polymers using as boiler compounds.

(b) Chelating agent based boiler compounds

In the chelating agent treatments, the hardness components coming into boiler with the feedwater are kept in their soluble states by the chelating agents, while in the treatments with phosphate based or polymer based boiler compounds, the hardness components are kept in stable suspensions in the form of hydroxyapatite or calcium carbonate. Typical chelating agents are ethylenediamine tetraacetic acid (EDTA), nitrilo triacetic acid (NTA) and their salts.

The EDTA combines with calcium ion and forms the water soluble complex salt in boiler water. The reaction of EDTA with calcium ion is a stoichiometry and the 3.8 mg/l of EDTA tetrasodium salt is required for chelating the 1 mg $CaCO_3/l$ of calcium hardness.

2.4.3 Sludge Dispersants

Hardness components and silica in boiler water

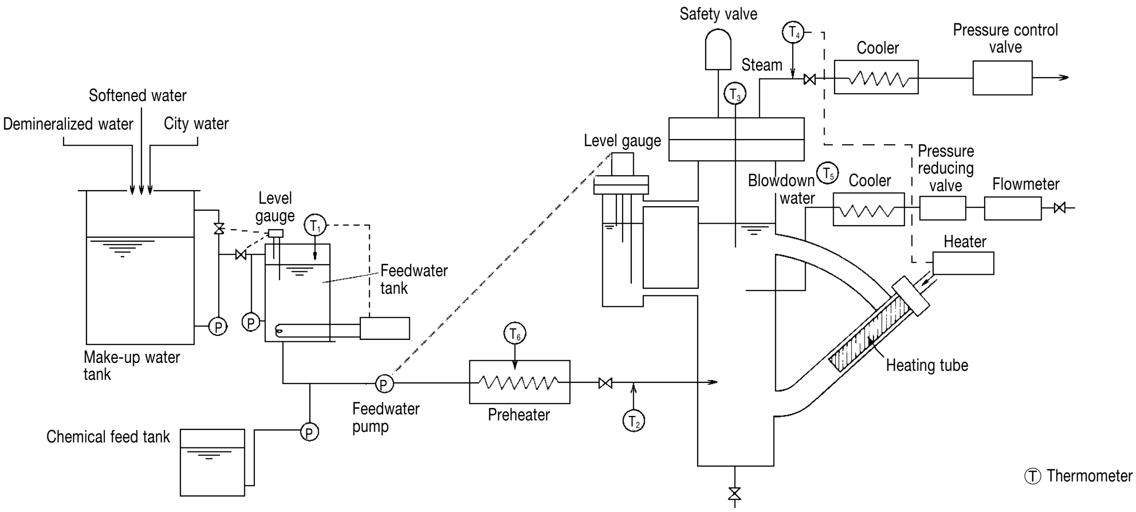


Fig. 2.44 Schematic flow diagram of a test boiler

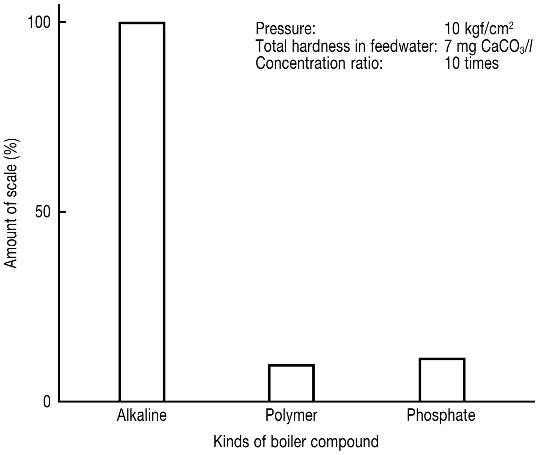


Fig. 2.45 Scale inhibition effects of a phosphate based and a polymer based boiler compounds comparing with an alkaline treatment

form the sludges of hydroxyapatite, magnesium hydroxide, magnesium silicate and so on by reacting with phosphate based boiler compounds. Most of them are stably suspended in the boiler water and are discharged with the blowdown water from the boiler. However, a small amount of them will accumulate on the heating surfaces or in the places of low water flow rate. As modern boilers have the high heat flux, a small amount of scale adhesion considerably reduces their efficiencies. Therefore, sludge dispersants (boiler sludge conditioners) are applied for preventing the accumulation of the sludges on the bottom of boiler drum and the scaling on the heating surface. The natural polymers, such as tannin, sodium ligninsulfonate and starch, were formerly used as sludge dispersants. However, as their effectivenesses were not sufficient, their application has become not-popular.

In the present, the application method of synthetic polymer dispersants is established and their applications become very popular. The effects of various sludge dispersants against hydroxyapatite in boiler water are shown in Figure 2.46.

Polymer E (a polyacrylate) shows the better sludge dispersing effect than that of polymer F (copolymer of acrylic acid and ethylene), polymer G (styrene sulfonate based polymer) or a natural polymer. The concentration of polymer E required for obtaining the sufficient dispersing effect on

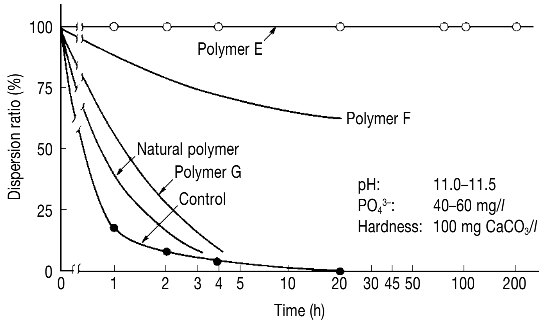


Fig. 2.46 Dispersing effects of various sludge dispersants against hydroxyapatite

hydroxyapatite sludge given by the following adsorption property equation.

$$P_{ad} = K_2 \times (P_T)^m \times (HAp)^{1-m} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (2.53)$$

where

P_{ad} = polymer concentration adsorbed (mg/*l*)

P_T = polymer concentration added (mg/*l*)

HAp = amount of hydroxyapatite deposited (mg/*l*)

K_2, m = constants

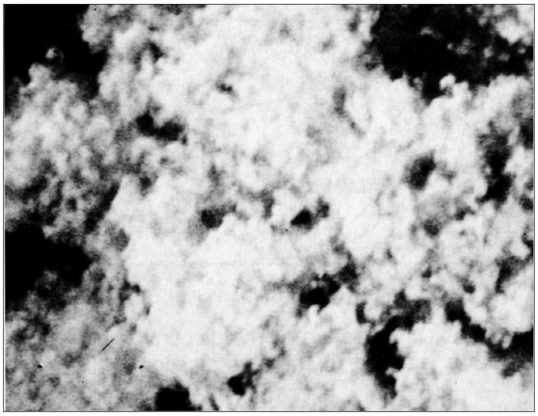
Particle size distribution of hydroxyapatite dispersing by the polymer E is shown in Figure 2.47. The normal and distorted crystal shapes are shown in Photographs 2.19 and 2.20. The crystal of hydroxyapatite becomes very small by the effect of polymer E comparing with the control test.

Further, the polymer E disperses iron oxide in boiler water and prevents its deposition on the heating surface.

Particle size distribution of iron oxide (Fe_2O_3) dispersing by the polymer E is shown in Figure 2.48. The normal and distorted crystal shapes are shown in Photographs 2.21 and 2.22. The particle size of iron oxide is reduced by the addition of polymer E and it reaches 0.25 µm in the mean size.

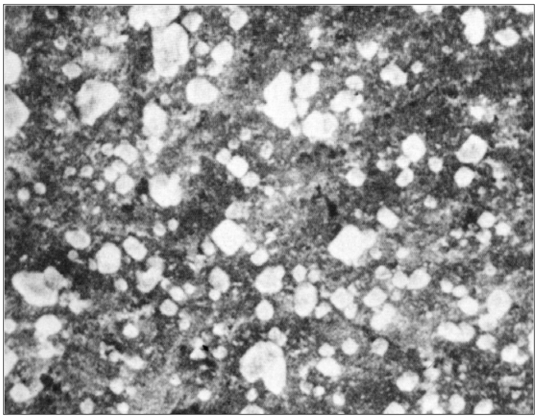
The dispersion effect of polymer E on hydroxyapatite sludge in a test boiler is shown in Photograph 2.23 (p. 2-70). Under a phosphate based treatment, the deposits of milky white scale are found, while no scale deposit is found under the polymer E treatment.

In food factories and hospitals and so on, as the safety of chemicals using for their boilers is very important, polymer H of food additive grade has been developed as the safe sludge dispersant. The



(x 10,000, electron microscopic photograph)

Photo 2.19 Precipitate of hydroxyapatite (without polymer dispersant)



(x 10,000, electron microscopic photograph)

Photo 2.20 Precipitate of hydroxyapatite distorted under the polymer E treatment

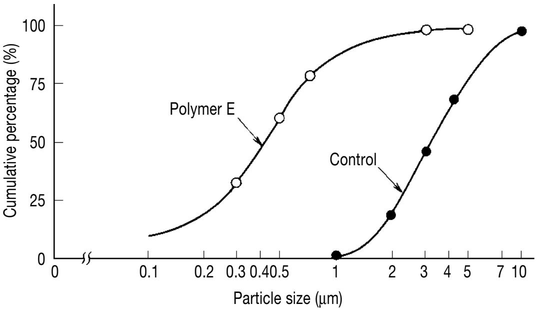


Fig. 2.47 Particle size distribution of hydroxyapatite under polymer E treatment comparing with a control test

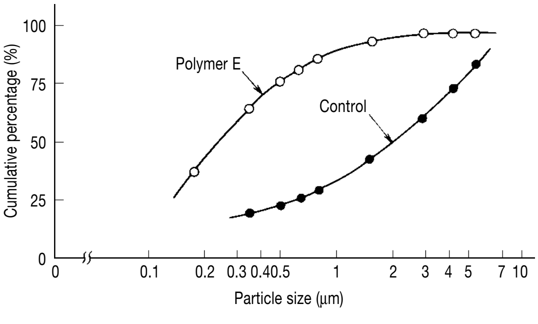
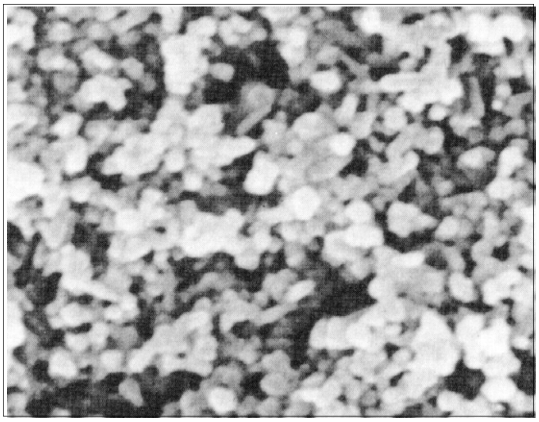
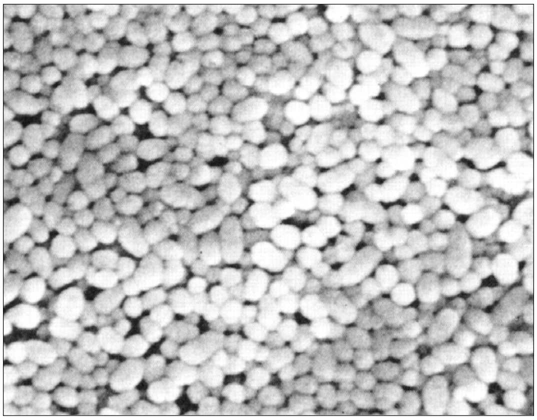


Fig. 2.48 Particle size distribution of iron oxide under polymer E treatment comparing with a control test



(x 10,000, electron microscopic photograph)
Photo 2.21 Particles of iron oxide (without polymer dispersant)



(x 10,000, electron microscopic photograph)
Photo 2.22 Particles of iron oxide distorted under polymer E treatment

required dosage of polymer H is determined by the same method as that of polymer E. The typical sludge dispersion effect of polymer H against hydroxyapatite is shown in Figure 2.49. As the polymer H removes the existing scale and disperses it, the dispersing ratio exceeds 100% as shown in Figure 2.49.

Recently, sludge dispersants are used for medium or high pressure boilers to prevent iron oxide sludge from the deposition on the heating surface and the accumulation. The use of polymer I disperses magnetite (Fe_3O_4) and changes the crystal shape as shown in Photographs 2.24 and 2.25.

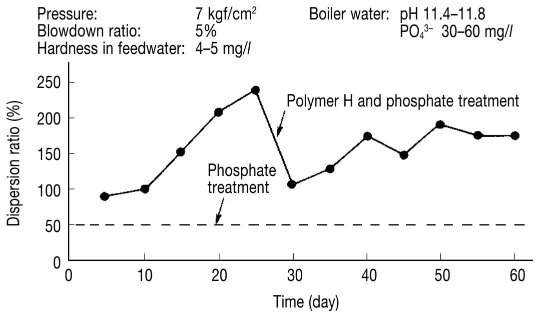
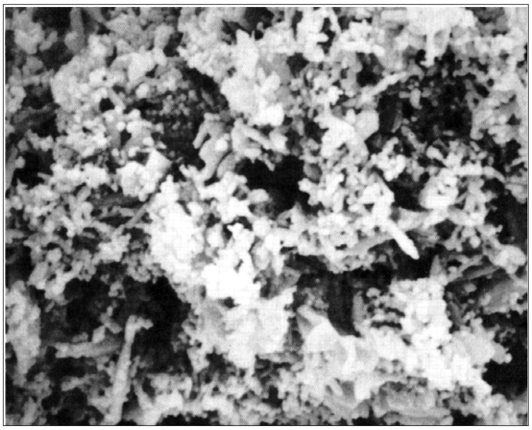
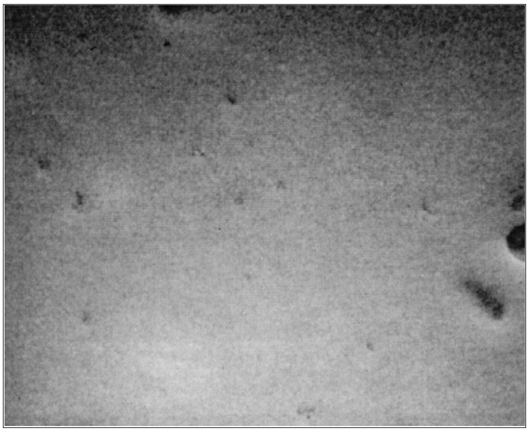


Fig. 2.49 Dispersing effect of polymer H on hydroxyapatite



(Secondary electron image x 10,000)
Photo 2.24 Particles of magnetite (without polymer dispersant)



(Secondary electron image x 10,000)
Photo 2.25 Particles of magnetite dispersed by polymer I treatment

2.4.4 Oxygen Scavengers

Oxygen scavengers are chemicals which remove dissolved oxygen from water by their reduction reactions, and thereby inhibit the corrosion caused by the oxygen and water.

The desirable properties of oxygen scavengers are as follows:

① Strong reducing power against oxygen,
② No aggressive action of the thermally decomposed products and the reaction products with oxygen against boilers, and the steam and condensate lines.

The types and chemical names of oxygen scavengers are shown in Table 2.14. The hydrazine shows the best performance among them, however, it is highly toxic. Therefore, the hydrazine based chemicals have been replaced with the other chemicals recently.

(1) Hydrazine

The chemical called hydrazine is normally hydrazine hydrate (hereafter referred to as hydrazine).

The reaction between hydrazine and oxygen is generally represented by the equation (2.54), but in boilers, it is reported that heterogeneous reactions, such as the equations (2.55) and (2.56), take place prior to the equation (2.54)[29].

(Homogeneous reaction)

$$N_2H_4 + O_2 \rightarrow N_2 + 2H_2O \quad \cdots\cdots (2.54)$$

(Heterogeneous reaction)

$$6Fe_2O_3 + N_2H_4 \rightarrow 4Fe_3O_4 + N_2 + 2H_2O \quad \cdots\cdots (2.55)$$

$$4Fe_3O_4 + O_2 \rightarrow 6Fe_2O_3 \quad \cdots\cdots (2.56)$$

Table 2.14 Oxygen scavengers

Type	Chemical names
Hydrazine based oxygen scavengers	Hydrazine hydrate Hydrazine sulfate Hydrazine phosphate
Sulfite based oxygen scavengers	Sodium sulfite Sodium hydrogen sulfite Sodium pyrosulfite
Other oxygen scavengers	Saccharides Tannins Hydrazide L-ascorbic acid Hydroquinone Alkanol amines

In both cases, as the reaction products of hydrazine and oxygen are nitrogen and water, no dissolved solid remains in the boiler water. Therefore, hydrazine is appropriate for high pressure boilers or once through boilers.

As the reaction rate of hydrazine with oxygen is slower than that of sodium sulfite, generally it is accelerated by using catalysts. Figure 2.50 shows the effect of an organic catalyst. The reaction is also accelerated by increasing the dosage of hydrazine, pH and temperature as shown in Figures 2.51 and 2.52[30].

Calculated from the equation (2.54), 1 mg/*l* of hydrazine is required to reduce 1 mg/*l* of oxygen. In boiler operation, hydrazine should be added in an excess of the theoretically required amount to keep the concentration in the boiler water over the lowest standard value.

Since it was previously considered that hydrazine would transfer to the steam phase in a deaerator, it was injected at the outlet of the deaerator. However, it is found that hydrazine is not consumed so much in the deaerator. Therefore, hydrazine is injected into the feedwater line before the deaerator to prevent the corrosion of the feedwater line and deaerator.

The equations (2.57) to (2.59) represent the thermal decomposition reactions of hydrazine. Among them, the reaction of the equation (2.57) generally proceeds in boilers[31)-33)].

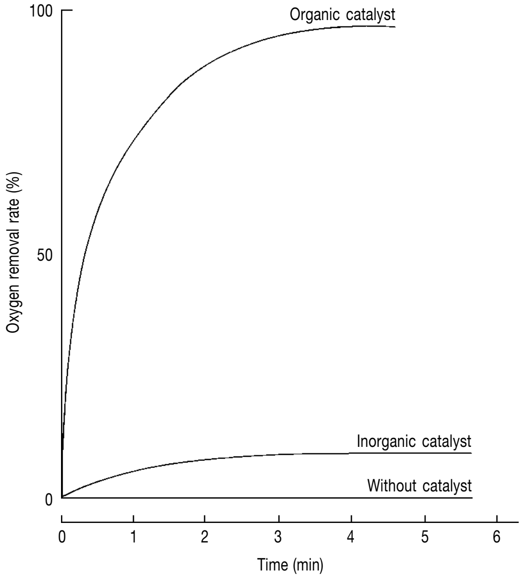


Fig. 2.50 Effects of catalysts on the oxygen removal reaction of hydrazine

$$3N_2H_4 \rightarrow 4NH_3 + N_2 \quad \text{.......} \quad (2.57)$$
$$2N_2H_4 \rightarrow 2NH_3 + N_2 + H_2 \quad \text{.......} \quad (2.58)$$
$$3N_2H_4 \rightarrow 2NH_3 + 2N_2 + 3H_2 \quad \text{.......} \quad (2.59)$$

Since ammonia is produced by the decomposition of hydrazine, in the systems where copper based materials are used in the steam and condensate lines, the excessive injection of hydrazine should be avoided for the corrosion prevention.

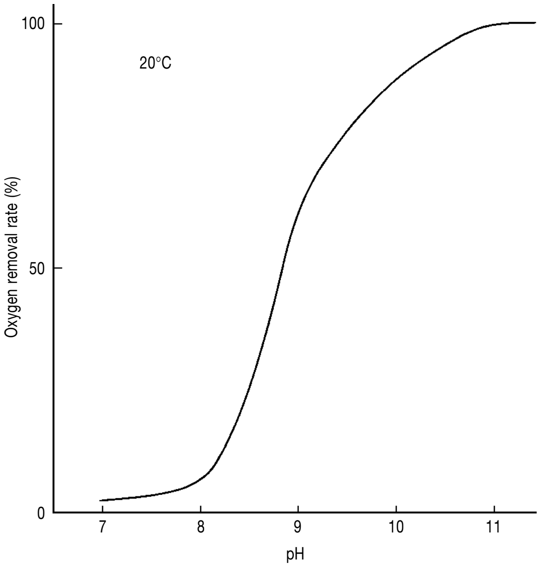


Fig. 2.51 Effect of pH on the oxygen removal reaction of hydrazine

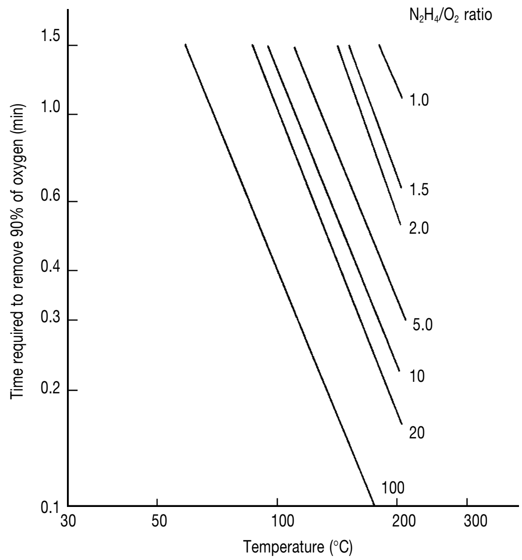


Fig. 2.52 Influences of temperature and the dosage of hydrazine on the oxygen removal reaction of hydrazine

(2) Sodium sulfite

The reaction between sodium sulfite and oxygen is represented in the equation (2.60).

$$2Na_2SO_3 + O_2 \rightarrow 2Na_2SO_4 \quad \text{.......} \quad (2.60)$$

As shown in Figure 2.53[34)], this reaction proceeds slowly either at low temperatures or in the pH ranges of lower than 4 or higher than 9. However, the reaction proceeds rapidly at higher temperature of above 50° C regardless of pH.

The 7.9 mg/*l* of sodium sulfite is required to remove the 1 mg/*l* of oxygen and the 8.9 mg/*l* of sodium sulfate (Na_2SO_4) yields as the reaction product. Therefore, total dissolved solids in boiler water increase when sodium sulfite is used.

When the dosage of sodium sulfite is insufficient and sulfate ion concentration increases with the presence of oxygen, carbon steel corrosion will be accelerated as shown in Figure 2.54[35)] and Photograph 2.26 (p. 2-71).

Therefore, sulfite should be added in an excess of the required amount against dissolved oxygen to keep the concentration in boiler water higher than the lower control limit.

Since sodium sulfite rapidly reacts with oxygen and the concentration gradually decreases in the chemical dissolving tank, the concentration in the tank should be periodically determined.

Recently, a sodium sulfite based oxygen scavenger including a stabilizer has been developed to prevent the reduction of the sulfite concentration in the dissolving tank. Figure 2.55 shows the effect of the stabilizer.

It was reported that the thermal decomposition

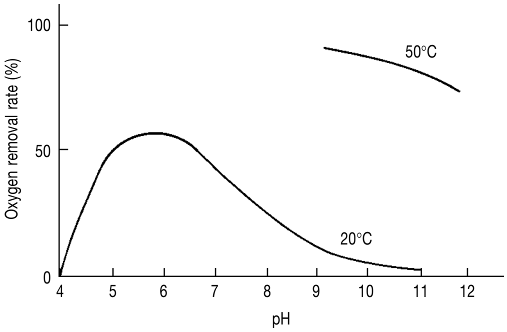


Fig. 2.53 Influences of pH and temperature on the oxygen removal reaction of sodium sulfite

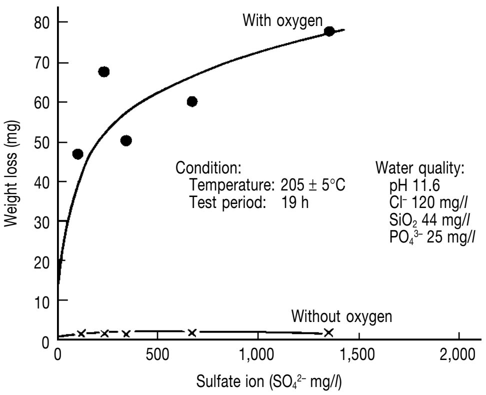


Fig. 2.54 Influence of sulfate ion concentration on the corrosion of carbon steel

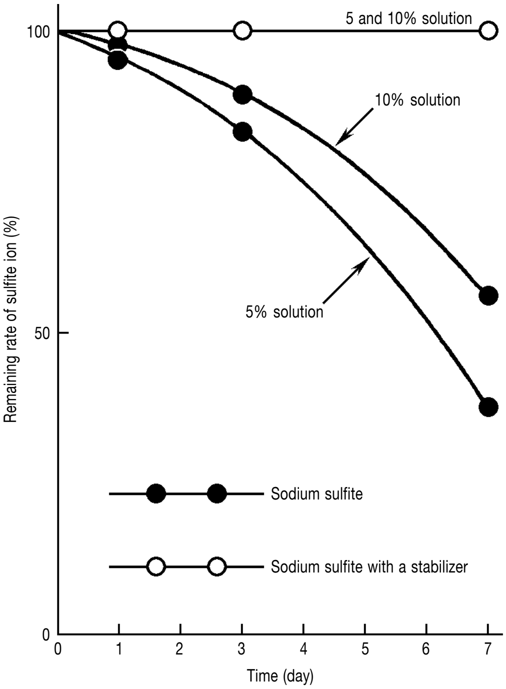


Fig. 2.55 Effectiveness of a stabilizer for sodium sulfite decomposition

of sodium sulfite was generally occurred at above 285° C as shown in Figure 2.56$^{36)}$. This reaction is represented by the equations (2.61) to (2.63).

$$4Na_2SO_3 \rightarrow Na_2S + 3Na_2SO_4 \quad \text{.....} \quad (2.61)$$

$$2Na_2S + 4Na_2SO_3 + 3H_2O \rightarrow 3Na_2S_2O_3 + 6NaOH \quad \text{.....} \quad (2.62)$$

$$Na_2SO_3 + H_2O \rightarrow 2NaOH + SO_2 \quad \text{.....} \quad (2.63)$$

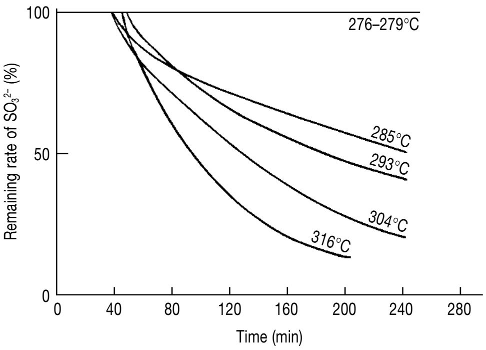


Fig. 2.56 Thermal decomposition of sodium sulfite

Since the decomposition products are sodium sulfide (Na_2S), sulfur dioxide (SO_2), etc., they corrode the boiler, and the steam and condensate lines. Therefore, sodium sulfite is never applied for boilers with the pressure of over 65 kgf/cm^2.

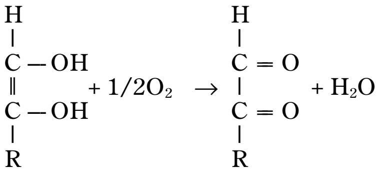
Sodium hydrogen sulfite ($NaHSO_3$), sodium pyrosulfite ($Na_2S_2O_5$) and so on are also used as the same type of oxygen scavengers to sodium sulfite. Since these compounds consume the alkalinity of boiler water, they are applied in combination with boiler compounds of high alkali content or applied for boilers using high M-alkalinity feedwater. As shown in the reactions (2.64) and (2.65), they change to sodium sulfite in boiler water and remove oxygen.

$$NaHSO_3 + NaOH \rightarrow Na_2SO_3 + H_2O \quad \text{.....} \quad (2.64)$$

$$Na_2S_2O_5 + 2NaOH \rightarrow 2Na_2SO_3 + H_2O \quad \text{.....} \quad (2.65)$$

(3) Saccharides and ascorbic acid

The reaction of saccharides or ascorbic acid with oxygen is represented in the equation (2.66).



$$\begin{array}{c} H \\ | \\ C-OH \\ \| \\ C-OH \\ | \\ R \end{array} + 1/2O_2 \rightarrow \begin{array}{c} H \\ | \\ C=O \\ | \\ C=O \\ | \\ R \end{array} + H_2O \quad \text{.....} \quad (2.66)$$

Since those oxygen scavengers generate no corrosive ion as the reaction products, they scarcely accelerate metallic corrosion even if they are insufficiently dosed.

Saccharides have been widely used for the boilers of food factories and hospitals because of their safeties. Photograph 2.27 (p. 2-71) shows the treatment result of saccharide in a smoke tube boiler. The excellent treatment result is obtained without any pitting corrosion by using this oxygen scavenger.

Ascorbic acid based oxygen scavengers are generally applied for medium or high pressure boilers substituting for toxic hydrazine based ones.

(4) Hydrazides

The reaction between hydrazide based chemicals and oxygen is represented in the equation (2.67).

$$R - CONHNH_2 + O_2 \rightarrow R - COOH + N_2 + H_2O \quad \ldots\ldots (2.67)$$

The oxygen scavenging reaction is progressed by the function of hydrazide group and its mechanism is the same as hydrazine.

Recently, polymers having hydrazide groups have been developed and used for medium or high pressure boilers as an oxygen scavenger with the function of sludge dispersion also.

(5) Other oxygen scavenger

Tannins, hydroquinone, aminoguanidines, diethyl-hydroxylamine and so on are also used as the non-hydrazine based oxygen scavengers for their safeties.

2.4.5 Corrosion Inhibitors for the Feedwater and Condensate Lines

Neutralizing amines (volatile amines) and filming amines are typically used as corrosion inhibitors to prevent the feedwater or the steam and condensate lines from the corrosion.

Volatile amines inhibit the corrosion by controlling the condensate pH. Filming amines form the water repellent film on metal surfaces and inhibit the corrosion by preventing the metals from contacting with the corrosive substances, such as oxygen and carbon dioxide.

(1) Corrosion inhibitors for the feedwater and condensate lines of low pressure boilers

Substances causing corrosion in the steam and condensate lines of low pressure boilers are mainly oxygen and carbon dioxide as described in the section 2.2.2.

The presence of a small quantity of carbon dioxide in the condensate decreases the pH as shown in the Figure 2.18 (p.2-13), and accelerates metallic corrosion. Under this corrosive environment, neutralizing (volatile) amines and/or filming amines are applied as corrosion inhibitors.

The application of neutralizing amines shows the excellent inhibition, but the effect is decreased by the presence of oxygen. The higher dosage is required when the M-alkalinity of feedwater is higher.

Filming amines are adsorbed on the metal surface even with a small dosage and form the water-repellent protective film. However, the film formation takes a long time if the metal surface is covered with the corrosion products.

The combined use of both types of amines shows the better and more stable corrosion inhibition comparing with their single use.

(a) Neutralizing amines

Cyclohexyl amine ($C_6H_{11}NH_2$), morpholine (C_4H_8ONH), monoisopropanol amine [$NH_2CH_2CH(CH_3)OH$] and so on are generally used as neutralizing amines for boiler systems. Ammonia is also used as a neutralizing agent. These neutralizing agents are usually dosed into the feedwater line but they are sometimes injected into the boiler or the steam and condensate lines. The amine added into the feedwater volatiles together with the steam generated in the boiler. When the steam condenses in the condensate line, the amine dissolves into the condensate and neutralizes the carbon dioxide (carbonic acid) in the condensate as shown in the reactions (2.68) to (2.70). As the result, the pH of the condensate is increased and the corrosion of metals is inhibited.

$$2NH_4OH + H_2CO_3 \rightarrow (NH_4)_2CO_3 + 2H_2O \quad \ldots\ldots (2.68)$$

$$2C_6H_{11}NH_3OH + H_2CO_3 \rightarrow (C_6H_{11}NH_3)_2CO_3 + 2H_2O \quad \ldots\ldots (2.69)$$

$$2C_4H_8ONH_2OH + H_2CO_3 \rightarrow (C_4H_8ONH_2)_2CO_3 + 2H_2O \quad \ldots\ldots (2.70)$$

Figure 2.57[37) shows the influence of condensate pH on the corrosion rate of carbon steel in a steam and condensate line. Since the condensate pH is increased by injecting the neutralizing amine, the corrosion rate of carbon steel decreases to an acceptable level at the pH 7 or higher. The corrosion rate of copper is low in the condensate of the pH 6 to 9 as shown in Figure 2.58, but the corrosion rate increases when the pH becomes below 6 or above 10. When ammonia is used as a neutralizing agent, the corrosion rate of copper is remarkably increased at the pH of above 9.

The required amounts of amines for the neutralization of carbon dioxide are different depend-

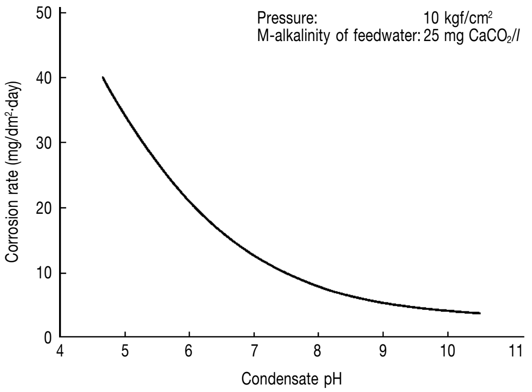


Fig. 2.57 Relationship between the corrosion rate of carbon steel and condensate pH

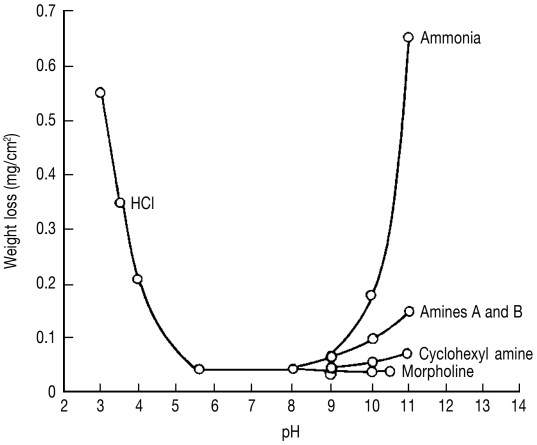


Fig. 2.58 Relationship between copper corrosion and condensate pH

ing on the basicities of amines. Table 2.15 shows the dissociation constants and the required amounts of amines for neutralizing 1 mg/*l* of carbon dioxide.

Among the characteristics of neutralizing amines, the distribution ratio is important for the condensate line treatment. The distribution ratio is the ratio of amine concentration in steam to that in condensate under a specified condition as shown in the equation (2.71).

$$\text{Distribution ratio} = \frac{\text{Amine concentration in steam}}{\text{Amine concentration in condensate}} \quad \cdots\cdots (2.71)$$

An amine with the high distribution ratio easily transfers to steam side, but it hardly transfers to the condensate side when the steam condenses. On the contrary, an amine with low distribution ratio hardly moves to steam side, but easily moves to condensate side.

The distribution ratio also varies depending on the temperature (steam pressure). Neutralizing amines are classified into three categories: the first ones, which the distribution ratios increase as temperature rises (such as alkanol amines); the second ones, which the distribution ratios are reduced as the temperature increases (such as ammonia); and third ones, which the distribution ratios reach the peaks at a certain temperature (such as cyclohexyl amine).

Figures 2.59 and 2.60 show the typical relationships between the distribution ratios of amines and temperature (steam pressure).

The amines with the low distribution ratios, such as morpholine and alkanol amine, are effective for preventing the corrosion of the initial condensation zone where is comparatively close to the boiler. The amines with high distribution ratios, such as cyclohexyl amine, are effective for preventing the corrosion of the condensate lines far from the boiler.

Ammonia is effective for neutralizing carbon dioxide as shown in Table 2.15, but it is not applicable for the boilers employing copper materials in the steam and condensate lines because of the corrosion acceleration against copper.

(b) Filming amines

Alkyl amines with the following chemical structure are used as filming amine based corrosion inhibitors.

$$R\text{-}NH_2$$

where

R = alkyl group with the carbon number of 10 to 22

Octadecylamine (ODA) which has eighteen carbon atoms, is generally used as filming amine. As the ODA is insoluble in water, it is generally used as the dispersion by using emulsifiers[38)].

The inhibition mechanism of ODA is shown in Figure 2.61. The amino group (-NH$_2$) of ODA adsorbs and forms mono or few molecular layer[39)] adsorption film on the metal surface. This film is a water repellent and prevents metal from the corrosion by disturbing the contact of condensate with the surface.

Photograph 2.28 (p. 2-72) shows the spherical

Table 2.15 Neutralizing effects and dissociation constants of neutralizing agents

Neutralizing agent	Required amount of amine for neutralizing 1 mg/*l* of carbon dioxide (mg/*l*)	Dissociation constant (Kb)
Ammonia	0.4	1.78×10^{-5}
Cyclohexyl amine	2.3	3.39×10^{-4}
Monoisopropanol amine	1.8	5.25×10^{-5}
Morpholine	2.0	2.09×10^{-6}
Alkanol amine A	1.4	3.15×10^{-5}
Alkanol amine B	2.1	5.62×10^{-5}

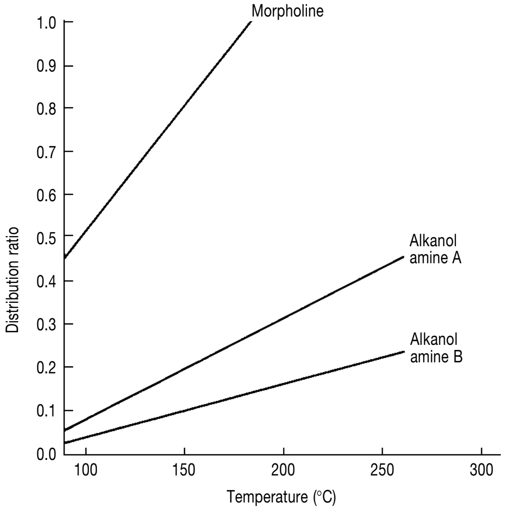


Fig. 2.59 Influence of temperature on the distribution ratios of neutralizing amines

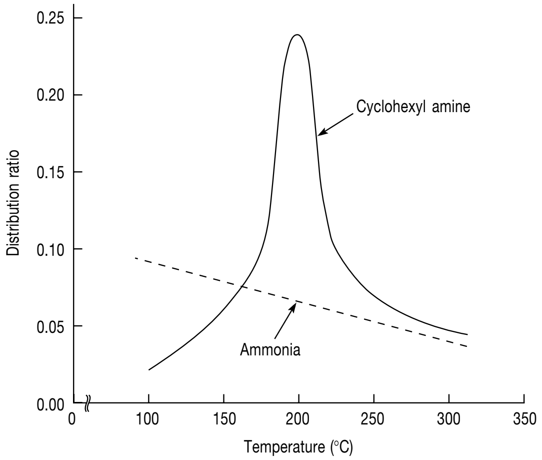


Fig. 2.60 Influence of temperature on the distribution ratios of ammonia and cyclohexyl amine

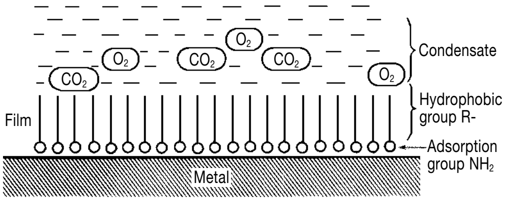


Fig. 2.61 Adsorption film of filming amine formed on metal surface

water drops repelled from the metal surface by the adsorption film formed by the ODA.

The factors which influence the corrosion inhibition provided by ODA are the dosage of ODA, M-alkalinity of feedwater, temperature of condensate and so on[37)].

Figure 2.62 shows the influence of feedwater M-alkalinity on the corrosion inhibition effect of ODA against carbon steel. When the 25 mg/*l* as a product of ODA suspension is injected into a feedwater with the M-alkalinity of 50 mg $CaCO_3/l$, the corrosion rate of carbon steel lowers below 10 mg/dm^2 day (mdd) after 2 days from the injection. When the M-alkalinity is increased to 100 mg $CaCO_3/l$, it is requires three days to decrease the corrosion rate below 10 mg/dm^2 day. The increase in the feedwater M-alkalinity deteriorates the initial corrosion inhibition provided by ODA, but it gives no bad influence after the adsorption film formation by ODA.

Condensate temperature affects the corrosion inhibition provided by ODA as shown in Figure 2.63. The ODA shows the better corrosion inhibition at the lower condensate temperature of below 45° C.

Dissolved oxygen in condensate accelerates the corrosion of the condensate line as shown in Figure 2.20 (p.2-13). Dissolved oxygen also influences the corrosion inhibition effect of ODA. Figure 2.64

shows the influence of dissolved oxygen in condensate on the corrosion inhibition provided by ODA on carbon steel. When the dissolved oxygen is sufficiently low (0.2 mg O/*l*), ODA shows the excellent inhibition, but high dissolved oxygen concentration (3 mg O/*l*) reduces the effectiveness. Therefore, it is necessary for the corrosion control by ODA to minimize the oxygen transferred from the boiler to the condensate line by applying the deaeration of feedwater and/or injecting oxygen scavengers.

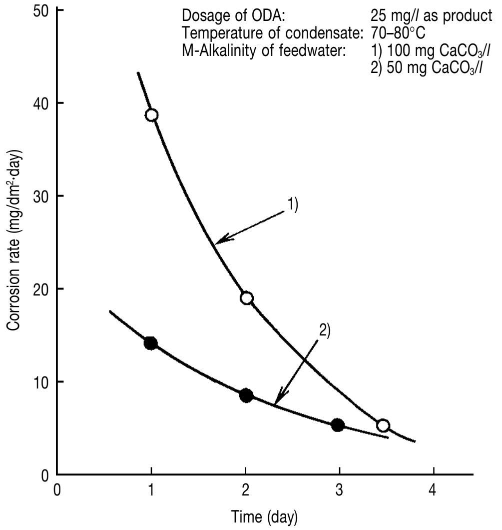


Fig. 2.62 Influence of feedwater M-Alkalinity on the corrosion inhibition effect of ODA against carbon steel

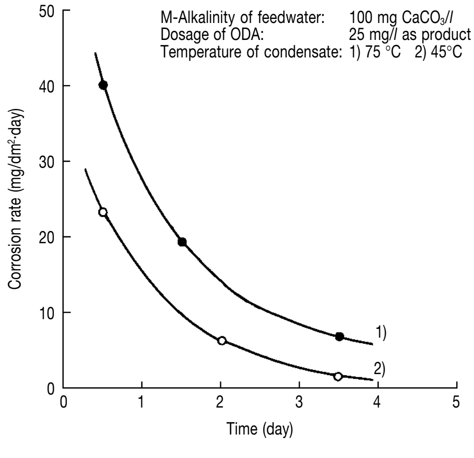


Fig. 2.63 Influence of condensate temperature on the corrosion inhibition effect of ODA against carbon steel

(c) Combined use of neutralizing amine and filming amine

A high dosage of neutralizing amine is required to control the corrosion of condensate line satisfactorily when the M-alkalinity of feedwater is high. On the other hand, filming amines require a longer period of time to form the protective film and to show the corrosion inhibition. The combined use of both types of amines improves their corrosion inhibitions.

Table 2.16[40)] shows the improved corrosion inhibition of the combined use comparing with their single uses. Under the neutralizing amine treatment, the corrosion rate of carbon steel decreases when the condensate pH is risen. Under the filming amine treatment, the corrosion rate is low even when the pH is low. The combined treatment remarkably improves the corrosion inhibition.

Even in the case of condensate including dissolved oxygen, the combined treatment shows the better corrosion inhibition compared with a filming amine treatment as shown in Figure 2.65.

(2) Corrosion inhibitors for feedwater and condensate lines of medium or high pressure boilers

Since demineralized water with a low temperature is generally supplied for medium or high pressure boilers, corrosion problems hardly occurs at the line before the inlet of the deaerator. However, the pipeline and the auxiliary equipments after the deaerator may sometimes corrode in the

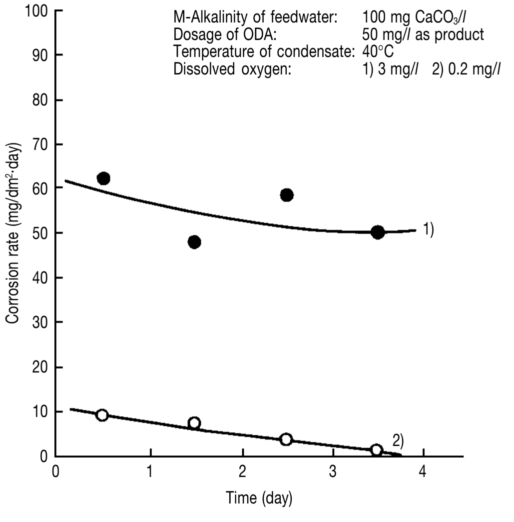


Fig. 2.64 Influence of dissolved oxygen in condensate on the corrosion inhibition effect of ODA on carbon steel

Table 2.16 Effectiveness of the combined use of a neutralizing amine and a filming amine

Chemical treatment	pH	Dosage of filming amine (mg/*l*)	Corrosion rate of carbon steel (mg/dm²·day)
None	5.3	0	124.5
Neutralizing amine	6.6	0	78.4
	7.0	0	54.8
Filming amine	5.3	20	32.1
Combined use of both amines	6.6	20	11.2
	7.0	20	11.8

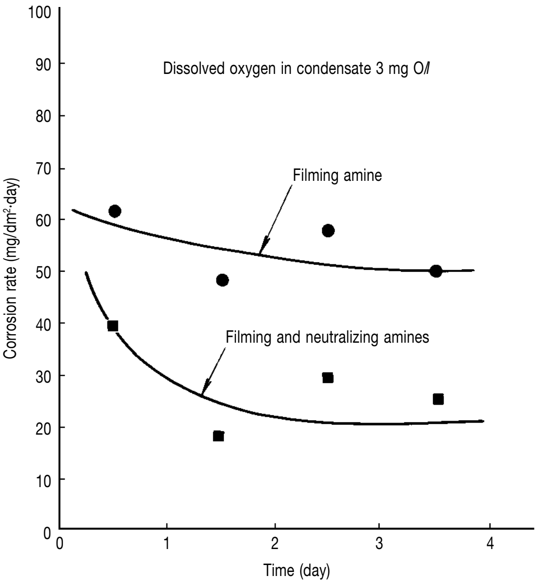


Fig. 2.65 Improvement of corrosion inhibition provided by a filming amine on carbon steel by the combined use of a neutralizing amine

case of a poor water quality control or an insufficient operation control of deaerator because of the increased temperature. Therefore, the corrosion control of feedwater line is important same as the steam condensate line. Neutralizing amines are used as the corrosion inhibitors for the feedwater and condensate lines.

The important characteristics of neutralizing amines for medium or high pressure boilers are the pH control effects and stabilities against thermal decompositions. Figure 2.66 shows the relationship between the pH of demineralized water, and the dosages of neutralizing amines and ammonia, which are calculated from their dissociation constants shown in Table 2.15(p.2-39).

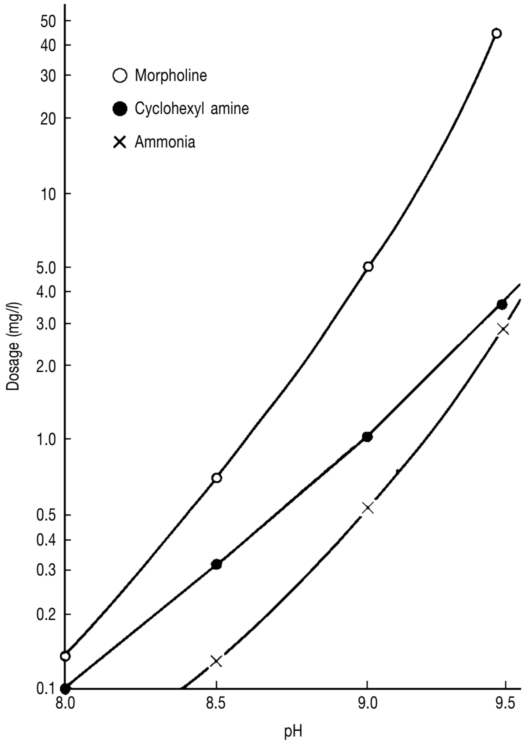


Fig. 2.66 Relationship between the pH of demineralized water, and the dosages of neutralizing amines and ammonia

Figure 2.67 shows the decomposition rate of morpholine in a test boiler reported by C. Jacklin[41]. He calculated the decomposition rate from the amount of NH_3 generated by the thermal decomposition of morpholine. In this case, the maximum decomposition rate is around 12% at the boiler pressure of 175 kgf/cm² and the steam temperature of 649° C.

On the other hand, the decomposition rate of morpholine in an actual boiler with the pressure of 96 kgf/cm² and the steam temperature of 513° C is reported 0.6 to 2.2% as the lower value than that in the test boiler.

The decomposition rate of cyclohexyl amine is sufficiently low and 5.0 to 5.8% in the above actual boiler under the same operational conditions.

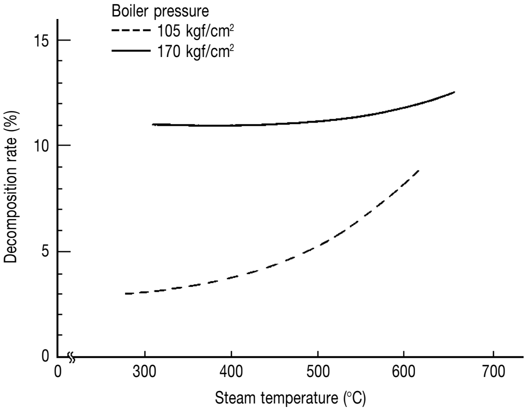


Fig. 2.67 Thermal decomposition of morpholine in a test boiler

The thermal decomposition rate of an alkanol amine is 12% at a pressure of 70 kgf/cm^2 under an autoclave test.

Neutralizing amines generally have high thermal stabilities and are used for medium or high pressure boilers widely. However, filming amines are scarcely used for medium or high pressure boilers because they are decomposed at the temperature of above 250° C.

2.4.6 On-Stream Scale Removers

On-stream scale remover (OSSR) is a chemical which removes scale deposited in a boiler during the operation without the stoppage.

Scale is composed of several substances, such as calcium carbonate ($CaCO_3$), calcium silicate ($CaSiO_3$), hydroxiapatite ($[Ca_3(PO_4)_2]_3{\cdot}Ca(OH)_2$), iron oxides ($Fe_2O_3$, Fe_3O_4) and zinc oxide (ZnO). The thermal conductivities of scales are quite small as shown in Table 2.3(p.2-6). Therefore, even a small amount of scale adhesion reduces the boiler efficiency and increases the fuel consumption.

Heavy scale formation in the evaporation tubes will cause the expansion and bursting. To solve those scale troubles, the adhered scale has to be removed.

To remove scale, chemical cleaning or mechanical cleaning is generally carried out. However, the boiler has to be stopped for the cleaning. If it is possible to remove the scale from the boiler during the operation, it will realize a considerable energy saving. Previously, chelating agents were used as the OSSR, but their performances for scale removing were insufficient. Recently, the combined treatment of a low molecular weight polymer and a chelating agent has been developed and it has shown the excellent effect as the OSSR.

Figure 2.68 shows the increase in the total hardness of boiler water when the OSSR is applied for a fire and flue-tube boiler with the scale of calcium silicate mainly. The sample A in Table 2.17 shows the composition of this scale. When the OSSR of 2,000 mg/*l* was injected into the boiler water, the total hardness was increased until 130 mg $CaCO_3$/*l* by the scale removal. After 4 months, the excellent scale removal effects was determined by inspecting the boiler inside as shown in Photograph 2.29 (p. 2-72).

The sample B in the Table 2.17 is a typical zinc base scale caused by a boiler water contamination with zinc coming from a condensate line made of galvanized steel. Figure 2.69 shows the increase of zinc concentration in the boiler water by applying the OSSR. The excellent scale removal effect was observed when the boiler was inspected 3 months later.

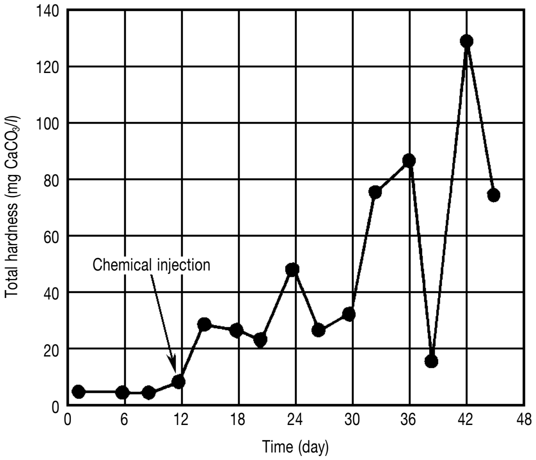


Fig. 2.68 Increase of total hardness in boiler water by applying an OSSR

Table 2.17 Typical boiler scale analyses (Unit: %)

Composition	Sample A	Sample B
CaO	31.7	4.6
Fe_2O_3	Trace	25.2
ZnO	0.5	47.1
Acid insoluble matter*	48.9	18.8
P_2O_5	2.3	4.5

* Mainly silica

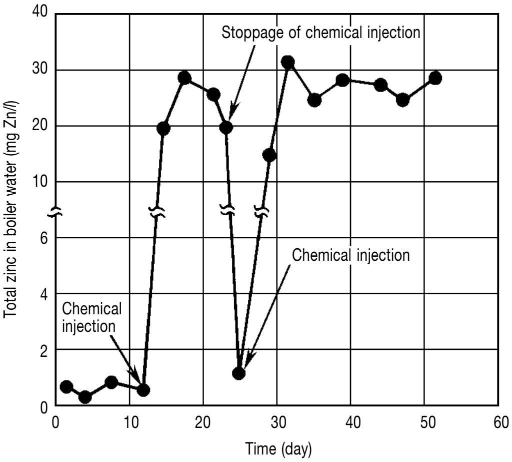


Fig. 2.69 **Increase of total zinc in boiler water by applying an OSSR**

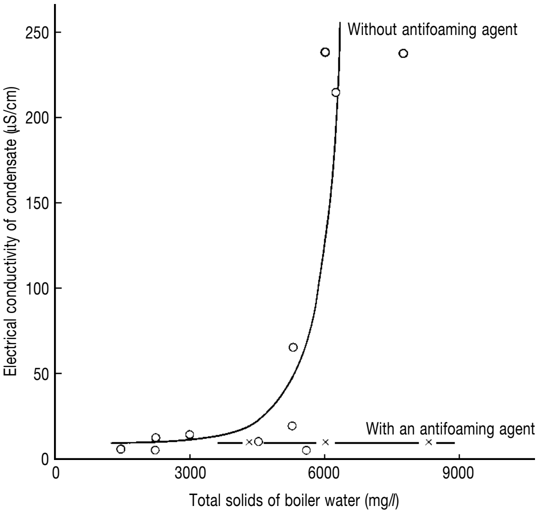


Fig. 2.70 **Effect of an antifoaming agent against carryover**

2.4.7 Antifoaming Agents

Antifoaming agents prevent the carryover problems of boilers by controlling a foaming caused by the increase of dissolved or suspended solid concentration in the boiler water, or by the contamination of boiler water with oils, fats and organic matters.

Castor oil and cottonseed oil were used as antifoaming agents in the past. However, as their effects were insufficient and sometimes promoted the foaming, they are not used presently. At present, some kinds of amines, alcohols, fatty acid esters and so on are used as the antifoaming agents. These chemicals show the excellent effects with their small dosages.

Figure 2.70 shows a typical application result of an antifoaming agent. The high cycle number operation of boilers is realized without the carryover by applying the antifoaming agents.

2.5 Water Treatment for Mini-Circulation Boilers

The mini-circulation boiler is essentially a kind of water tube boiler having a steam and water separator, and the hot water divided by the separator returns to the evaporation tubes. The amount of the separated hot water is generally below 50% of the maximum feedwater volume.

The heat transfer area of mini-circulation boiler is below 80 m^2, but most boilers have the heat transfer area of below 10 m^2 and the pressure of below 10 kgf/cm^2. Mini-circulation boilers include the single-tube type and the multiple-tube type with the header. At present, the multiple-tube type with 2 headers, one on top and another at the bottom, is commonly used.

In case of the mini-circulation boilers, the concept of water treatment to prevent the corrosion and scale problems is basically the same as that of the water tube boilers.

However, it is necessary to consider the special structure and characteristics of the mini-circulation boiler for the safety operation.

2.5.1 Scale Inhibition

The heating surface area of mini-circulation boilers is generally smaller than 10 m^2. However, the steam generation capacity per unit area is big and the heat flux is similar to that of the water tube boiler. In the case of same steam generation capacity, the holding water volume of a mini-circulation boiler is 1/2 to 1/10 of that of cylindrical boiler or water tube boiler. Therefore, if the feedwater quality is changed, the boiler water quality is also changed in a shorter time compared to the water tube boilers and so on. For example, if the hardness leakage from the softener happens, the hardness in the boiler water is more rapidly increased and causes severer scaling problems comparing with the other type of boilers.

Figure 2.71 shows the rapid increase in the cycles of concentration of a mini-circulation boiler

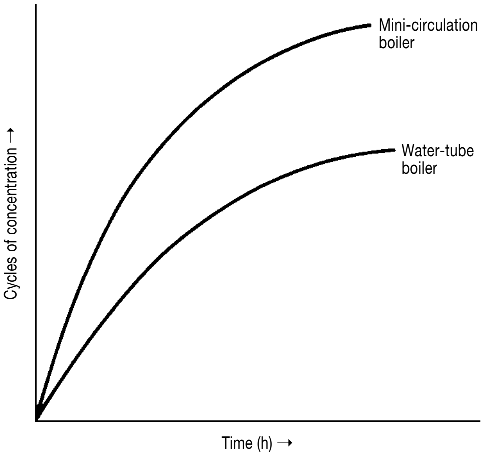


Fig. 2.71 Relationship between the type of boilers and the change in the cycles of concentration of boiler water with time

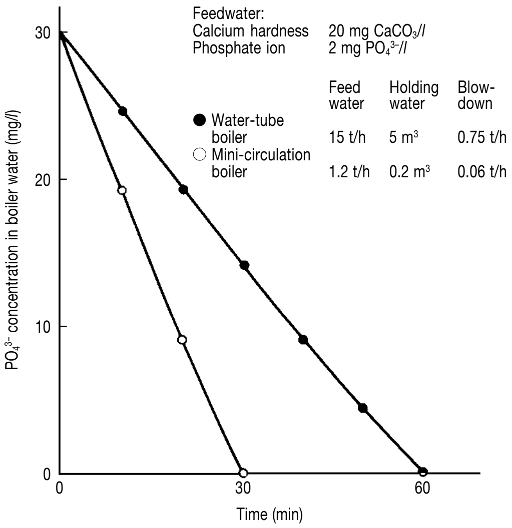


Fig. 2.72 Change of phosphate ion concentration in boiler water when a hardness leakage happens in feedwater

compared to a water tube boiler. Figure 2.72 shows the more rapid reduction of phosphate ion in the boiler water of a mini-circulation boiler than that of a water tube boiler when a hardness leakage happens in the feedwater.

To inhibit scaling in mini-circulation boilers, the control of water-softening and chemical injection has to be tightly carried out comparing with the other type of boilers, such as cylindrical boilers and water tube boilers.

Automatic operation control of softeners is commonly used for mini-circulation boilers. However, following cares should be paid for the safe operation of softeners:

① Check the hardness of the softened water sufficiently.
② Check whether the timer for the regeneration is correctly set or not.
③ Ensure that the regenerant is properly put into the tank.

2.5.2 Corrosion Inhibition

In the case of a mini-circulation boiler, the corrosion is caused by dissolved oxygen and following two types of corrosion are found:

① Corrosion of the bottom header,
② Corrosion of whole boiler system.

(1) Corrosion of bottom header

The corrosion of the bottom header is usually found in boilers having the structure shown in Figure 2.73. The corrosion is caused by the dissolved oxygen in feedwater and by the reduction of boiler water pH because of feedwater supply.

Table 2.18 shows the corrosion rates of carbon steel test coupons installed in a water tube of a mini-circulation boiler as shown in Figure 2.74. A higher corrosion rate is detected near the bottom header than those at the upper and middle parts.

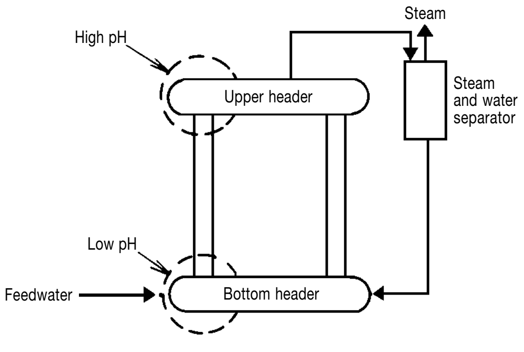


Fig. 2.73 Unbalance of boiler water pH in a mini-circulation boiler

Table 2.18 Corrosion rates of carbon steel test coupons in the water tube of a mini-circulation boiler

Position of test coupon	Upper	Middle	Bottom
Corrosion rate (mg/dm²·day)	3.5	3.8	70.1

Measures to inhibit the corrosion near the bot-

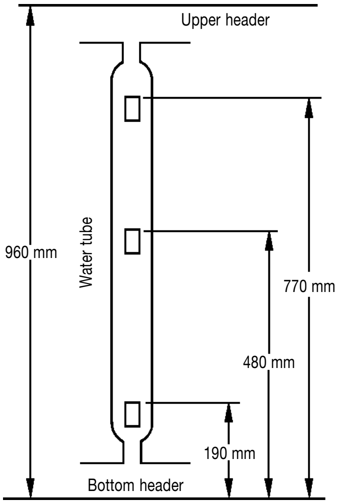


Fig. 2.74 Positions of test coupons in a water tube of a mini-circulation boiler

tom header are as follows:

① Increase of feedwater pH using a suitable boiler compound,
② Increase of boiler water pH by the initial dosing of a boiler compound from the operation start-up,
③ Prevention of feedwater entering into boiler during the operation stoppage by closing the valves and so on.

(2) Corrosion of whole boiler system

Generally no continuous blowdown equipment is installed in mini-circulation boilers. Since the intermittent blowdown is conducted and the holding water volume is a small, the sufficient control of blowdown is difficult.

Therefore, the blowdown of total holding water (total blowdown) is often done when the boiler operation is stopped.

However, the supply of feedwater at the operation start-up often causes the corrosion of whole boiler system. The cause of this corrosion is the dissolved oxygen and the low pH of the feedwater.

The measures to prevent this type of corrosion are as follows:

① Total blowdown is carried out just before starting the boiler operation.
② After the total blowdown, the initial dosing of boiler compound must be done.
③ Installation of a continuous blowdown equipment and minimization of the intermittent blowdown.

2.6 Preservation of Boilers during Stoppage

2.6.1 Corrosion of Boilers during Stoppage

Generally, water treatment is appropriately applied for boilers during the operation, but it sometimes becomes insufficient during the stoppage. Problem occurring in the boiler stoppage is mainly corrosion problem.

After stopping a boiler operation, the boiler water temperature drops and the steam in the boiler is condensed. Thus the boiler pressure becomes lower than the atmospheric pressure and air comes into the boiler through the steam valves, inspection holes and so on. As the result, the corrosion caused by oxygen occurs at the vapor phase and the waterline. Then the corrosion proceeds below the waterline.

Photograph 2.30 (p. 2-73) shows an example of boiler corrosion occurred during the stoppage.

Proper preservation treatment should be applied to prevent the corrosion during the operation stoppage in consideration of the preservation period.

2.6.2 Preservation Treatments for Boilers during Stoppage

The preservation treatments of boilers are classified into the wet preservation and the dry preservation. An appropriate preservation method should be chosen considering the term of preservation, the structure of boiler, air temperature and so on.

(1) Preservation during short term

When a boiler is stopped and preserved in a short period, the same chemicals using for the boiler operation are applied for the preservation. When the boiler pressure becomes approximately 1 kgf/cm^2 after the stoppage, water and chemicals are injected into the boiler to fill the boiler with water and to adjust the water quality to an appropriate one for the preservation.

Tables 2.19 to 2.21 show the relationship among the chloride and sulfate ion concentrations of boiler water at the stoppage, the duration of preservation, the pH of boiler water and chemical concentrations for the preservation. When the boiler operation is started again, the water level is reduced to the normal level of the operation by blowdown and the operation starts up.

Table 2.19 Preservation methods of boilers by using hydrazine during short period

Cl^- and SO_4^{2-} concentration of boiler water (mg/*l*)	Preservation period (day)	Chemical concentration and pH of boiler water		
		N_2H_4 (mg/*l*)	PO_4^{3-} (mg/*l*)	pH
Cl^-: below 100 SO_4^{2-}: below 100	Within 14	More than 0.1	60–100	12.0
Cl^-: 101–300 SO_4^{2-}: 101–300	Within 3	More than 1.0		
	4–7	More than 10		
	8–14	More than 100		
Cl^-: 301–500 SO_4^{2-}: 301–500	Within 3	More than 10		
	4–7	More than 50		
	8–14	More than 100		

Table 2.20 Preservation methods of boilers by using sodium sulfite during short period

Cl^- and SO_4^{2-} concentration of boiler water (mg/*l*)	Preservation period (day)	Chemical concentration and pH of boiler water		
		SO_3^{2-} (mg/*l*)	PO_4^{3-} (mg/*l*)	pH
Cl^-: below 100 SO_4^{2-}: below 100	Within 2	More than 10	60–100	12.0
Cl^-: 101–300 SO_4^{2-}: 101–300	Within 2	More than 100		
	3–5	More than 300		

Table 2.21 Preservation methods of boilers by using a saccharide during short period (within 10 days)

Cl^- and SO_4^{2-} concentration of boiler water (mg/*l*)	Chemical concentration and pH of boiler water		
	Saccharide (mg/*l*)	PO_4^{3-} (mg/*l*)	pH
Below 300	500–3,000	60–100	12.0

(2) Preservation during long term

(a) Wet preservation

The wet preservation of boilers to be filled with water, is widely applied. This method is suitable for boilers which the perfect blowdown of the holding water is impossible or an urgent restart-up is expected. However, in the case that the freezing of boiler water is anticipated, the dry preservation has to be applied.

Hydrazine or nitrite based chemicals are generally applied for the wet preservation. For boilers installed in hospitals, food factories and so on, nontoxic chemicals, such as organic acids, are applied for the preservation. Table 2.22 shows the preservation conditions with each chemicals. The term of preservation is usually up to six months, but it can be prolonged by the additional dosing of those chemicals to maintain the dosages shown in the Table 2.22.

The chemicals for the preservation are continuously injected into the feedwater so as to be kept the specified concentration in the boiler. After the chemical dosing, it is desirable to mix the chemical sufficiently by the water convection caused by the residual heat of boiler water or by the water circulation using a temporary circulation pump.

For the monitoring of the preservation condition, the pH, total iron and the chemical concentration are analyzed once or twice a month to keep the water quality in the control range. When the water quality is out of the range, the chemicals should be dosed to keep the water quality within the specified range.

In case that the mixing of chemicals with the boiler water is difficult or the total iron of boiler water tends to increase, all the water is discharged and the boiler should be filled with new feedwater including the specified concentration of the chemical.

Before the start-up of the boiler operation, all the water is discharged and the inside of boiler should be inspected.

(b) Dry preservation

Dry preservation is suitable for the boilers that the freezing of boiler water is anticipated or have to be preserved during long term. Two kinds of dry preservation using desiccants and sealing with nitrogen gas are usually used.

Table 2.22 Conditions of the wet preservation of boilers for long term

Kind of factory		General factories				Food factories and hospitals
Chemical		Hydrazine based		Nitrite based		Carboxylate based
Kind of feedwater		Softened	Demineralized	Softened	Demineralized	Softened or demineralized
Control range of boiler water quality	pH	above 9*	above 9*	above 7	above 7	above 11.5
	Chemical concentraion (mg/*l*)	above 200 as N_2H_4	above 100 as N_2H_4	above 200 as NO_2^-	above 100 as NO_2^-	above 5,000 as product
	Total iron	No trend of increase				

* It is preferable to use boiler compounds or volatile amines together with those chemicals.

For the application of dry preservation, all the boiler water is blowdown when the water temperature drops around 90 to 95° C, and the boiler inside is dried with the residual heat. The amounts of the desiccants required for the dry preservation are shown in Table 2.23.

The desiccant should be inspected periodically (once or twice a month) and the desiccant losing the moisture absorbing capacity should be replaced with a new one at once.

In the case of preservation sealing with nitrogen gas, the gas is introduced into the boiler to replace the water with the gas before the pressure in the boiler reaches the atmospheric pressure.

The pressure of the nitrogen gas in the boiler should be maintained at about 0.5 kgf/cm^2 and the gas should be injected if the pressure reduces around 0.3 kgf/cm^2.

2.7 Water Quality Control for Boiler System

Most of problems caused by water in boiler systems may be prevented if the daily water quality control is properly conducted. In order to prevent the problems and to operate the boiler system safely, the application of adequate water treatment and the sufficient water quality control are necessary. When a boiler water chemical treatment is planned, the control range of water quality is firstly determined according to the boiler structure and the operating conditions. Secondly, the treatment method by means of equipments and chemicals, and the control method of the cycles of concentration of boiler water are decided to maintain the control range.

Table 2.23 Required amounts of desiccants for the dry preservation of boilers

Kind of desiccants	Dosage (kg/m^3 boiler capacity)
Quicklime	3–5
Silica gel	1.5
Activated alumina	1.3
Calcium chloride	1.0
Synthetic zeolite	1.5

To confirm that the boiler water quality is kept within the control range, the water analysis should be carried out. When the water quality is out of the range, the operation conditions of the equipments for feedwater treatment, the chemical injection system, the blowdown condition and so on have to be checked to improve the operation condition for preventing the trouble occurrence.

2.7.1 Standard Water Quality Control Range

(1) Determination of water quality control range

A boiler water quality control range is set on the basis of the standard criteria and, the structure and operation conditions of a boiler.

In Japan, "The quality of boiler feedwater and boiler water (JIS 8223-1989)" of Japan Industrial Standard is generally used as the standard values. Also, the recommended standard values are proposed by boiler manufactures and water treatment chemical suppliers.

"The quality of boiler feedwater and boiler water (JIS B 8223-1989)" is shown in the pages A-31 to A-34 of the Appendices.

Generally, the steam purity is maintained when the boiler water and feedwater qualities are controlled in the ranges. In the case that the condensate is recovered as the feedwater, the condensate should be treated to satisfy the feedwater quality standard.

(2) Chemical treatment of boiler water

The chemical boiler water treatment methods in Japan are classified into the alkaline phosphate treatment, coordinated phosphate treatment and volatile treatment. In Germany and Russia, oxygen treatment is also applied for once through boilers in the power plants.

Recently, the oxygen treatment has been applied for boilers in power plans on trial in Japan. Therefore, the JIS 8223-1989 includes the standard qualities of boiler feedwater and boiler water for the oxygen treatment.

(a) Alkaline phosphate treatment

In the alkaline phosphate treatment, the pH of boiler water is adjusted by using sodium hydroxide and so on, and the Na/PO_4 mole ratio in the boiler water is controlled at 3.0 or higher.

In the case of low pressure boilers to be fed raw water or softened water, the boiler water pH is maintained in the range of 11.0 to 11.8 to prevent the scale and corrosion problems. In this case, the P-alkalinity of boiler water is supplied by the boiler compounds and the alkali generated from the thermal decomposition of carbonates including in the feedwater. In the case of medium pressure boilers to be fed demineralized water, the pH of boiler water is adjusted with sodium hydroxide and sodium phosphate.

For medium pressure boilers, the alkaline phosphate treatment or the coordinated phosphate treatment is generally applied. However, in case that the feedwater includes colloidal silica or organic matter like humic acid, the alkaline phosphate treatment is applied for obtaining the stable corrosion and scale inhibition by keeping the higher pH of boiler water comparing with the coordinated phosphate treatment.

(b) Coordinated phosphate treatment

The coordinated phosphate treatment is the method of adjusting the pH of boiler water by using trisodium phosphate and/or disodium hydrogen phosphate without free alkali to prevent the alkaline corrosion of boilers.

This method is applied for medium or high pressure boilers using demineralized water as the feedwater and the Na/PO_4 mole ratio in the boiler water is generally controlled within the range of 2.6 to 3.0.

If the hide-out of sodium phosphate occurs, free sodium hydroxide will remain in the boiler water and cause the alkaline corrosion in case that the Na/PO_4 mole ratio is higher than 2.85 at 300° C of water temperature and higher than 2.65 at 365° C[42) respectively. Therefore, the Na/PO_4 mole ratio should be controlled lower than those values to prevent the alkaline corrosion if the hide-out occurs.

(c) Volatile treatment

The volatile treatment is the method of adjusting the pH of boiler water by using only volatile substances like hydrazine, ammonia and volatile amines to prevent the alkaline corrosion and the hide-out problems. In the case of high pressure boilers, the amount of impurities in the feedwater should be strictly lowered, and the total solids in the boiler water should be controlled at the lowest level to minimize scaling on the heat transfer surfaces and to keep the steam purity.

In the case of once through boilers, the volatile treatment has to be applied because the structure requires to eliminate any solid substances, such as phosphates, from the boiler water.

In this treatment, since the pH of boiler water is low and nearly the same as the feedwater pH, the presence of silica and dissolved oxygen in the feedwater may cause the carryover and corrosion problems. Therefore, sufficient control of the feedwater quality is essential under the volatile treatment.

(d) Oxygen treatment

The oxygen treatment is classified into two categories of the neutral water treatment and the combined water treatment. In the case of neutral water treatment, neutral demineralized water is used as the feedwater and the dissolved oxygen is controlled at 20 ppb or higher. Under the combined water treatment, the feedwater pH is controlled within the range of 8.0 to 8.5 and the dissolved oxygen is maintained in rather higher range of 100 to 200 ppb. The oxygen treatment inhibits the corrosion of steels by passivating them with dissolved oxygen and prevents the scaling of iron oxides in the boilers.

Therefore, the oxygen treatment requires more strict control of feedwater quality than that of volatile treatment. This treatment has been developed and applied for once through boilers in Germany and Russia during these ten years or longer, and the trial application has been carried out in Japan recently.

(3) Control items for feedwater quality

Table 2.24 shows the control items of feedwater quality and their purposes. The aims of controlling feedwater quality are classified into corrosion inhibition, scale inhibition and the maintenance of steam purity

(a) pH

As the water pH becomes higher, the corrosion rate of carbon steel lowers. On the other hand, the corrosion rate of copper tends to increase at

Table 2.24 Control items of feedwater quality and their purposes

Control item	Purpose
pH	Corrosion inhibition Prevention of scaling caused by corrosion products
Total hardness	Scale control on heat transfer surface Reduction of sludge formation
Oils and fats	Prevention of foaming and carryover in boiler Prevention of carbon scale on heat transfer surface
Dissolved oxygen	Corrosion inhibition
Total iron and total copper	Prevention of scaling on heat transfer surface Prevention of under deposit corrosion
Hydrazine	Corrosion inhibition of feedwater line, boiler and condensate line
Electrical conductivity	Corrosion and scale control Maintenance of steam purity
Silica	Scale prevention on heat transfer surface Maintenance of steam purity

the pH of higher than 9 as shown in Figure 2.58(p.2-38). Therefore, the pH of feedwater, should be controlled in an appropriate range depending on the kinds of materials constituting a system.

For boilers feeding fresh or softened water, the pH of the feedwater is controlled in the range of 7 to 9. When the boiler is equipped with a feedwater heater or an economizer, the pH is controlled at about 9 to inhibit the corrosion.

In the case of medium or high pressure boilers feeding demineralized water, it is more important to control the corrosion of feedwater line because scaling due to corrosion products coming into the boiler with the feedwater becomes severer as the pressure increases. The pH of feedwater is generally controlled in the range of 8.5 to 9.0 for the system using copper and copper alloys, and 9.0 to 9.5 for the systems without copper materials.

In the oxygen treatment, the pH of feedwater is controlled in the range of 6.5 to 9.0 by using volatile amines or ammonia if the pH adjustment is necessary.

(b) Total hardness

In the case of recent low pressure boilers of 20 kgf/cm^2 or lower, since the evaporation rate is high and exceeds 50 kg/m^2·h, they tend to suffer the scaling problems. When the water blowdown is reduced to save energy, the total hardness of feedwater has to be severely controlled below 1 mg $CaCO_3/l$ for the non-scale operation.

For the boilers with the pressure of higher than 20 kgf/cm^2, the demineralized water of zero hardness has to be used as the feedwater, because of the higher scaling tendency.

(c) Oils and fats

Oils and fats in the feedwater should be controlled as nearly as possible to zero.

Since the operations of high pressure boilers are greatly suffered by the fouling of the heat transfer surface with oils and fats, their entering into boilers has to be prevented.

(d) Dissolved oxygen

In the boilers without deaerator, dissolved oxygen concentration in the feedwater is generally high. Therefore, to keep the dissolved oxygen in the feedwater as low as possible, the increase of feedwater temperature at the open section like the feedwater tank is an effective measure.

In the case of water-tube boilers with the pressures of higher than 20 kgf/cm^2, deaerators should be equipped because of the heavy corrosion caused by the dissolved oxygen. The upper limit of dissolved oxygen concentration in feedwater is generally determined according to the guaranteed value of the deaerator.

In the oxygen treatment, the dissolved oxygen has to be controlled in the range of 0.02 to 0.2 mg/l by injecting oxygen gas or hydrogen peroxide into the feedwater at the outlet of deaerator.

(e) Total iron and total copper

To eliminate the problems caused by total iron, the total iron in the feedwater should be controlled lower than the allowable upper limit according to the type and pressure of the boiler.

The copper in the feedwater should be controlled as low as possible because it may deposit on the inside of boilers as metallic copper and it forms the galvanic couple with steel. A higher heat flux of medium or high pressure boilers accelerates the scaling by the iron and copper oxides (corrosion products) on the heating surface and the scaling seriously reduces the boiler efficiency. Therefore, the severer upper limits for total iron and total copper in the feedwater should be applied for boilers with the higher pressure.

(f) Hydrazine

In the case of boilers equipped with deaerators, the hydrazine concentration in feedwater is controlled at around twice of mole equivalent concentration against the dissolved oxygen concentration of feedwater to remove the oxygen sufficiently and to maintain the residual hydrazine in the feedwater. The overdosing of hydrazine sometimes increases the condensate pH excessively because the hydrazine changes to ammonia through the thermal decomposition in the boiler water. In that case, the dosage of hydrazine in the feedwater should be controlled according to the condensate pH.

(g) Electrical conductivity

In water-tube boilers with the pressure of 125 kgf/cm^2 or higher, the electrical conductivity of feedwater is specified to keep the total dissolved solid in the boiler water as low as possible.

In once through boilers with the pressure of 75 kgf/cm^2 or higher, the total dissolved solids in the feedwater should be strictly controlled because almost all the solids deposit on the inside surface of evaporation tubes. The total dissolved solid of boiler water is generally controlled by analyzing the electrical conductivity.

The electrical conductivity of the feedwater is increased by the presence of hydrazine, ammonia, or volatile amines. Therefore, the conductivity is measured after removing those substances from the sample by using a strongly acidic cation exchange resin of the H-form.

As the oxygen treatment requires a much better water quality, the electrical conductivity of feedwater should be controlled below 0.2 μS/cm.

(h) Silica

In once through boilers with the pressure of 75 kgf/cm^2 or more, the silica concentration in the feedwater should be controlled less than 0.02 mg/*l* as SiO_2 to prevent the carryover of silica into the steam.

(4) Control items for boiler water quality

Table 2.25 shows the control items of boiler water quality and their purposes.

Table 2.25 Control items of boiler water quality and their purposes

Control item	Purpose
pH	Corrosion inhibition Scale prevention due to silica and hardness
P-alkalinity	Prevention of silica scaling
Electricalconductivity or Total dissolved solids	Control of corrosion, sludge and scale Prevention of carryover
Chloride ion	Corrosion inhibition Determination of the cycles of concentration of boiler water
Phosphate ion	Inhibition of calcium scale Control of boiler water pH
Sulfite ion or hydrazine	Corrosion inhibition
Silica	Prevention of silica scale Prevention of carryover

(a) pH

The corrosion rate of carbon steel at high temperature is minimized in the pH range of 11 to 12 as shown in Figure 2.75[43)]. Thus the corrosion of boilers is prevented by controlling the pH between 11 to 12.

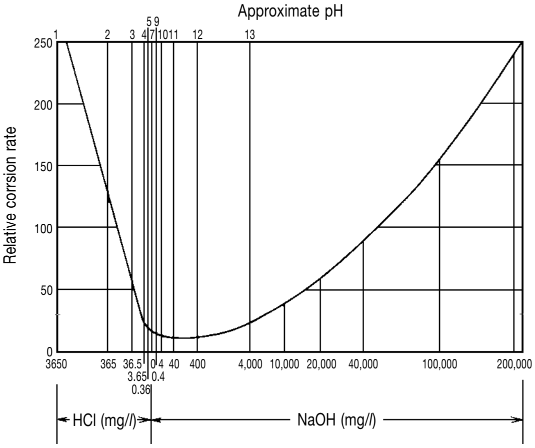


Fig. 2.75 Relationship between pH and the corrosion rate of carbon steel at 310°C

However, the pH on the boiler tube surface becomes higher than that of boiler water because the concentration film is formed on the heating surface as shown in Figure 2.6 (p.2-6). Therefore, the boiler water pH is controlled lower than 11 in case of medium or high pressure boilers.

The pH of boiler water is mainly adjusted by using sodium hydroxide for low pressure boilers applying the alkaline phosphate treatment. Under the coordinated phosphate treatment for medium or high pressure boilers, trisodium phosphate and/or disodium hydrogen phosphate are used for the pH control to avoid the alkaline corrosion. For preventing the hide-out of sodium phosphate, the boiler water pH is adjusted by using volatile substances like hydrazine, ammonia, or volatile amines.

To minimize the silica transfer from the boiler water into the steam in medium or high pressure boilers, the boiler water pH is controlled at the upper limit of the control range.

To prevent the scaling of hardness components or silica in low pressure boilers, the boiler water pH is controlled in the range of 11 to 12 under the presence of a sufficient concentration of phosphate ion.

(b) Alkalinity

Substances analyzed as alkalinity of boiler water include sodium hydroxide, sodium carbonate, sodium phosphate, sodium silicate and so on. These substances originate from the feedwater or additives, such as boiler compounds.

In the case of boilers feeding raw or softened water including higher silica, the scale with a large silica content tends to be formed. To prevent silica scaling, the P-alkalinity (mg $CaCO_3/l$) of boiler water should be controlled at 1.7 times or more of the silica concentration (mg SiO_2/l), as well as controlling the silica concentration of boiler water. The softening of feedwater is also effective to prevent silica scale.

The pH and P-alkalinity of boiler water are important factors to prevent the corrosion and scaling problems. However, the increase of silica concentration in boiler water decreases the boiler water pH under the same P-alkalinity level as shown in Figure 2.76. Therefore, in the case of high silica boiler water, both the pH and P-alkalinity of boiler water should be strictly controlled.

In the case of boilers feeding with demineralized water, the alkali of boiler water is supplied by only boiler treatment chemicals and the silica concentration is kept at very low level. In that case, since the pH and P-alkalinity have the close correlation, the pH control of boiler water results to control the P-alkalinity.

(c) Total solids or electrical conductivity

The total solids in boiler water consist of dissolved solids and suspended solids.

The increase of the total solids causes the deposition and scaling of the dissolved solids with lower solubilities on the heat transfer surfaces. The suspended solids may accumulate at the sections with the low water flow velocity and disturb the water circulation in the evaporation tubes. Therefore, the total solid concentration should be controlled below a specified upper limit.

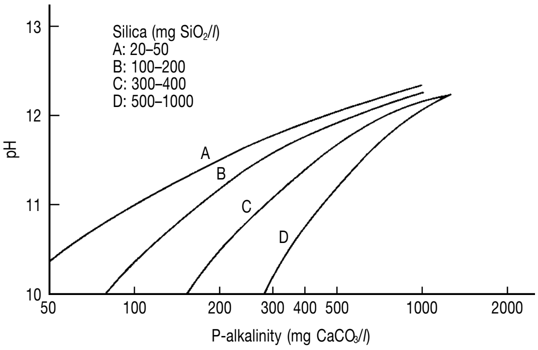


Fig. 2.76 Influence of silica concentration on the relationship between the pH and P-alkalinity of boiler water

In addition, a higher total solids cause the carryover and lower the steam purity. The total solids of the boiler water should be kept at the lower level to maintain the steam purity as the pressure becomes higher.

Since almost all of the dissolved solids are electrolytes, the electrical conductivity of boiler water increases as the total solid concentration increases. Therefore, the total solid concentration is appropriately controlled by controlling the electrical conductivity analyzed easily.

(d) Chloride ion

Since the chloride ion always exists in the dissolved state without precipitation, the cycles of concentration of boiler water is calculated from the chloride ion concentrations of feedwater and boiler water.

Since the anions, such as chloride and sulfate ions, in the boiler water deteriorates the passivation film of steel, they promotes the corrosion under the presence of oxygen as shown in the Figure 2.17(p.2-12). Thus the chloride ion concentration in the boiler water is maintained as low as possible.

(e) Phosphate ion

In boilers feeding with softened water, phosphate ion concentration should be controlled at the upper limit to cope with any unexpected leakage of hardness from the softener. In boilers fed with fresh water, phosphate ion concentration in boiler water is maintained in the range of 20 to 100 mg PO_4/l considering the fluctuation in the hardness of feedwater.

In water tube boilers feeding with demineralized water, since the feedwater includes no hardness, phosphate is used for controlling the boiler water pH mainly. In that case, the boiler water pH is determined by the Na/PO_4 ratio of the phosphate and the phosphate ion concentration. The lower pH and the lower phosphate concentration ranges are applied for boilers with the higher pressure.

(f) Oxygen scavengers

(i) Hydrazine

In the case of boilers with the pressure below 20 kgf/cm^2, the boiler corrosion is prevented by keeping the hydrazine in the boiler water above 0.1 mg/l regardless of the installation of deaerator.

The hydrazine is generally injected into the feedwater to maintain the specified concentration in the boiler water.

In the boiler of which the pressure is higher than 20 kgf/cm^2 and the deaerator is installed, the dosage of hydrazine in the feedwater is specified in the range of above 0.01 mg/l to above 0.2 mg/l according to the pressure range.

(ii) Sulfite

The control range of sulfite ion concentration in boiler water is also specified according to the boiler pressure. The upper limit becomes lower as the pressure increases. The installation of deaerator also decreases the upper limit.

Sulfite based oxygen scavengers are generally injected into the feedwater after the outlet of deaerator.

Sulfite decomposes and yields corrosive sulfur dioxide gas and hydrogen sulfide gas at the temperature of above 280° C. Therefore, the sulfite is generally applied for the boiler of the pressure below 65 kgf/cm^2.

(iii) Saccharides and the other organic compounds

Recently, saccharides and the other organic compounds, such as ascorbic acid and alkanol amines, are used as oxygen scavengers substituted for toxic hydrazine. As the JIS B 8223-1989 has no control limit for those new oxygen scavengers, the suppliers of those chemicals determine own control limits for them.

(g) Silica

The silica concentration is generally high in the boiler water of low pressure boilers fed with softened water. For preventing the silica scale, the P-alkalinity of boiler water is maintained more than 1.7 times of the concentration of silica to keep the silica as water soluble sodium metasilicate.

The Japanese Industrial Standard, "Feedwater and Boiler Water Quality for Boilers" (JIS B8223-1989) gives no control limit of the silica concentration in boiler water for cylindrical boilers and water-tube boilers of 20 kgf/cm^2 or lower. In those cases, the required P-alkalinity of boiler water is determined by the same calculation method for the boilers fed with softened water. For cylindrical boilers with the lower heat flux than the water-tube boilers, the upper limit of silica in the boiler water is extended up to 450 mg SiO_2/l.

In the boilers fed with demineralized water, the silica concentration is generally kept in the very low level. However, the silica concentration in boiler water should be controlled below the specified concentration to keep the silica concentration in the steam lower than 0.02 mg SiO_2/l for preventing the silica scaling on turbine blades and so on. The upper limit of silica in boiler water has to be lowered as the boiler pressure increases, because the solubility of silica increases as the steam temperature increases.

2.7.2 Control of Boiler Water Blowdown

(1) Purpose of blowdown

The purpose of boiler water blowdown is to control the concentration of boiler water and to discharge sludge. Substances including in the feedwater and chemicals applied are concentrated as the dissolved solids or suspended solids in the boiler water.

The increase of dissolved solids and suspended solids in boiler water causes the following problems:

① Reduction of steam quality, scaling in superheaters and turbine blades, and the reduction of their efficiencies by the foaming or carryover,

② Acceleration of corrosion by increasing in chloride and sulfate ion concentration,

③ Scaling on the heating tube by increasing in the concentration of dissolved solids with the low solubilities,

④ Reduction of boiler efficiency and occurrence of under deposit corrosion by the sludge accumulation in boiler.

To prevent these troubles, it is essential to discharge the concentrated boiler water for controlling the concentration of total dissolved solids in the boiler water within the control limit.

(2) Determination of blowdown rate

Relationship among the blowdown rate, the amount of blowdown and the amount of feedwater are expressed by following equations:

$$X = \frac{B}{F} \times 100 \qquad \text{.....} \quad (2.72)$$

$$B = \frac{X \times F}{100} \qquad \text{.....} \quad (2.73)$$

where

X = blowdown rate (%)

B = amount of blowdown (t/h)

F = amount of feedwater (t/h)

When the total solid concentration of boiler water is kept at a constant level, the amount of total solids coming into the boiler with the feedwater is equal to the amount of total solids discharged from the boiler by blowdown.

$$F \times F_s = B \times B_s \quad \text{.....................................} \quad (2.74)$$

where

F_s = total solid concentration of feedwater (mg/*l*)

B_s = total solid concentration of boiler water (mg/*l*)

Then, the concentration ratio of dissolved solids in boiler water (cycles of concentration) is obtained from the equation (2.75).

$$N = \frac{B_s}{F_s} = \frac{F}{B} \quad \text{.....................................} \quad (2.75)$$

where

N = cycles of concentration of boiler water

In the case of low pressure boilers fed with softened or raw water, the blowdown is carried out to keep the concentrations of total solids (or electrical conductivity), chloride ion and silica within their control limits. Therefore, the maximum value among three blowdown rates obtained from the following equations should be chosen as the most appropriate blowdown rate:

$$B_{TS} = \frac{F_{TS}}{S_{TS}} \times 100 \quad \text{................................} \quad (2.76)$$

$$B_{Cl^-} = \frac{F_{Cl^-}}{S_{Cl^-}} \times 100 \quad \text{................................} \quad (2.77)$$

$$B_{SiO_2} = \frac{F_{SiO_2}}{S_{SiO_2}} \times 100 \quad \text{................................} \quad (2.78)$$

where

B_{TS} = blowdown rate obtained from the total solids (%)

B_{Cl^-} = blowdown rate obtained from the chloride ion (%)

B_{SiO_2} = blowdown rate obtained from silica (%)

F_{TS} = total solid concentration of feedwater (mg/*l*)

F_{Cl^-} = chloride ion concentration of feedwater (mg/*l*)

F_{SiO_2} = silica concentration of feedwater (mg SiO/*l*)

S_{TS} = control limit of total solid for boiler water (mg/*l*)

S_{Cl^-} = control limit of chloride ion for boiler water (mg/*l*)

S_{SiO_2} = control limit of silica for boiler water (mg SiO_2/*l*)

The addition of boiler compound and so on increases the total solids and the electrical conductivity of boiler water. Especially when high concentration of sodium sulfite based oxygen scavengers is used, the total solids and electrical conductivity of boiler water are considerably increased by yielding sodium sulfate as shown in Figure 2.77. In that case, the actual blowdown rate should be determined considering the increases in the total solids and the conductivity.

In the case of medium or high pressure boilers fed with demineralized water, the blowdown is usually conducted by referring to the silica concentration in boiler water. The blowdown rate is generally 0.5 to 2.0%.

(3) Blowdown method

Blowdown methods of boiler water are divided into the continuous blowdown and intermittent blowdown.

(a) Continuous blowdown

The continuous blowdown usually carries out to discharge water from the upper layer of boiler water and it is effective for discharging the floating suspended matters.

This method easily controls the boiler water quality within the control range and reduces the blowdown amount comparing with the intermittent blowdown. The thermal energy of blowdown water is readily recovered by using a heat exchanger for preheating the feedwater.

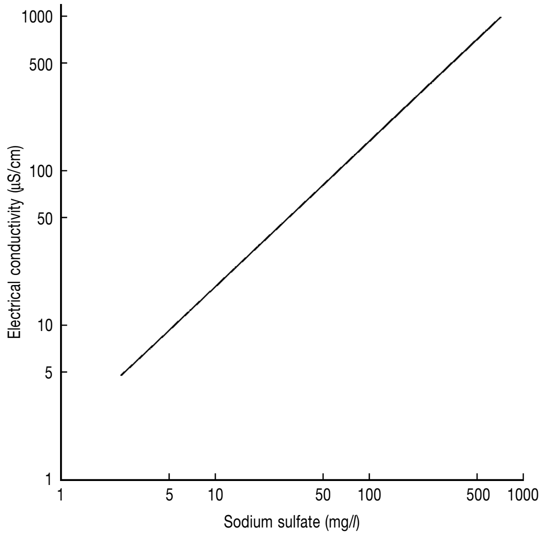


Fig. 2.77 Relationship between the sodium sulfate concentration and electrical conductivity of boiler water

The fuel cost saving by the reduction of blowdown or by the recovery of thermal energy from the blowdown water is referred to the section 2.8.

(b) Intermittent blowdown

The intermittent blowdown generally carried out to discharge water from the bottom of boiler drum and it is effective to discharge the sludge accumulated at the bottom.

This method is difficult to keep the boiler water quality constantly and to recovery the thermal energy comparing with the continuous blowdown.

2.7.3 Control of Chemical Injection

(1) Purpose

The purpose of chemical injection control is mainly to make boiler treatment chemicals to show the sufficient effects by controlling the water quality in the specified ranges.

Some chemicals hardly show their sufficient effects and sometimes may promote the problems caused by water if their dosages, injection points, injection methods and so on are not adequate. Therefore, the functions and characteristics of chemicals mentioned in the section 2.4, should be fully understood to carry out the appropriate chemical injection control.

(2) Dissolving or dilution of chemicals

Chemicals for boiler treatment are generally injected after being dissolved or diluted with water to the specified concentrations. Hardness components in the water for dissolving or dilution react with alkali or phosphate ion in the chemical injection tanks or chemical feed lines, and produce the insoluble matters which cause the clogging of injection pumps or the feed lines. Therefore, water including no hardness must be used for chemical dissolving or dilution.

Sodium sulfite based oxygen scavengers should be dissolved with water at 40° C or lower because the sulfite is rapidly consumed reacting with the dissolved oxygen in water of higher temperature.

Recently, liquid type multifunctional boiler chemicals having various functions of boiler compound, oxygen scavenger, sludge dispersant, etc., are widely used. These chemicals realize the easy handling and injection control without any dissolving and dilution processes.

The frequency of dissolving or dilution of chemicals is generally once every one to ten days. Sodium sulfite based oxygen scavengers should be dissolved at least once a day because the effective concentration is rapidly lowered after dissolving. The addition of some stabilizers prevents the reduction of sulfite concentration and keeps the concentration in the chemical tank during one week or more as shown in Figure 2.55(p.2-36).

(3) Determination of chemical dosages

Chemical dosages are different for the initial treatment at the start-up time of boilers, such as after scheduled overhaul, and for the maintenance treatment during the normal operation.

(a) Initial dosage

The initial dosing is performed to obtain the same water quality at start-up as that in normal operation. The initial dosage is calculated against the holding water volume of the boiler.

The initial dosage of boiler compound is usually determined on the basis of phosphate ion concentration by using the following equation:

$$C_I = \frac{(F_{CaH} \times 0.57 + B_{PO_4}) \times 100 \times HW}{C_{PO_4}} \quad \text{..................................} \ (2.79)$$

where

C_I = initial dosage of boiler compound (g)

F_{CaH} = calcium hardness in feedwater (mg $CaCO_3/l$)

B_{PO_4} = phosphate ion concentration to be kept in boiler water (mg PO_4/l)

C_{PO_4} = content of phosphate ion in boiler compound (% as PO_4)

HW = holding water volume of boiler (m^3)

No initial dosing is carried out in the case of acidic boiler compounds because they reduce the boiler water pH at the boiler start-up and cause the corrosion. In that case, an alkaline boiler compound is used for the initial treatment and it is changed to the acidic one under the normal operation.

The initial dosage of oxygen scavenger should be two or three times of the concentration required for removing the dissolved oxygen in boiler water at the start-up.

The initial dosage of volatile amines is the amount required to adjust the pH of the feedwater and condensate within the specified value, that is, same to the maintenance dosage.

(b) Maintenance dosage

The maintenance dosing of chemicals aims to adjust the quality of boiler water within the specified range during the normal operation. The maintenance dosage is usually calculated against the amount of feedwater.

The maintenance dosing of boiler compounds is determined on the basis of the concentration of phosphate ion by using the following equation:

$$C_M = \left(F_{CaH} \times 0.57 + \frac{B_{PO_4}}{N}\right) \times \frac{100 \times F_W}{C_{PO_4}} \quad \text{.....................................} \ (2.80)$$

where

C_M = maintenance dosing rate of boiler compound (g/h)

N = cycles of concentration of boiler water

F_W = amount of feedwater (m^3/h)

The maintenance dosage of oxygen scavenger is determined based on the dissolved oxygen in the feedwater. For a boiler equipped with a deaerator, the maintenance dosage is generally two to three times of the concentration required to remove the oxygen in the feedwater as shown in the equation (2.81). The guaranteed concentration of oxygen at the deaerator outlet by the manufacturer is usually used as the oxygen concentration of feedwater.

$$S_M = D_{O1} \times (2 \text{ to } 3) \times S_O \times F_w \quad \text{.....................} \ (2.81)$$

where

S_M = maintenance dosing rate of oxygen scavenger (g/h)

D_{O1} = guaranteed value of dissolved oxygen at the outlet of deaerator (mg/*l*)

S_O = dosage of oxygen scavenger required to remove 1 mg/*l* of dissolved oxygen (mg/*l*)

For boilers without deaerator, the concentration of dissolved oxygen in the feedwater is analyzed or estimated from the saturated dissolved oxygen concentration at the water temperature in the feedwater tank. Then the oxygen scavenger is added with the dosage of 1 to 1.5 times of that required to remove the dissolved oxygen as shown in the equation 2.82. The relationship of temperature and the saturation concentration of dissolved oxygen is shown in Figure 2.78[44].

$$S_M = D_{O2} \times (1 \text{ to } 1.5) \times S_O \times F_w \quad \text{..................} \ (2.82)$$

where

D_{O2} = concentration of dissolved oxygen in feedwater (mg/*l*)

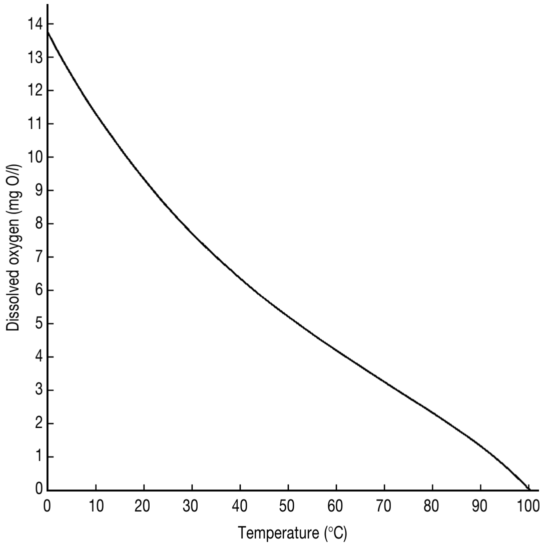


Fig. 2.78 Relationship between water temperature and the saturation concentration of dissolved oxygen (atmospheric pressure)

For the maintenance dosing of volatile amines, the dosage required to adjust the pH of condensate within a specified pH is determined from the curves indicating the relationship among condensate pH, the dosage of amines and the CO_2 content of condensate. Figure 2.79 shows a typical relationship among the dosage of amines, condensate pH and the CO_2 content. The relationship between the dosages of typical amines and condensate pH in the absence of CO_2 gas shown in Figure 2.66(p.2-41).

(4) Injection points of chemicals

Boiler compounds are injected into the boiler drum or into the nearest feedwater line to the drum. When an acidic boiler compound is injected into the feedwater line, it lowers the pH of feedwater after the injection point and corrodes the feed-water piping. Therefore, the piping after the injection point should be made of a corrosion-resistant material, such as stainless steel.

Oxygen scavengers are generally injected into the feedwater line at the most distant point from the boiler. However, sodium sulfite based oxygen scavengers is never injected into an open system like a feedwater tank.

For boilers equipped with deaerators, hydrazine based oxygen scavengers are injected at the inlet of the deaerator, while sodium sulfite based ones are injected at the outlet.

As shown in Figure 2.80, in the case that the feedwater is injected into the desuperheater, sodium sulfite based oxygen scavengers and boiler compounds have to be injected into the feedwater line to the boiler.

Volatile amines are usually injected into the feedwater line at a point as far as possible from the boiler. They can be injected together with hydrazine based oxygen scavengers.

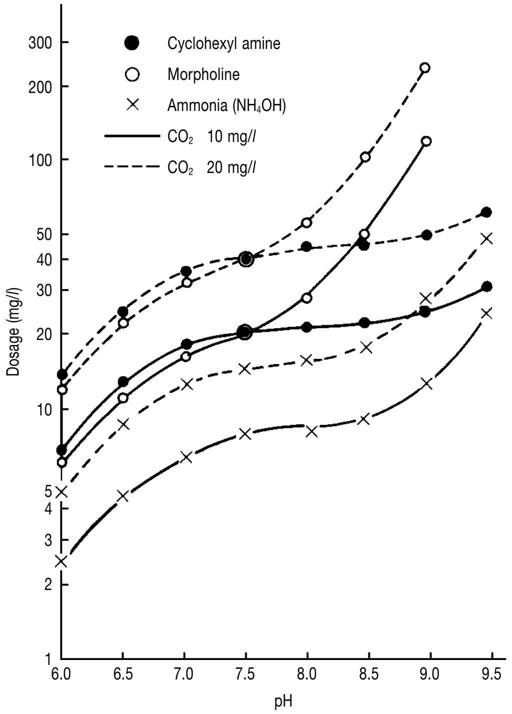


Fig. 2.79 Relationship among the dosages of volatile amines, condensate pH and the CO_2 content

(5) Injection methods of chemicals

Chemical injection methods are divided into the continuous and intermittent injections.

The continuous injection is easy to control the water quality of boiler system within the control range. The continuous injection carried out at a constant rate or at a proportional rate to the amount of feedwater using an automatic control system. Among them, the injection with a constant rate using a metric pump is generally employed.

In case that the level of the boiler water is regulated with a level controller of float type or electrode type, the amount of feedwater is controlled by switching on and off the feedwater pump. Then the feedwater containing a constant concentration of chemical is always fed to the boiler by injecting the chemical with the dosage adjusted to the capacity of feedwater pump.

In the boiler of which the water level is regulated using a thermal expansion tube type level controller, since the feedwater quantity is controlled by changing the opening of the control valve, the chemical injection with a constant rate results in an excess or shortage of chemical dosage in the boiler water. Therefore, the proportional injection of chemicals to the amount of feedwater is recommended for a boiler having the relatively large load fluctuation.

The intermittent chemical injection is difficult to maintain a constant quality of water in the boiler system and the chemical consumption becomes larger than that in the case of the continuous injection. When the intermittent injection is applied, the injection frequency should be increased to compensate the disadvantage. Intermittent injection of oxygen scavengers and neutralizing amines must be avoided because it reduces their performances.

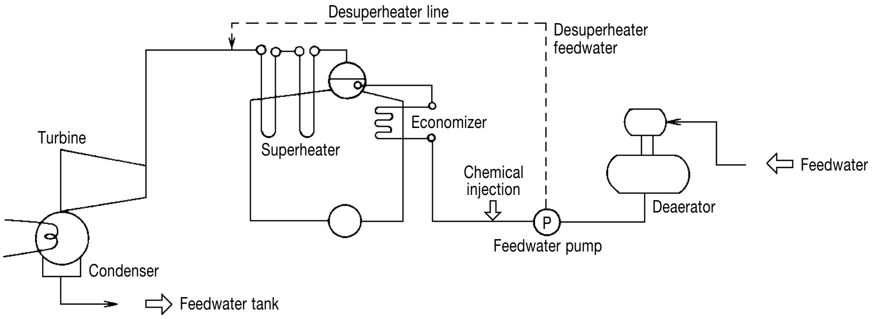


Fig. 2.80 Injection point for sodium sulfite based oxygen scavengers and boiler compounds in case of a boiler equipped with a desuperheater

2.8 Energy Conservation for Boilers

Through two times of oil crisis in 1973 and 1979, it has been difficult to get abundant and cheap crude oils which had been the driving force of the economic growth in Japan. In Japan, "Law Concerning the Rationalization of the Use of Energy" has enforced to establish concrete and effective measures for saving energy. As the result of employing the measures for saving energy and for diversifying energy resources, the consumption of crude oil in Japan has reduced beyond the expectation of the government accompanied by the structural reforms of industries.

However, Japan still largely depends on foreign countries for the energy resources. Therefore, it is necessary to encourage the energy conservation in order to keep the economical growth.

Measures for energy saving in boiler systems include various ways: the reduction of blowdown, the recovery of condensate, the prevention of thermal efficiency drop caused by scaling, the heat recovery from blowdown water, the prevention of steam leakage, etc.

Methods for saving energy by applying appropriate water treatments are presented below.

2.8.1 Recovery of Condensate

Condensate recovery is the most effective energy saving method for boiler system. In the total heat (energy) of steam, the latent heat is mainly utilized in the industrial processes and the sensible heat is scarcely utilized. As the heat remaining in the condensate is 20 to 30% of the total heat of steam, the recovery of condensate results in a considerable fuel saving.

The advantages of condensate recovery are as follows:

① Fuel saving,
② Feedwater saving,
③ Blowdown saving.

The quality of condensate is similar to a demineralized water. So the recovery of condensate as boiler feedwater is able to reduce the blowdown by increasing the cycles of concentration.

(1) Required conditions for condensate recovery

Although the recovering of condensate is very effective for saving energy and water, the recycling of condensate including high total iron is difficult without the reduction of iron content, because the iron deposits on the heat transfer surface of boiler and causes the under deposit corrosion.

Accordingly, the iron content has to be reduced by preventing the corrosion of steam and condensate line for recycling the condensate. The use of dispersants for iron is also recommended to increase the allowable limit in feedwater.

(2) Unit heat price of condensate

The unit heat price of condensate is represented by the equation (2.83).

$$Q_C = \frac{1{,}000 \times (I_C - I_F)}{\frac{n}{100} \times C} \times a \quad \text{..................} \ (2.83)$$

where

Q_C = unit heat price of condensate (yen/t)
I_C = enthalpy of condensate (kcal/kg)
I_F = enthalpy of feedwater (kcal/kg)
n = boiler efficiency (%)
C = lower heat value of fuel (kcal/kg)
a = unit price of fuel (yen/kg)

The unit heat price of one ton of condensate at 90° C is calculated from the equation (2.83) assuming a feedwater temperature of 20° C, boiler efficiency of 85%, and the use of heavy oil with the lower heat value of 10,000 kcal/kg and the unit price of 30 yen/kg:

$$Q_C = \frac{1{,}000 \times (90 - 20)}{\frac{85}{100} \times 10{,}000} \times 30 = 247 \quad \text{.......} \ (2.84)$$

Namely, one ton of the condensate has the unit heat price of 247 yen.

(3) Example of energy saving by condensate recovery

Since A company used no corrosion inhibitor for the steam and condensate line in the past, the condensate line was corroded and the total iron content of condensate was high. Consequently, the recycling of condensate was difficult.

Then a corrosion inhibitor for the steam and condensate line, and an iron dispersant were applied to reduce the total iron of condensate. As the result, the recovering of condensate by 40% has realized for saving a large amount of fuel and water.

The boiler operation conditions of A company are shown in Table 2.26. Table 2.27 shows the necessary data for calculating the fuel and water costs of A company.

The fuel consumption of boiler is obtained from the equation (2.85).

$$F = \frac{E \times 1{,}000 \times (I_S - I_F)}{\frac{n}{100} \times C} + \frac{B \times 1{,}000 \times (I_B - I_F)}{\frac{n}{100} \times C} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(2.85)}$$

where
F = fuel consumption (kg/day)
E = evaporation rate (t/day)
B = blowdown (t/day)
I_S = enthalpy of generated steam (kcal/kg)
I_F = enthalpy of feedwater (kcal/kg)
I_B = enthalpy of boiler water (kcal/kg)
n = boiler efficiency (%)
C = lower heat value of fuel (kcal/kg)

The equation (2.85) gives the daily fuel consumption of A company at 7,736 kg. Accordingly, the monthly fuel consumption and fuel cost become as follows:

Fuel consumption (t/month)

$$= \frac{7{,}736 \times 25}{1{,}000} = 193.4 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(2.86)}$$

Fuel cost (10^3 yen/month) = 193.4 × 30 = 5,802 .... (2.87)

Table 2.26 Boiler operational conditions of A company

Treatment	Old	Improved
Type of boiler	Cylindrical	
Normal operation pressure (kgf/cm^2)	7	
Evaporation rate (t/day)	100	
Blowdown (t/day)	11.1	6.7*1
Blowdown rate (%)	10	6.3
Feedwater (t/day)	111.1	106.7
Recovery of condensate (t/day)	0	40
Recovery ratio of condensate (%)	0	40
Water consumption (t/day)	111.1	66.7
Kind of feedwater	Softened water	Softened water and condensate
Condensate temperature (°C)	—	90
Feedwater temerature (°C)	20	46.2*2

*1: Generally, the quantity of blowdown is decreased from B (t/day) to $B\left(1 - \frac{\alpha}{100}\right)$ (t/day), if α% of the condensate against evaporation is recovered.

*2: Assuming the temperatures of supply water and condensate to be 20°C and 90°C respectively, the temperature of feedwater after the recovery of 40% of condensate becomes:

$$\frac{20 \times 66.7 + 90 \times 40}{66.7 + 40} = 46.2°\text{C}$$

Table 2.27 Data for fuel and water cost estimation

Duration of boiler operation (day/month)	25
Boiler efficiency (%)	85
Kind of fuel	Heavy oil
Price of fuel (Yen/kg)	30
Lower heat value of fuel (kcal/kg)	10,000
Cost of feedwater (Yen/t)	400
Boiler water temperature (°C)	171.3
Enthalpy of steam (kcal/kg)	660.8 (at 171.3°C)

The fuel consumption and cost after the condensate recovery are calculated by the same way as follows:

Fuel consumption (t/month); 183.2
Fuel cost (10^3 yen/month); 5,496

The condensate recovery has led to the fuel savings by 10.2 ton per month and the cost saving by 306 thousand yen per month.

Further, the condensate recovery reduces the water consumption from 2,778 to 1,668 t/month and saves the water cost of 444 thousand yen/month. The relationship between the condensate recovery ratio, and the saving of fuel and water costs in A company is shown in Figure 2.81.

2.8.2 Prevention of Steam Leakage

The corrosion of a steam and condensate line sometimes causes a steam leakage at the joints of pipings, branch pipings and so on with the thin wall thicknesses. Sufficient countermeasures against the corrosion should be taken because the steam leakage leads to a great energy loss.

(1) Unit price of steam

The unit heat price of steam is expressed by equation (2.88).

$$Q_S = \frac{1{,}000 \times (I_S - I_F)}{\frac{n}{100} \times C} \times a \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots (2.88)$$

where

Q_S = unit heat price of steam (yen/t)
I_S = enthalpy of steam (kcal/kg)
I_F = enthalpy of feedwater (kcal/kg)
n = efficiency of boiler (%)
C = lower heat value of fuel (kcal/kg)
a = unit price of fuel (yen/kg)

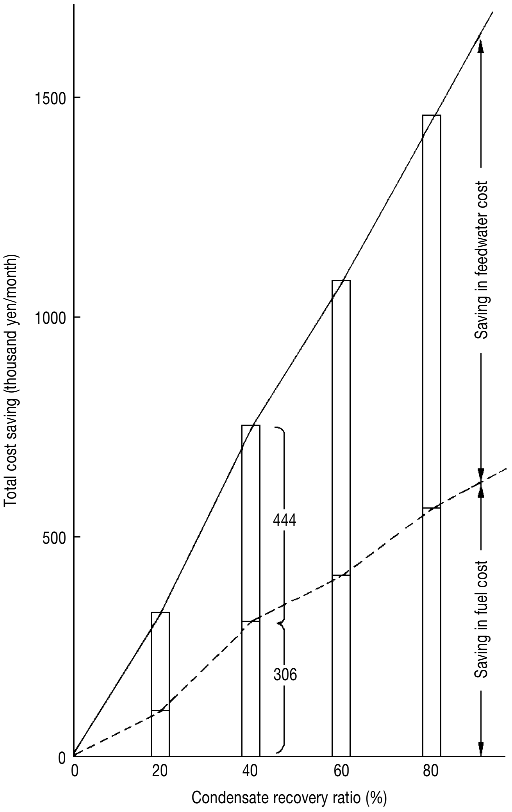


Fig. 2.81 **Relationship between the condensate recovery ratio, and the saving of fuel and water costs in A company**

The unit heat price of steam under the conditions of Table 2.27 is calculated by using equation (2.88):

$$Q_S = \frac{1{,}000 \times (660.8 - 20)}{\frac{85}{100} \times 10{,}000} \times 30 = 2{,}262$$

$$\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (2.89)$$

The unit price of 1 ton of steam is 2,262 yen.

(2) Steam loss by leakage

The quantity of steam leaking from a small hole in a pipe line is calculated by equation (2.90).

$$G = 0.5626 \times D^2 \times \sqrt{\frac{P+1}{V}} \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots (2.90)$$

where

G = leakage of dry saturated steam (kg/h)
D = diameter of hole (mm)
P = steam pressure (kgf/cm^2)
V = specific volume of dry saturated steam (m^3/kg)

The relationship between steam pressure and steam leakage obtained from the equation (2.90) is shown in Figure 2.82.

(3) Example of heat loss by steam leakage

B company operated a boiler with the pressure of 7 kgf/cm^2 and met the steam leakage from a hole in the piping. The hole was formed by the corrosion and its diameter was 3 mm. The energy loss by steam leakage is calculated below.

The leakage of steam is calculated from the equation (2.90).

$$G = 0.5626 \times 3^2 \times \sqrt{\frac{7+1}{0.245}} = 28.9 \text{ (kg/h)}$$

$$\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (2.91)$$

The V value is shown in the A-4 of Appendices in this handbook.

When the boiler is operated for 25 days a month, the steam loss per month becomes 17.3 t/month.

Assuming the unit heat price of steam to be 2,262 yen, the loss of fuel cost is 39 thousand yen per month.

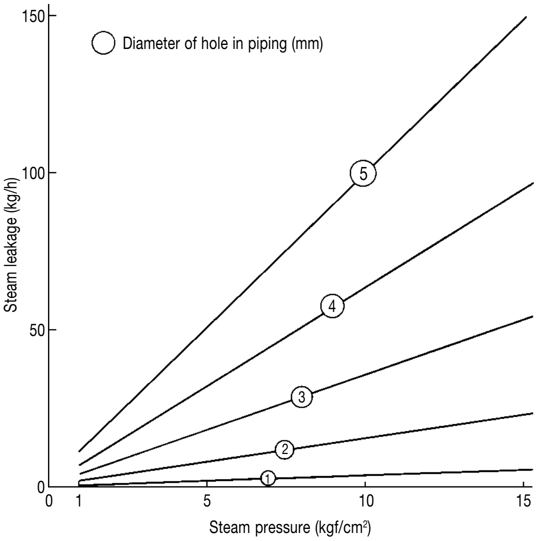


Fig. 2.82 Relationship between steam pressure and steam leakage from a hole in piping

In the case of B company, the relationship between the diameter of hole in a steam piping and the loss of fuel cost is shown in Figure 2.83.

2.8.3 Prevention of Thermal Efficiency Drop of Boiler Due to Scaling

Hardness in the feedwater for the small and medium size boilers are generally removed by using softeners. However, the hardness leakage sometimes occurs due to the insufficient maintenance and it causes scale deposition on the heat transfer surfaces of boilers. Even a small amount of scale deposition causes a remarkable decrease in the thermal efficiency because the scales have the small thermal conductivities at 1/20 to 1/100 of that of boiler tube materials as shown in Table 2.3(p.2-6).

The heat loss due to the scale deposition gives a great influence on the fuel consumption.

(1) Heat loss by scale deposition

(a) Fundamentals of boiler heat transfer

The heat transfer condition of a fire and flue-tube boiler is schematically shown in Figure 2.84. Approximately 50% of the heat is utilized in the furnace section. The gas temperature at the outlet of the furnaces is approximately 1,200° C. In the flue section, 40% of the heat is utilized and, the rest of around 10% is discharged.

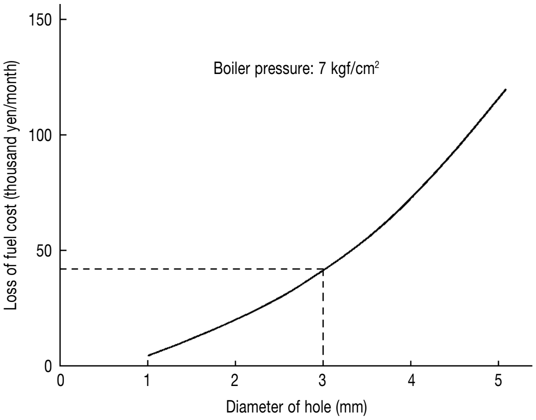
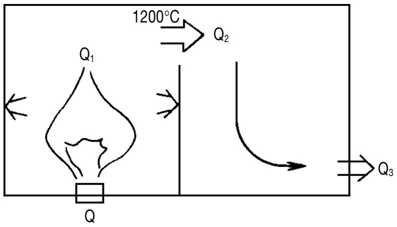


Fig. 2.83 Relationship between the diameter of hole in steam piping and the loss of fuel cost in B company



Q: Overall heat of boiler (100%)
Q_1: Heat flux by radiation in furnace section (Approx. 50%)
Q_2: Heat flux by conduction in flue section (Approx. 40%)
Q_3: Exhaust heat (Approx. 10%)

Fig. 2.84 Heat transfer in boiler

The heat transfer in the furnace is mainly carried out by radiation because of high gas temperature, the presence of luminous flame and the thick gas layer. In the flue part, the heat is transferred by the conduction between the gas and tube, because the gas temperature becomes lower and the gas layer is reduced.

In the radiation heat transfer section, the scaling hardly affects the heat transfer, while in the conduction heat transfer section, the scale deposition considerably lowers the heat transfer efficiency.

(b) Heat balance in conduction heat transfer section

The quantity of heat transfer from combustion gas to boiler water in a conduction heat transfer section is expressed by the following equation:

$$Q = U \times \Delta tl_m \times A \quad \text{.....................................} \quad (2.92)$$

where

Q = heat flux (kcal/h)
U = overall heat transfer coefficient (kcal/m²·h·° C)

Δtl_m = logarithmic mean temperature difference (°C)
A = heat transfer surface area (m^2)

The overall heat transfer coefficient is calculated by equation (2.93). Figure 2.85 illustrates the heat transfer condition from combustion gas to boiler water through boiler tube and scale.

$$U = \frac{1}{\frac{1}{h_1} + \frac{D_1}{k_1} + \frac{D_2}{k_2} + \frac{1}{h_2}} \quad \text{.................... (2.93)}$$

where
h_1^{*1} = heat transfer coefficient at gas side ($kcal/m^2 \cdot h \cdot °C$)
h_2^{*2} = heat transfer coefficient at water side ($kcal/m^2 \cdot h \cdot °C$)
k_1^{*3} = thermal conductivity of boiler tube ($kcal/m \cdot h \cdot °C$)
k_2 = thermal conductivity of scale ($kcal/m \cdot h \cdot °C$)
D_1 = thickness of tube wall (m)
D_2 = thickness of scale (m)

*1 h_1 = 60–100 $kcal/m^2 \cdot h \cdot °C$
*2 h_2 = 8,000–10,000 $kcal/m^2 \cdot h \cdot °C$
*3 k_1 = 40–60 $kcal/m \cdot h \cdot °C$ (in the case of carbon steel)

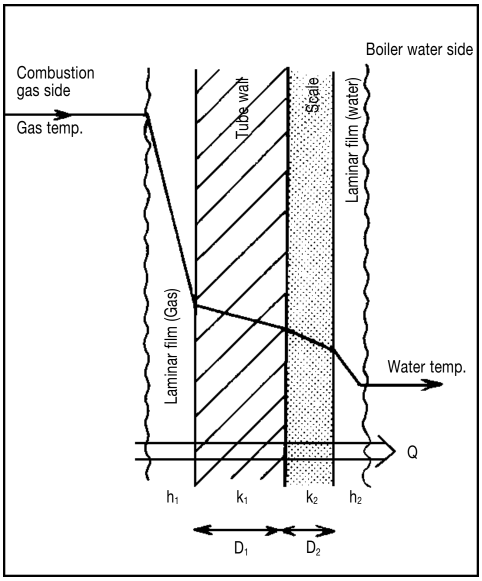


Fig. 2.85 Schematic model of heat transfer through a boiler tube and scale

When the gas temperature is changed as shown in Figure 2.86, the logarithmic mean temperature difference is calculated by using equations (2.94) to (2.96).

$$\Delta tl_m = \frac{\Delta t_1 - \Delta t_2}{\ln \frac{\Delta t_1}{\Delta t_2}} \quad \text{.................................... (2.94)}$$

$$\Delta t_1 = T_1 - t_0 \quad \text{.................................... (2.95)}$$

$$\Delta t_2 = T_2 - t_0 \quad \text{.................................... (2.96)}$$

where
T_1 = gas temperature at the inlet (°C)
T_2 = gas temperature at the outlet (°C)
t_0 = boiler water temperature (°C)

The quantity of heat released from the gas in the conduction heat transfer section is expressed by equation (2.97).

$$Q = (T_1 - T_2) \times C_G \times G \quad \text{............................ (2.97)}$$

where
Q = heat flux (kcal/h)
C_G = average specific heat of gas (approximately 0.33 $kcal/Nm^3 \cdot °C$)
G = flow rate of gas (Nm^3/h)

The Q in the equation (2.92) is equal to the Q in the equation (2.97).

Figure 2.87 illustrates the relationship between the thickness of scale with the thermal conductivity of 0.5 kcal/m·h·°C and the increase of fuel consumption calculated from the equations (2.92) and (2.97). Scale deposition with the thickness of 0.3 mm increases the fuel consumption by approximately 1%.

The scale deposition not only causes the heat loss but also causes the local superheating of boiler tube at the deposited portion, which sometimes leads to a trouble, such as the embrittlement and bursting of boiler tubes. The scale

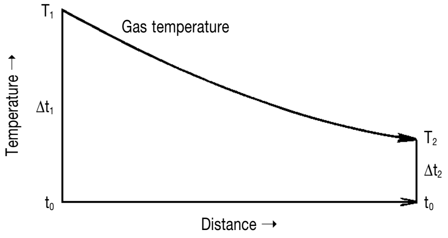


Fig. 2.86 Change of combustion gas temperature under a fixed boiler water temperature

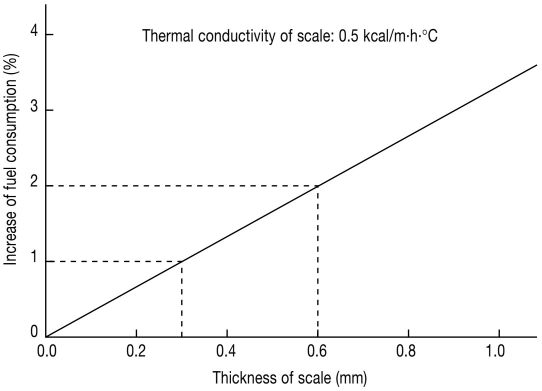


Fig. 2.87 Relationship between the thickness of scale and the increase of fuel consumption

deposition will cause the fatigue of tube material because it will give the repetition of the expansion and contraction to the tube, exceeded the allowance.

(2) Energy saving by preventing scale deposition

In C company, the hardness leakage into the boiler feedwater occasionally occurred and scaling with about 0.5 mm thickness was observed on the heating surfaces when the boiler was inspected.

Then, after the acid cleaning of boiler, a chemical treatment using a scale dispersant was applied. When the boiler was inspected one year later, the heat transfer surface was found to be clean and fuel cost has been saved.

The boiler operation conditions of C company is shown in Table 2.28. The data shown in the Table 2.27 are used for calculating the fuel cost saving in C company.

The fuel consumption in the case of no scale deposition is calculated from the equation (2.85):

$$F = \frac{40 \times 1{,}000 \times (660.8 - 20) + 3 \times 1{,}000 \times (171.3 - 20)}{\frac{85}{100} \times 10{,}000} \times 25 \times 10^{-3} = 76.7 \text{ (t/month)} \quad \text{........... (2.98)}$$

In the previous treatment, since the scale with the thickness of 0.5 mm was deposited on the boiler tube, the fuel consumption increased by approximately 1.7% comparing with the no scale operation as shown in Figure 2.87. Namely, the increases of fuel consumption and fuel cost by scale adhesion become 1.3 t/month and 39 thousand yen/month respectively.

Table 2.28 Boiler operational conditions of C company

Type of boiler	Cylindrical boiler
Normal operation pressure (kgf/cm^2)	7
Evaporation rate (t/day)	40
Blowdown (t/day)	3
Feedwater (t/day)	43
Kind of feedwater	Softened water
Temperature of feedwater (° C)	20

2.8.4 Reduction of Blowdown

The blowdown of boiler water is indispensable in order to maintain the dissolved solids concentration in boiler water within the control limit and to prevent the trouble occurrence.

The improvement in the performance of small size boilers has brought the increase of the evaporation rate per unit heat transfer surface recently. This high efficiency will cause the scaling problems even in a case of a slight hardness leakage into the feedwater. Therefore, some increase of blowdown is carried out for the safe operation of such type of boilers.

However, the amount of blowdown is reduced by using an appropriate chemical, such as dispersants effective for hardness components and iron sludges.

(1) Unit heat price of blowdown water

The unit heat price of blowdown water is expressed by equation (2.99).

$$Q_B = \frac{1{,}000 \times (I_B - I_F)}{\frac{n}{100} \times C} \times a \quad \text{.................... (2.99)}$$

where

Q_B = unit heat price of blowdown water (yen/t)
I_B = enthalpy of boiler water (kcal/kg)
I_F = enthalpy of feedwater (kcal/kg)
n = efficiency of boiler (%)
C = lower heat value of fuel (kcal/kg)
a = unit cost of fuel (yen/kg)

Using the equation (2.99), the unit heat price of blowdown water for a boiler operated at the pressure of 7 kgf/cm^2 is calculated.

Assuming the feedwater temperature of 20° C, boiler efficiency of 85%, and the use of heavy oil with the lower heat value of 10,000 kcal/kg and the price of 30 yen/kg, the unit heat price becomes approximately 534 yen/t.

$$Q_B = \frac{1{,}000 \times (171.3 - 20)}{\frac{85}{100} \times 10{,}000} \times 30 = 534 \quad \cdots\cdots\cdots\cdots (2.100)$$

The reduction of blowdown contributes to energy savings as well as water savings.

(2) Energy saving by reduction of blowdown

In D company, the boiler was operated at the blowdown rate of 12% because of occasional hardness leakages.

The chemical water treatment program was changed from a conventional method using a boiler compound and an oxygen scavenger to the new program including an excellent sludge dispersant. The new program was able to reduce the blowdown rate to 7%.

The reduction of the fuel and water costs is calculated based on the operation conditions of D company, shown in Table 2.29. The necessary data for the calculation are shown in the Table 2.27.

The monthly fuel cost saving by the reduction of blowdown is calculated by around 40,000 yen/month from the unit heat price of blowdown and the operation period of the boiler.

Then, the monthly saving of the feedwater is 30,000 yen/month.

Accordingly, D company saves the fuel and make-up water cost of approximately 70,000 yen/month by lowering the blowdown rate.

Table 2.29 Boiler operational conditions of D company

Treatment	Conventional	Improved
Type of boiler	Water tube boiler	
Normal operation pressure (kgf/cm^2)	7	
Evaporation rate (t/day)	50	
Blowdown (t/day)	6.8	3.8
Blowdown rate (%)	12	7
Feedwater (t/day)	56.8	53.8
Kind of feedwater	Softened water	
Feedwater temperature (° C)	20	

The saving in the fuel and water costs by reducing the blowdown rate is shown in Figure 2.88 in the case of D company.

2.8.5 Heat Recovery from Blowdown Water

The heat exchange between feedwater and blowdown water using a continuous blowdown equipment recovers the heat energy in the blowdown water and saves the fuel cost of boiler.

(1) Unit price of heat recovery from blowdown water

The heat of blowdown water is recovered by using a continuous blowdown equipment shown in Figure 2.89.

The theoretical maximum heat recovery from

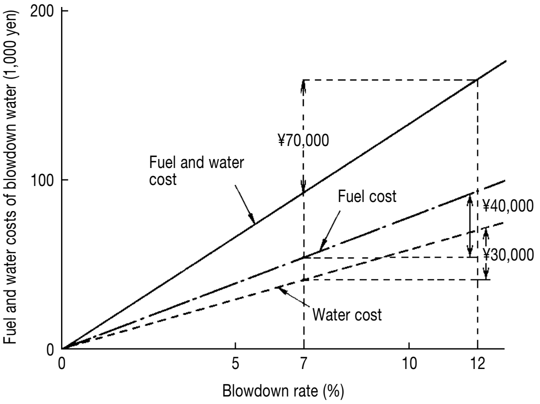


Fig. 2.88 Saving in the fuel and water costs by reducing the blowdown rate in D company

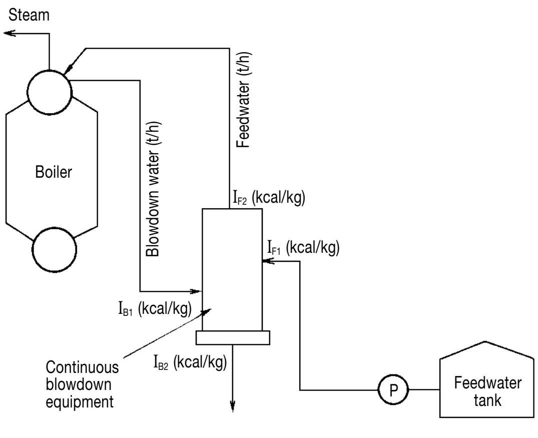


Fig. 2.89 Flow diagram of a countinuous blowdown equipment

blowdown water is calculated by the equation (2.101).

$$Q_{max} = B \times 1,000 \times (I_{B1} - I_{F1}) \quad \text{.................} \quad (2.101)$$

where

Q_{max} = theoretical maximum heat recovery (kcal/h)

B = blowdown (t/h)

I_{B1} = enthalpy of blowdown water at heat exchanger inlet (kcal/kg)

I_{F1} = enthalpy of feedwater at heat exchanger inlet (kcal/kg)

The practical heat recovery is calculated by equation (2.102) or (2.103).

$$Q = B \times 1000 \times (I_{B1} - I_{B2}) \quad \text{......................} \quad (2.102)$$

$$Q = F \times 1000 \times (I_{F2} - I_{F1}) \quad \text{.......................} \quad (2.103)$$

where

Q = practical heat recovery (kcal/h)

I_{B2} = enthalpy of blowdown water at heat exchanger outlet (kcal/kg)

F = feedwater (t/h)

I_{F2} = enthalpy of feedwater at heat exchanger outlet (kcal/kg)

When the heat recovery efficiency of continuous blowdown equipment is b, the relationship between the Q_{max} and Q is expressed by equation (2.104).

$$Q = Q_{max} \times \frac{b}{100} = B \times 1000 \times (I_{B1} - I_{F1}) \times \frac{b}{100} \quad \text{...................................} \quad (2.104)$$

where

b = heat recovery efficiency of continuous blowdown equipment (%)

Therefore, the cost of recovered heat is calculated by equation (2.105).

$$Q_C = \frac{Q}{\frac{n}{100} \times C} \times a = \frac{B \times 1,000 \times (I_{B1} - I_{F1})}{\frac{n}{100} \times C} \times \frac{b}{100} \times a \quad \text{...................................} \quad (2.105)$$

where

Q_C = cost of recovered heat (yen/h)

n = boiler efficiency (%)

C = lower heat value of fuel (kcal/kg)

a = unit cost of fuel (yen/kg)

b = heat recovery efficiency of continuous blowdown equipment (%)

When the continuous blowdown equipment with the heat recovery efficiency of 60% is installed under the conditions shown in Table 2.27, the unit cost of the recovered heat from the blowdown water of 1 ton is calculated by 320 yen as shown below:

$$Q_C = \frac{1,000 \times (171.3 - 20)}{\frac{85}{100} \times 10,000} \times \frac{60}{100} \times 30 = 320 \quad \text{...................................} \quad (2.106)$$

(2) An example of heat recovery from blowdown water

In E company, the boiler was operated at the blowdown rate of 10% and employed a continuous blowdown equipment to save energy.

The operating conditions of the boiler are shown in Table 2.30. The data for calculating the cost saving by the heat recovery from blowdown water are shown in Table 2.27. The heat recovery efficiency of the continuous blowdown equipment is 60%.

The monthly saving in the fuel cost is calculated as follows:

$$Q_C = \frac{2.2 \times 1,000 \times (171.3 - 20)}{\frac{85}{100} \times 10,000} \times \frac{60}{100} \times 25 \times 30 = 17,600 \text{ yen/month} \quad \text{...........................} \quad (2.107)$$

Table 2.30 Boiler operational conditions of E company

Type of boiler	Cylindrical boiler
Normal operation pressure (kgf/cm^2)	7
Evaporation rate (t/day)	20
Blowdown (t/day)	2.2
Blowdown rate (%)	10
Feedwater (t/day)	22.2
Kind of feedwater	Softened water
Feedwater temprature (°C)	20

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3. Cooling Water Treatment

Cooling water is used directly or indirectly to cool chemical products, steel products, etc.

Generally, cooling water is used indirectly to cool process fluids (liquids and gases) through heat exchangers. This system is called an indirect cooling system. Solid products are often cooled directly by spraying water through nozzles. This system is termed a direct cooling system and is used in plants handling solid products, such as iron works and food factories.

Cooling water systems are classified as shown in Table 3.1.

In Japan, approximately 149 million m^3/day[1)] of fresh water was consumed for industrial purposes and about 70%[1)] of that was used as cooling water in 1996. Thus, the demand for cooling water has a great influence on the entire industrial water supply. To reduce the water requirements for cooling systems, the change from once through to recirculating cooling systems, the reduction of blowdown by increasing the cycles of concentration in open recirculating cooling systems and so on have been made.

Such effective utilization of cooling water causes the concentration of dissolved solids, resulting in the frequent problems with corrosion, scale and slime (boifouling) in cooling water systems. Various cooling water treatment chemicals are used to prevent these problems. The development of these chemicals and the related technology has realized more effective utilization of cooling water. The recent developments have made it possible to prevent the thermal efficiency drop of heat exchangers even under lower water flow rates and higher outlet water temperatures. The application of advanced cooling water treatment technology provides "energy saving operation" of cooling systems by reducing the rotating speed of cooling tower fans and by decreasing the number of water circulation pumps in operation.

Cooling water treatment chemicals have a probability to cause environmental pollution because they are discharged with the blowdown water. Therefore, non-polluting chemicals have been developed.

Recently, petroleum refineries and petrochemical factories tend to extend their continuous operation periods from 1 year to 2 to 4 years for increasing productions and reducing total operation costs. In those cases, chemicals for cooling water systems are required to provide the higher performances comparing with conventional ones.

The cooling water treatment chemicals and technologies described here are mainly concerned with indirect cooling systems. The treatment of indirect cooling water systems is presented in Chapter 8., Water Treatment for Iron and Steel Making Plants.

3.1 Outline of Cooling Water Systems

3.1.1 Types and Features of Cooling Water Systems

(1) Open recirculating cooling water system

Table 3.1 Classification of cooling water systems

Cooling water system	Indirect cooling water system	Open recirculating cooling water system
		Closed recirculating cooling water system
		Once through cooling water system
	Direct cooling water system	Open recirculating cooling water system
		Once through cooling water system

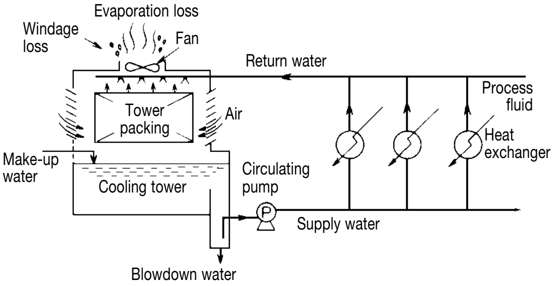


Fig. 3.1 Flow diagram of an open recirculating cooling water system

A typical flow diagram of an open recirculating cooling system is shown in Figure 3.1. In this system, cooling water removes heat from process fluids passing through heat exchangers and the temperature is risen. The hot water is cooled in a cooling tower by the partial evaporation and the release of the latent heat of evaporation. Thus the water is recirculated and reused. This system is widely used to cool products, refrigerants, etc., in petroleum refineries, petrochemical and other plants. Fresh water is usually used in this system.

(2) Closed recirculating cooling water system

Figure 3.2 shows an example of flow diagram of a closed cooling water system. In this system, the water heated by passing through heat exchangers or other equipments is cooled by secondary coolers using seawater, air or the cooling water from an open recirculating cooling water system. It is then recirculated and reused.

The water loss is usually small in this system and the concentration of dissolved solids by evaporation scarcely occurs. The closed system includes cooling systems for engines, bearings, etc., chilled water systems for air conditioning and so on.

(3) Once through cooling water system

In an once through cooling water system, the water after being heated is discharged directly into a receiving stream without recirculation. As this system requires a large amount of water, it is being used less frequently except the system of seawater supply. Figure 3.3 illustrates the flow diagram of this system.

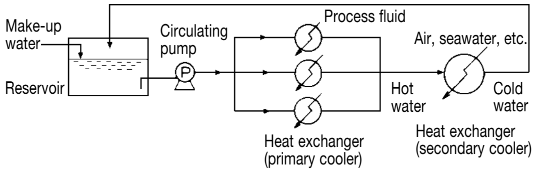


Fig. 3.2 Flow diagram of a closed recirculating cooling water system

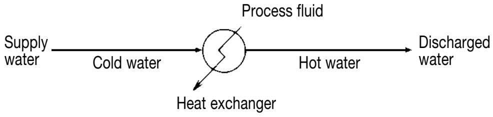


Fig. 3.3 Flow diagram of an once through cooling water system

This system is used for cooling products in factories or closed recirculating cooling water with the secondary coolers. In Japan, thermal power plants frequently install once through systems using seawater because they generally locate near seacoasts.

3.1.2 Equipments and Materials in Cooling Water Systems

(1) Cooling towers

Cooling tower is used to cool hot water for the recycling. In the cooling tower, hot water contacts with cold air and some portion of the water evaporates. As the result, the hot water is cooled by releasing the latent heat of evaporation.

Cooling towers are classified into two major types. One is the natural draft type where air is supplied by natural convection and the other is the mechanical draft type where air is supplied by fan.

The mechanical draft type includes forced draft

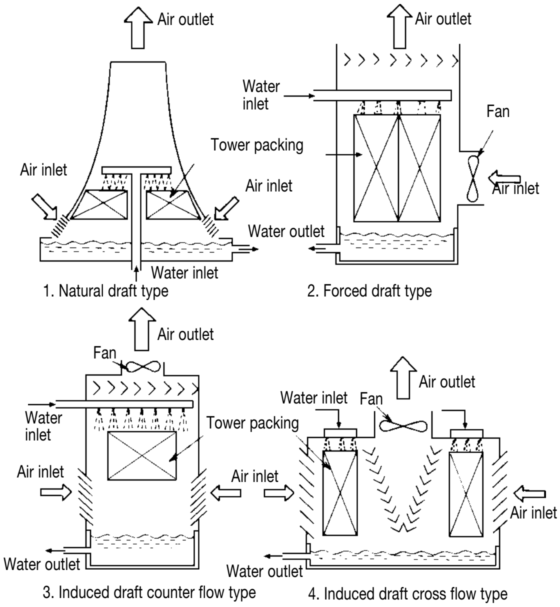


Fig. 3.4 Types of cooling towers

and induced draft types. Also, they are classified into counter flow and cross flow types according to the flow directions of water and air. In a counter flow tower, air moves upward through the tower packing, counter to the downward flow of water. In a cross flow tower, air flows horizontally across the downward flow of water. Figure 3.4 illustrates these types of cooling towers. As each type has its advantages and disadvantages, the most suitable type is selected depending on conditions such as tower capacity, the installation area, etc.

In Japan, round counter flow type cooling towers (Figure 3.5) are used for small scale systems with the circulation rate of less than about 300 m^3/h. Square cross flow type cooling towers (Figure 3.6) are used for larger size systems.

(2) Heat exchangers

(a) Structures and features

Heat exchangers are used as coolers, heaters, condensers or evaporators depending on the requirement.

By structure, they are classified as tubular heat exchangers, double tube heat exchangers, spiral tube heat exchangers, irrigation coolers, plate heat exchangers, and air fin coolers. The tubular heat exchanger is most widely used. It includes horizontal and vertical types. The horizontal type is generally used although the vertical type has the advantage of a smaller installation area.

Typical structures and features of horizontal tubular heat exchangers are shown in Figure 3.7 and Table 3.2. Cooling water flows through either tube inside or shell side. The flows of cooling water in tubular heat exchangers and their characteristics are listed in Table 3.3.

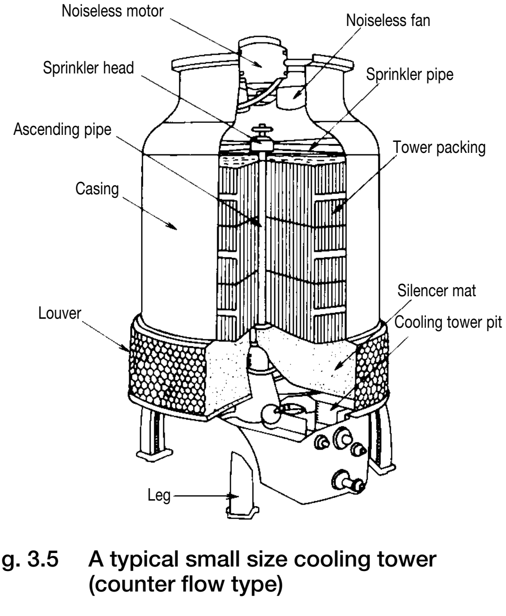


Fig. 3.5 A typical small size cooling tower (counter flow type)

(b) Heat flux

Heat flux is defined as the heat removed from the process fluid by the cooling water per unit area and per unit time. It is calculated by the following equation:

$$Q = \frac{\Delta T \times C \times R \times 10^3}{A} \quad \cdots\cdots (3.1)$$

where

Q = heat flux ($kcal/m^2 \cdot h$)

ΔT = temperature difference of the cooling water between the inlet and the outlet of heat exchanger (°C)

R = flow rate of cooling water (m^3/h)

C = specific heat of water at constant pressure ($kcal/kg \cdot °C$)

A = heat transfer area (m^2)

The higher heat flux, the greater possibility of scale or corrosion problems in heat exchangers.

(c) Over-all heat transfer coefficient

Over-all heat transfer coefficient (U-value) is an index of thermal efficiency, and it is determined by the following equation:

$$U = \frac{1}{\frac{1}{\alpha_1} + \gamma_1 + \frac{l}{\lambda_1} + \frac{1}{\alpha_2} + \gamma_2} \quad \cdots\cdots (3.2)$$

where

U = over-all heat transfer coefficient ($kcal/m^2 \cdot h \cdot °C$)

α_1 = heat transfer coefficient of laminar film at the process side ($kcal/m^2 \cdot h \cdot °C$)

α_2 = heat transfer coefficient of laminar film at the cooling water side ($kcal/m^2 \cdot h \cdot °C$)

λ = thermal conductivity of tube material ($kcal/m \cdot h \cdot °C$)

l = tube wall thickness (m)

γ_1 = fouling factor at the process side ($m^2 \cdot h \cdot °C/kcal$)

γ_2 = fouling factor at the cooling water side ($m^2 \cdot h \cdot °C/kcal$)

The U-value is decreased by fouling with scale, corrosion products and slime during the operation of heat exchanger. The reduction rate in U-value becomes bigger for the heat exchanger of higher U-value under the same level of fouling.

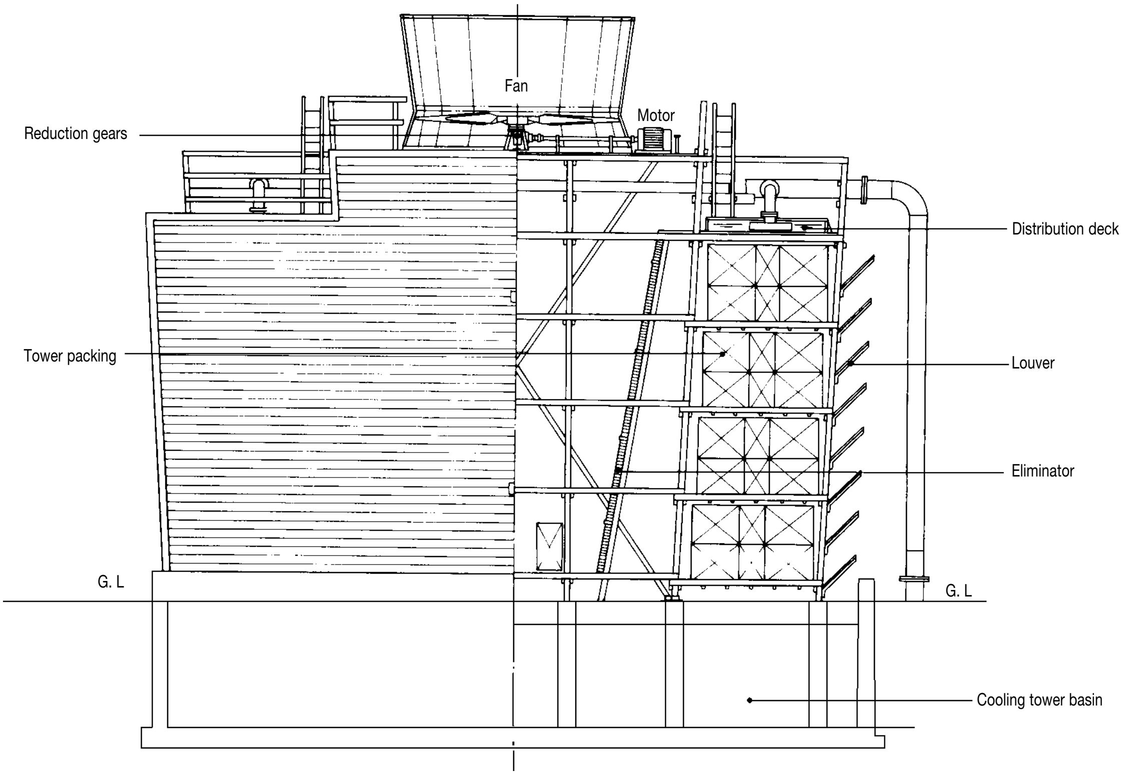
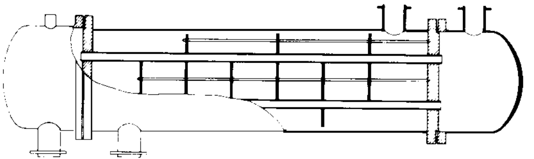
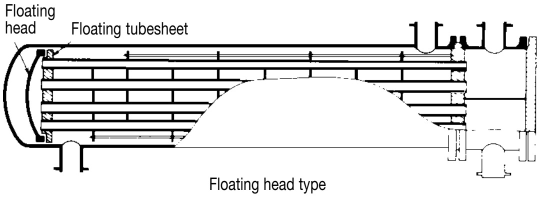


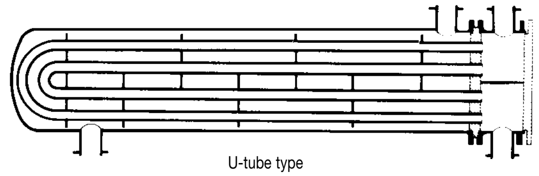
Fig. 3.6 A typical large size cooling tower (cross flow type)



Fixed tubesheet type



Floating head type



U-tube type

Fig. 3.7 Typical structures of tubular heat exchangers

Figure 3.8 shows an example of relationship between the thickness of fouling and the reduction of U-value.

(d) Fouling factor

Fouling factor indicates the degree of fouling by scale and other deposits in the heat exchanger.

The factor is calculated by the following equation:

$$\gamma = \gamma_1 + \gamma_2 = \frac{1}{U_f} - \frac{1}{U_o} \quad \cdots\cdots\cdots\cdots (3.3)$$

where

γ = over-all fouling factor (m^2·h·°C/kcal)

γ_1 = fouling factor at the process side (m^2·h·°C/kcal)

γ_2 = fouling factor at the cooling water side (m^2·h·°C/kcal)

U_f = over-all heat transfer coefficient with fouling (kcal/m^2·h·°C)

U_o = initial over-all heat transfer coefficient (without fouling) (kcal/m^2·h·°C)

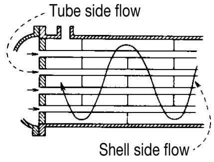
The fouling factor is also determined by the thermal conductivity and the thickness of fouling material using the following equation:

$$\gamma_1 = \frac{L_1}{\lambda_1}, \ \gamma_2 = \frac{L_2}{\lambda_2} \quad \cdots\cdots\cdots\cdots (3.4)$$

Table 3.2 Types and features of tubular heat exchangers

Type	Features
Fixed tube-sheet	(1) Easy to manufacture; less expensive (2) Difficult to clean the shell side because of the impossibility of removing the tube bundle
Floating head	(1) Applied to cases of large difference in temperature between the tube and shell side fluids or in thermal expansion coefficient between tube and shell materials (2) Possible to clean the shell side by removing the tube bundle
U-tube	

Table 3.3 Flows of cooling water in tubular heat exchangers and their characteristics

Water flow		Characteristics
	Tube side	Easy to get good effects of cooling water treatment because the flow rate is usually more than 0.5 m/s
	Shell side	Likely to cause fouling problems due to sludge accumulation because of the low and complicated water flow

Note: In general, corrosive fluids, fluids of high fouling potential or fluids under high pressure flow through the tube side. However, recently heat exchanger using cooling water have been frequently designed with the tube side water flow because of the easy maintenance.

where

L_1 = fouling thickness at the process side (m)

L_2 = fouling thickness at the cooling water side (m)

λ_1 = thermal conductivity of fouling at the process side (kcal/m·h·°C)

λ_2 = thermal conductivity of fouling at the cooling water side (kcal/m·h·°C)

Heat exchangers are commonly designed with the water side fouling factors (designed γ_2) in the range of 0.0002 to 0.0006 $m^2 \cdot h \cdot {}^\circ C/kcal$, depending on the expected fouling tendency of the cooling water. Therefore, the γ_2 in service must be maintained below the designed γ_2.

The permissible scale thickness is estimated from the designed γ_2 and λ_2. The λ_2 is reasonably estimated from the cooling water quality and the chemical treatment program.

(3) Cooling water circulation pump

Turbine pumps are usually used for circulating water in cooling water systems.

(4) Metals in general use

Equipments in contact with the cooling water are heat exchangers, pipings, pumps, cooling towers, cooling tower basins and the sensors of measuring instruments. Except for the cooling tower, most of the other equipments are made of metals. Table 3.4 shows the characteristics of metals widely used in pipings and heat exchangers.

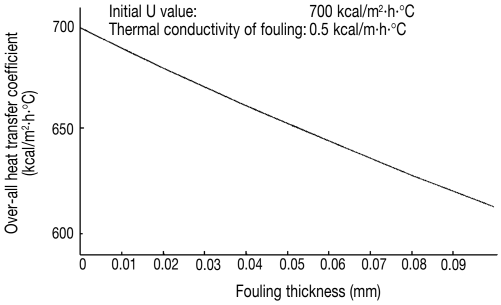


Fig. 3.8 **Relationship between the fouling thickness of an heat exchanger and the reduction of the overall heat transfer coefficient**

3.1.3 Water Balance in Cooling Water Systems

(1) Water balance in open recirculating cooling water system

Figure 3.9 illustrates the water flow in an open recirculating cooling water system. Evaporation loss, windage loss, blowdown, and make-up water quantities are generally obtained by calculation. Table 3.5 presents common terms and their symbols related to the water balance calculation in the cooling water system.

(a) Evaporation loss

When the total heat quantity removed by the cooling water from the process fluid is equal to the total heat quantity released from the cooling water by the evaporation in the cooling tower, the following equation is satisfied:

Table 3.4 Metals used for pipings and heat exchangers

Metal		Characteristics
Piping	Carbon steel pipe (JIS G3452; SGP)	Economical and good workability but corrodible. Grooving is sometimes observed at welded part of electric-resistance welded pipe even under an appropriate cooling water treatment.
	Galvanized pipe (JIS G3442; SGPW)	Corrosion resistant while galvanized zinc remains. Corrosion may be caused when the potential of zinc becomes higher than iron at the temperature of 50℃ or over.
	PVC-lined carbon steel pipe	Corrosion resistant but expensive. Widely used in small cooling water systems.
Heat exchanger	Carbon steel tube (JIS G3461; STB) Steel plate (except heat exchanger tube) (JIS G3101; SS, JIS G3106; SM)	Economical, good workability and reliable quality. Widely used unless process fluid is corrosive to iron. Seamless tubes should be used for heat exchanger tubes.
	Stainless steel tube (JIS G3463; SUS-TB)	Corrosion resistant. Widely used because of excellent mechanical and physical properties, and highly reliability. Some possibility of stress corrosion cracking, pitting and crevice corrosion.
	Copper (JIS H3300)	Excellent mechanical properties, heat conductivity, workability, weldability and corrosion resistance under various conditions. Corrosive in oxidizing atmosphere or in the presence of ammonia. Some possibility of impingement attack at a high flow rate and pitting corrosin under deposits.
	Brass (Copper-zinc alloy, e.g. aluminum brass)	
	Bronze (Copper-tin alloy)	
	Cupronickel	

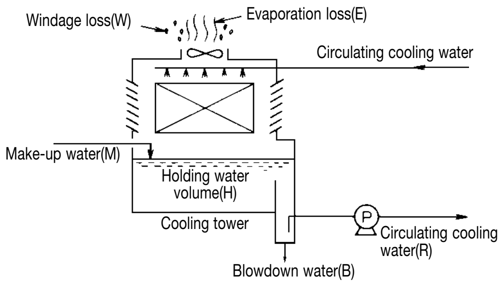


Fig. 3.9 Water flow in an open recirculating cooling water system

$$R \times 10^3 \times \Delta T \times C = E \times 10^3 \times H_L \quad \text{......} \quad (3.5)$$

where

C = specific heat of water at constant pressure (kcal/kg·°C) (0.998 kcal/kg·°C at the water temperature of 40°C)

H_L = latent heat of water evaporation (kcal/kg) (approximately 578 kcal/kg at 40°C)

Then, equation (3.6) is derived from the equation (3.5):

$$E \cong \frac{\Delta T}{5.8} \times R \times \frac{1}{100} \quad \text{......} \quad (3.6)$$

Therefore, when 1 percent of circulating water evaporates, the temperature difference becomes approximately 5.8°C. However, the actual evaporation loss becomes smaller than the calculated one in winter because the water is also cooled by the cold air itself. Table 3.6 shows the relationship between the actual and the calculated evaporation losses in each season in Japan.

Equation 3.7 is an equation to calculated more exact evaporation loss by considering the influence of air temperature (dry bulb temperature) on the water evaporation in cooling tower.

$$E = \frac{(0.575 + 0.011\,T_d) \times R \times \Delta T}{580} \quad \text{......} \quad (3.7)$$

where

T_d = air temperature (dry bulb temperature) (°C)

(b) Windage loss

The amount of windage loss depends on the designed and operating conditions of cooling tower. In general, the windage loss is 0.05 to 0.2% of the circulation rate of cooling water in forced draft cool-

Table 3.5 Terms and symbols related to the water balance calculation of open recirculating cooling water systems

Circulating water quantity (R), (m^3/h)	Total cooling water quantity circulated by pumps per hour
Holding water volume (H), (m^3)	Total water volume held in the cooling water system including the piping, the cooling tower basin and so on
Evaporation loss (E), (m^3/h)	Water lost by evaporation per hour
Windage loss (W), (m^3/h)	Water lost by windage or drift per hour
Blowdown water quantity (B), (m^3/h)	Water quantity discharged from system in order to control the cycles of concentration
Make-up water quantity (M), (m^3/h)	Water volume supplied to the cooling water system per hour
Temperature drop of water across cooling tower (ΔT), (℃)	Difference of cooling water temperature between the cooling tower inlet and outlet
Cycles of concentration (number of cycles) (N)	Concentration rate of dissolved solids in circulating water compared with those in make-up water
Retention time (T_R), (h)	Time required to exchange the holding water by water supply corresponding to blowdown and windage loss
Half life time (T_H), (h)	Time it takes the dosed chemical concentration to be reduced 50% without additional chemical dosing

ing towers.

(c) Blowdown water quantity

Blowdown rate is determined in consideration of corrosion and scale inhibition as well as available make-up water quality and quantity. The calculation method of blowdown water quantity is described below in the paragraph (e).

(d) Make-up water quantity

In cooling water system, the holding water volume is kept at a constant under the normal operating condition. Therefore, the make-up water quantity is equivalent to the total amount of water lost from the system by evaporation, windage and blowdown.

$$M = E + B + W \quad \text{.......} \quad (3.8)$$

(e) Cycles of concentration (number of cycles)

Cycles of concentration indicates the ratio of dissolved solids concentration in the circulating water to that of the make-up water, and is defined by the following equation:

$$N = \frac{C_R}{C_M} \quad \text{.......} \quad (3.9)$$

where

C_R = dissolved solids concentration in circulating water

C_M = dissolved solids concentration in make-up water

Under a steady state condition, the amount of dissolved solids which is supplied into the system by the make-up water is equivalent to the amount of dissolved solids which are discharged from the system by water blowdown and windage.

$$C_M \times M = C_R \times (B + W) \quad \text{.......} \quad (3.10)$$

Equation (3.11) is derived from the equations (3.9) and (3.10):

$$N = \frac{C_R}{C_M} = \frac{M}{B + W} \quad \text{.......} \quad (3.11)$$

Equation (3.12) is obtained by the substitution of the equation (3.8) into the equation (3.11):

$$N = \frac{E + B + W}{B + W} \quad \text{.......} \quad (3.12)$$

Therefore, the value of N is calculated from the water balance in the cooling water system.

In addition, the cycles of concentration at a given time during the operation of a cooling water system is calculated by using the following equation:

Table 3.6 Relationship between actual and calculated evaporation losses in each season in Japan

	Summer	Spring and autumn	Winter
Actual evaporation loss as compared with calculated evaporation loss	90–100%	70–80%	50–60%

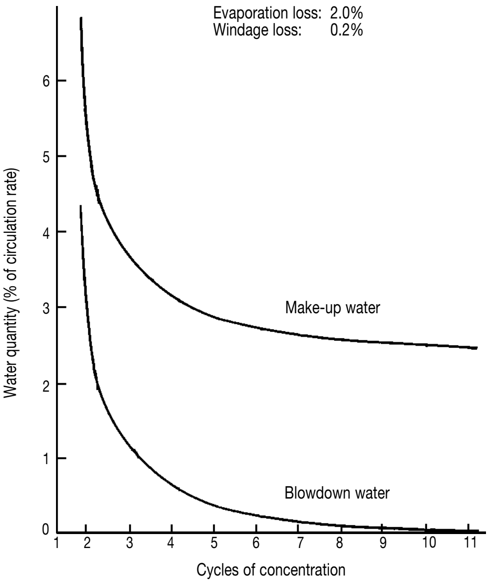


Fig. 3.10 Relationship among make-up water, blowdown water and cycles of concentration

$$N_t = \frac{M - \{M - (B + W)\, N_o\}\, e^{-t/T_R}}{B + W} \quad \text{............ (3.13)}$$

where

N_t = cycles of concentration after t hours
N_o = cycles of concentration at the start of system operation (usually, 1)
e = base of natural logarithm
t = operating time (h)
T_R = retention time (h)

The cycles of concentration is controlled by adjusting the blowdown water because the evaporation and windage losses are constant when the operating conditions are constant.

Figure 3.10 shows a typical relationship between the cycles of concentration and make-up water quantity calculated by using the equation (3.11). An increase in the cycles of concentration brings a reduction of blowdown water and a saving in make-up water. As shown in the Figure 3.10, make-up water is considerably decreased until the cycles of concentration reaches 5, but not at over 5.

On the other hand, the operation of cooling water systems at higher cycle of concentration may cause the deterioration of cooling water quality and various problems. Moreover, water treatment chemicals have the certain limits of their effectiveness, so an appropriate cycles of concentration must be determined. Thus, cooling water systems are usually operated with the cycles of concentration of 3 to 5.

(f) Retention time and half life time

Retention time (T_R) is calculated from the equation (3.14):

$$T_R = \frac{H}{B + W} \quad \text{.. (3.14)}$$

The retention time is increased by reducing blowdown water.

When chemical injection is stopped in a cooling water system operating under a steady state, the chemical concentration of after t hours is calculated from the equation (3.15):

$$X_t = X_o \times e^{-t/T_R} \quad \text{... (3.15)}$$

where

X_t = chemical concentration after t hours from chemical injection stoppage (mg/*l*)
X_o = chemical concentration when the injection is stopped (mg/*l*)

The time when the X_t becomes a half of X_o is called the half life time (T_H). The equation (3.16) is obtained when the half life time is calculated by using the equation (3.15):

$$T_H = 0.7 \times T_R \quad \text{.. (3.16)}$$

(2) Water balance in closed recirculating cooling water system

In closed recirculating cooling water system, the water is scarcely lost by evaporation and windage. The water loss in this system is generally corresponded to the leakage from circulation pumps. Thus, water is supplied to make-up this leakage.

3.1.4 Problems Occurred in Cooling Water Systems

Problems occurred in cooling water systems are generally classified into the following three categories:

① Corrosion,
② Scale,
③ Biofouling (slime and sludge).

As shown in Table 3.7, corrosion shortens the lives of the equipments in cooling systems and causes the leakage of products or cooling water from heat exchangers. The adhesion of corrosion

Table 3.7 Troubles occurred in cooling water systems and their causes

Trouble	Cause
(1) Shortened operation lives of heat exchangers, pipings, etc.	(a) Corrosion (b) Corrosion occurred under deposits such as slime and sludge (c) Corrosion under porous scale
(2) Reduction of heat exchanger thermal efficiency	(a) Adhesion of corrosion product, scale and slime (b) Accumulation of sludge
(3) Increase of pressure drop and reduction of cooling water circulation rate in system (increase in electric power consumption of pumps)	(a) Adhesion of corrosion product, scale and slime (b) Accumulation of sludge (c) Tube clogging with foreign matters
(4) Leakage of products and contamination of products with cooling water	(a) Penetration of heat exchanger tube by corrosion and under deposit corrosion
(5) Adsorption and waste of water treatment chemicals	(a) By corrosion products, scale, slime and sludge (b) By suspended solids in cooling water

Table 3.8 Frequency of trouble occurrence in each type of cooling water systems

Type of cooling water system / Problems	Once through	Closed re-circulating	Open re-circulating
Corrosion	○	◎	◎
Scale	△	△	◎
Slime	○	△	◎

Note: Frequency of problems ◎ (higher) ← ○ → △ (lower)

products also causes problems such as the reduction of heat exchanger thermal efficiency and water circulation rate.

Scale deposition and slime adhesion in heat exchangers not only lower the thermal efficiency but also frequently cause local corrosion under the deposits.

These problems scarcely occur independently and are usually caused with a mutual relationship.

Table 3.8 shows the frequency of these problems in each type of cooling water system. The problems occur most frequently in open recirculating cooling water systems, since the dissolved solids are concentrated in the cooling water by the water evaporation.

3.2 Corrosion and Corrosion Prevention

3.2.1 Mechanisms of Corrosion and Corrosion Inhibitors

(1) Mechanism of corrosion

The corrosion of carbon steel is described here because carbon steel is the most widely used for heat exchangers and pipings in open recirculating cooling water systems.

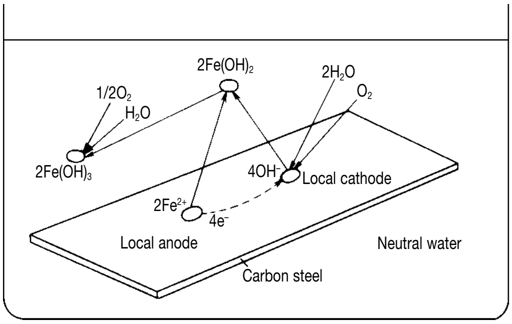


Fig. 3.11 Corrosion reactions of carbon steel in neutral water

When carbon steel is in contact with water, many minute spots with lower electrical potential (local anodes) and many spots with higher potential (local cathodes) are formed on the steel surface because of the ununiformity* of the steel surface. Then electrochemical reactions take place. The reaction (3.17) proceeds at the anodes of the local cells while reactions (3.18) and (3.19) at the cathodes:

$$\text{On the anode;}\quad Fe \rightarrow Fe^{2+} + 2e^- \quad \ldots\ldots\ldots\ldots (3.17)$$

$$\text{On the cathode;}\quad 1/2O_2 + H_2O + 2e^- \rightarrow 2OH^- \quad (3.18)$$

$$2H^+ + 2e^- \rightarrow H_2 \quad \ldots\ldots\ldots\ldots (3.19)$$

---

* On the carbon steel surface, the difference of composition (especially impurity concentration) between crystals and crystal boundaries, the disorder of crystal structure, the presence of non-uniform oxide film and so on cause the ununiformity. At the water side contacting with carbon steel, there are the ununiformities of dissolved solids concentration, temperature, water flow rate, etc.

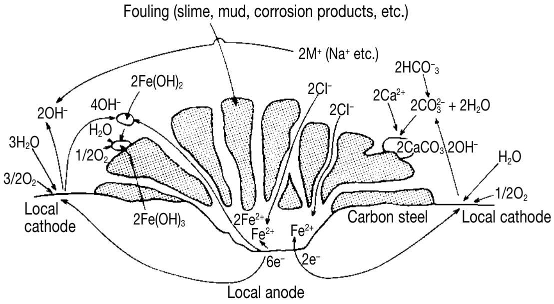


Fig. 3.12 Mechanism of carbon steel pitting corrosion under fouling

The main reaction at the cathode is the oxygen reduction expressed in the reaction (3.18) because the cooling water is usually neutral or weakly alkaline and has low H^+ ion concentration. Further, reactions (3.20) and (3.21) follow:

$$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2 \quad \text{..........................} \quad (3.20)$$

$$2Fe(OH)_2 + 1/2O_2 + H_2O \rightarrow 2Fe(OH)_3 \text{ or } Fe_2O_3{\cdot}3H_2O \quad \text{....................} \quad (3.21)$$

When the surface of carbon steel contacts water containing dissolved oxygen, the above corrosion reactions proceed. Figure 3.11 schematically shows these corrosion reactions of carbon steel.

When slime (fouling mainly composed of microorganisms) adheres to the metal surface and produces anaerobic conditions under the fouling, sulfate reducing bacteria grow and the cathodic reaction (3.22) proceeds. Then, the corrosion reaction is accelerated by hydrogen sulfide (H_2S) produced in some cases:

$$SO_4^{2-} + 10H^+ + 8e^- \rightarrow H_2S + 4H_2O \quad \text{..............} \quad (3.22)$$

When fouling materials, such as corrosion product, slime and sludge, ununiformly adhere on carbon steel surface, a local anode is produced under the fouling because of the lower oxygen concentration, and the surrounding areas with higher oxygen concentration become local cathodes. Thus, the carbon steel is attacked by the local corrosion (pitting corrosion) under the fouling.

In the pit, the concentration of cations (ferrous ions, Fe^{2+}) becomes higher than the bulk water. Therefore, in order to keep the electrical neutrality in the pit, anions move from the water to the pit through the fouling layer and concentrate there. Among anions, chloride ion with higher diffusion rate than the others is most easily concentrated in the pit. Since ferrous chloride concentrated in the pit yields hydrogen ions by the hydrolysis reaction, the pH in the pit is decreased and the pitting corrosion is further accelerated. Figure 3.12 schematically illustrates the process of pitting corrosion developed under fouling. The pitting corrosion under the deposits will be sometimes found even in the case of corrosion resistant materials such as copper, copper alloys and stainless steel.

The corrosion rate of carbon steel is usually 50 to 150 mg/dm^2·day (mdd) (0.24 to 0.72 mm/y) in the open recirculating cooling water systems if no inhibitor is used. Copper, copper alloys and stainless steels show their corrosion resistance abilities because they are passivated by dissolved oxygen and form tight oxides films on their surfaces in cooling water. Therefore, their average corrosion rates are usually very low in cooling water system, but they have some risk of pitting corrosion under fouling as mentioned above.

(2) Functional mechanisms of corrosion inhibitors

Corrosion inhibitors for cooling water systems are water soluble, however, they form insoluble films on metal surfaces. This film is called protective film and inhibits corrosion reaction by preventing the hydration of metal ions or the reduction of dissolved oxygen on the metal surface. The function of the protective film is closely related to the effect of corrosion inhibitors. Table 3.9[2)] shows the classification of corrosion inhibitors based on the characteristics of the protective films.

Corrosion inhibitors of the oxide film type including chromates and nitrites are also called passivators. They shift the corrosion potential of carbon steel to a higher level and rapidly oxidize the ferrous ions produced by the anodic reaction of corrosion. As the result, an oxide film mainly composed of γ-Fe_2O_3* is formed on the surface of carbon steel and inhibits the corrosion. In the case of chromates, the protective film also contains the reduction product, Cr_2O_3. Since the oxide type protective film is fine and thin, and has good adhesion on metal surfaces, it scarcely lowers the thermal efficiency of heat exchangers. Most corrosion inhibitors of this type show the excellent corrosion inhibition effects.

However, it is their disadvantage that the passivators have the tendency to cause local corro-

---

* Hydrated ferric oxide ($Fe_2O_3{\cdot}nH_2O$), corrosion product, is porous and non-protective. However, γ-Fe_2O_3 film is non-porous, so that it shows the excellent corrosion inhibition effect.

Table 3.9 Classification of corrosion inhibitors

Type of corrosion inhibitor		Example of corrosion inhibitor	Characteristics of protective film
Oxide film type (passivation film type)		Chromates, Nitrites, Molybdates	Fine and thin film (30–200Å), closely adherence to metal, excellent corrosion protection
Precipitation film type	Chemicals forming the insoluble salts with calcium ions, etc., in water	Polyphosphates, Orthophosphates, Phosphonates, Zinc salts	Relatively porous and relatively thick film, slightly poor adherence to metal, fairly good corrosion protection
	Chemicals forming water insoluble salts with the protected metal ion	Mercaptobenzothiazole, Benzotriazole, Tolyltriazole	Relatively close and relatively thin film, fairly good corrosion protection
Adsorption film type		Amines, Surfactants	Formation of perfect adsorption layer on clean metal surface in acid or non-aqueous solution and formation of non-uniform adsorption layer on unclean surface in fresh water

sion if applied in low concentrations. In addition, the passivators have the other problems in their application, for example, chromates are highly toxic and their discharge is strictly regulated. Nitrites are readily oxidized by nitrification bacteria in open re-circulating cooling water systems and change to nitrates which have no corrosion inhibition effect.

Polyphosphates, typical precipitation film type inhibitors, firstly form the protective film composed of iron oxide and iron phosphate*[1] on the carbon steel surface. Then, they combine with calcium ions in water and form calcium phosphate layer*[2] on the first layer. Auger Electron Spectroscopy (AES) analysis proves that the protective film formed by polyphosphates has such double layers as shown in Figure 3.13[3)]. In this case, the film thickness is around 60 nm. This AES analysis, the other electrochemical test results and so on suggest that the two layers of the films will play the different roles to prevent the carbon steel corrosion.

The iron oxide and iron phosphate rich layer on the carbon steel increases the electrical potential of steel to the passivation region and inhibits the dissolution of iron [equation (3.17)]. The upper calcium phosphate rich layer prevents the oxygen reduction [equation (3.18)] by disturbing oxygen diffusion to the carbon steel surface. The upper layer also disturbs the diffusion of chloride and sulfate ions through the film. As the result, the under layer is protected from the destruction by these aggressive ions.

Under the combined use of polyphosphates with zinc salts, the main components of the upper layer become the mixture of calcium and zinc phoshates but the under layer is scarcely changed in its composition.

Polyphosphates show the insufficient corrosion inhibition in softened or demineralized water including no bivalent metal ions such as calcium

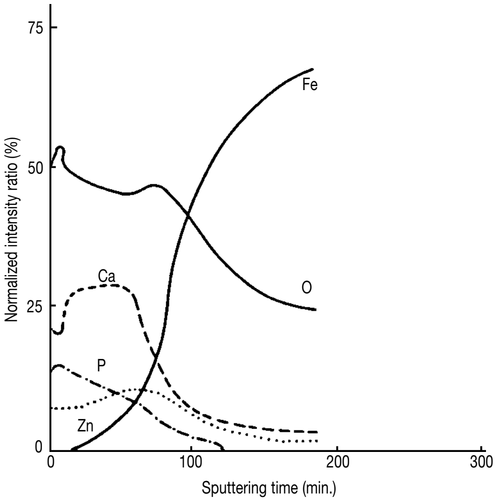


Fig. 3.13 AES depth profile of a protective film on carbon steel surface treated with a polyphosphate-zinc based inhibitor

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*[1] Mixture of amorphous iron-polyphosphate and iron-orthophosphate with higher content of polyphosphate than orthophosphate yielded by the hydrolysis of polyphosphate.

*[2] Mixture of amorphous calcium polyphosphate and calcium orthophosphate with different compositions depending on the hydrolysis rate of polyphosphate.

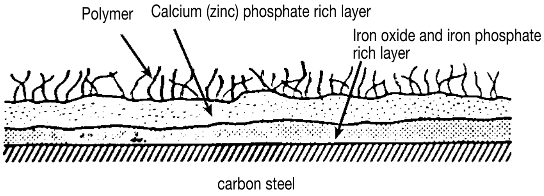

Fig. 3.14 Schematic structure of protective film formed by a phosphate-polymer treatment

and zinc ions. Because no calcium phosphate rich layer is formed, the iron oxide and iron phosphate rich layer may become not stable in those waters.

However, the corrosion inhibition provided by polyphosphates tends to inferior to passivators because the calcium phosphate film is usually not uniform and porous comparing with oxide film. When the dosage of polyphosphate is increased for improving the corrosion inhibition, the film grows too thick and sometimes causes scale* problems.

The corrosion inhibition mechanism of orthophosphates and phosphonates is similar to that of polyphosphates.

The combined use[4)] of phosphates together with water soluble low molecular weight polymers is very effective to make the calcium phosphate film on metal surface non-porous and to prevent the excess growth causing the scaling problems. The adsorption of polymers on calcium phosphate lowers the growth rate and make it amorphous precipitate. As the result, the calcium phosphate film becomes thin and non-porous. Since the polymers adsorbed on the film surface prevent the further deposition of calcium phosphate and the sedimentation of suspended solids in cooling water, the excess growth and contamination of the film are prevented. Figure 3.14[5)] shows the schematic structure of protective film formed by phosphate and polymer treatments, which is estimated from AES analysis and so on. This protective film formed by phosphate-polymer treatments shows the same or better corrosion inhibition comparing with the oxide type protective film formed by chromate treatment.

Photograph 3.1 shows the X-ray microanalyzer (XMA) analysis of protective film on a carbon steel heat exchanger tube, which is formed by a polyphosphate-zinc-polymer treatment during one year operation.

This film is mainly composed of Ca, Zn and P, and the main chemical compositions are assumed calcium and zinc phosphates (polyphosphates). In this film, iron, a corrosion product, is distributed in a small amount and chloride is hardly detected. Therefore, it is proved that the protective film has the excellent corrosion inhibition effect and prevents the aggressive chloride ions from being concentrated in the film.

In this case, the film thickness grows to approximately 70 μm and it is difficult to detect the presence of the very thin iron oxide and iron phosphate rich layer by XMA analysis.

Some precipitation film type corrosion inhibitors form insoluble salts with the ions of the metal to be protected. Such inhibitors form a protective film at the anodic areas where the metal is actively dissolved and the ion concentration becomes higher. In this case, the growth of the protective film is stopped after the formation because the film prevents any new metal dissolution. Therefore, the film does not change to scale even if the corrosion inhibitor is added in excess. Typical corrosion inhibitors of this type are benzotriazole and mercaptobenzothiazole which show the excellent corrosion inhibition effects on copper and copper alloys. An effective corrosion inhibitor of this type for carbon steel has not been developed yet.

Most corrosion inhibitors of the adsorption film type, such as amines, have functional groups which are able to adsorb on metal surfaces and also hydrophobic groups in their molecular structures. These corrosion inhibitors prevent corrosion by adsorbing on the clean metal surfaces with their functional groups and retarding the diffusion of water and dissolved oxygen to the metal surfaces with their hydrophobic groups. In neutral water, such as cooling water, these corrosion inhibitors show the insufficient effects because the carbon steel surfaces are usually not clean, thus the formation of the perfect adsorption film is difficult.

Many corrosion inhibitors which are not listed in Table 3.9, such as silicates, borates and benzoates, are used in closed recirculating cooling water systems and so on, however, their inhibition mechanisms are not so clear.

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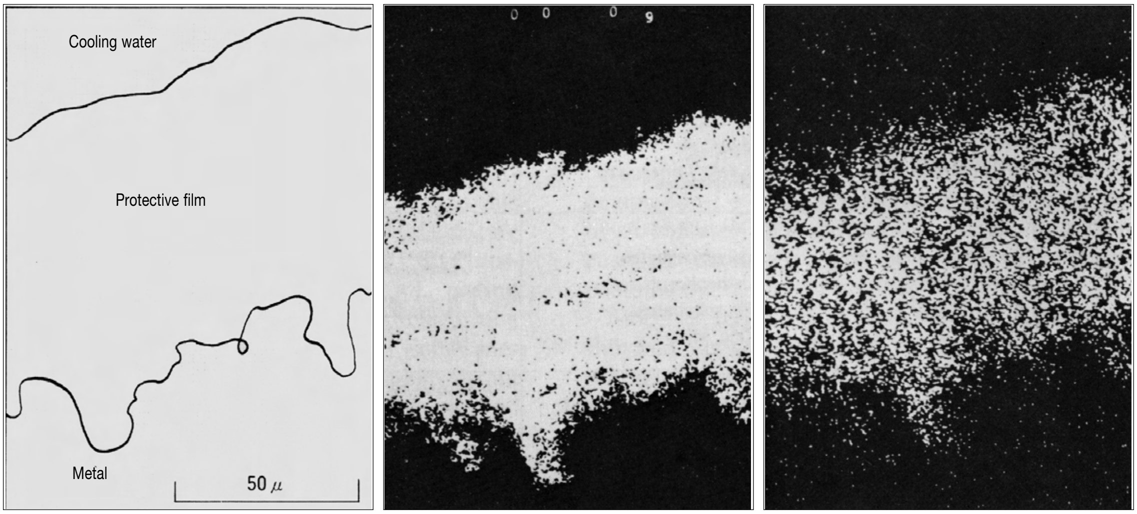
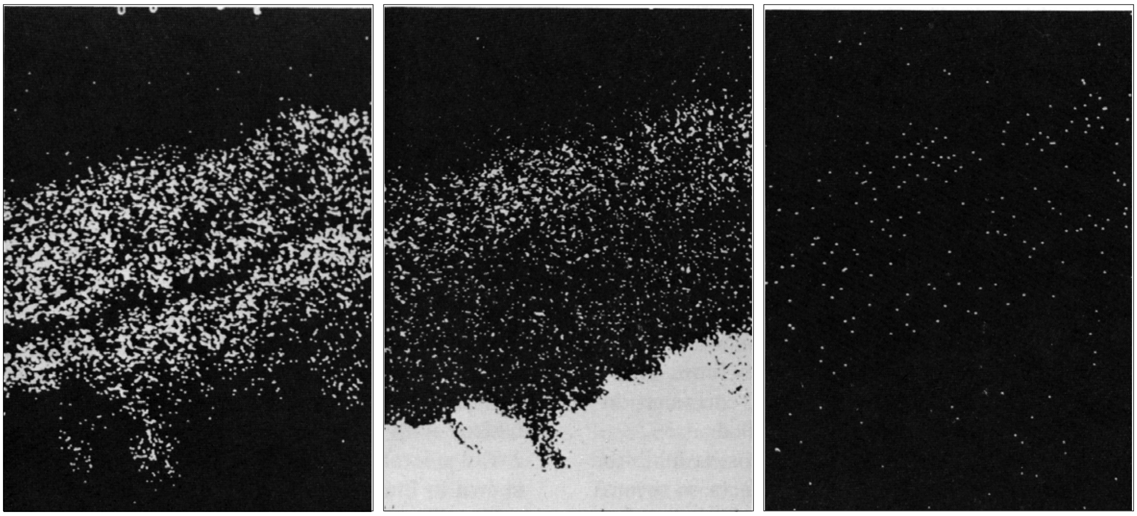
* The water side fouling factor of heat exchanger is usually designed within the range of 4×10^{-4} to 6×10^{-4} m²·h·°C/kcal. Since the thermal conductivity of calcium phosphate is approximately 0.8 kcal/m·h·°C, the permissible scale thickness of heat exchangers becomes 0.3 to 0.5 mm under the normal designed conditions. Therefore, when the film thickness exceeds 0.3 to 0.5 mm, scale troubles will be happened.



a) Illustration of the protective film studied by XMA*
* X-ray microanalyzer

b) Distribution of calcium
White spots indicate the presence of each element.

c) Distribution of zinc



d) Distribution of phosphorus

e) Distribution of iron

d) Distribution of chloride

Photo 3.1 Element distributions in a protective film (a polyphosphate-zinc polymer treatment)

3.2.2 Kinds of Metals and Forms of Corrosion

(1) Carbon steel

As expressed by the previous equations, (3.17) to (3.21), carbon steel is corroded by dissolved oxygen in neutral water. The corrosion rate is as high as 50 to 150 mg/dm²·day (0.24 to 0.72 mm/year)[4] in the absence of corrosion inhibitors.

When no corrosion inhibitor is used, carbon steel surface is covered with the corrosion product (rust). However, the adhesion of corrosion product is not uniform and the surface condition of carbon steel itself is not uniform also. Thus, the carbon steel is usually corroded ununiformly with local corrosion (Photographs 3.2 and 3.3, p.3-73). In general, the maximum penetration rate at the site of local corrosion of carbon steel is several times of the average rate and reaches 1 to 2 mm/year[5].

In the case of electrical resistance welded pipes, the corrosion potential is lower at the welded part than at the parent metal because the metal structure is changed by heating in welding process and by the rapid cooling thereafter.

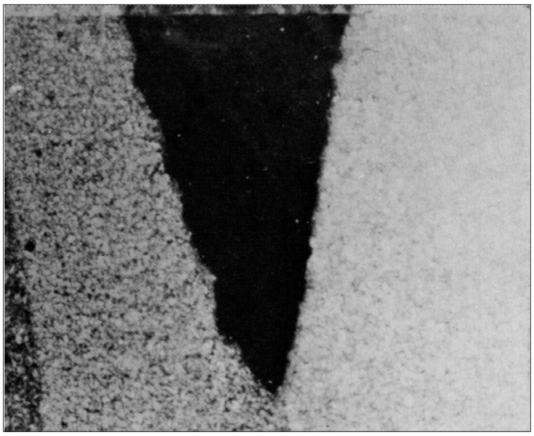


Photo 3.4 Grooving at the welded part of carbon steel

Therefore, the welded part sometimes corrodes rapidly because the part acts as a fixed anode. The maximum penetration rate of welded parts was reported to reach 8.4 mm/year⁶⁾, which is much greater than the rate of the parent metal. The typical corrosion form of the welded part is grooving as shown in Photograph 3.4.

In cooling water systems, the target corrosion rate of carbon steel is usually below 10 mg/dm²·day (0.048 mm/y) with the application of corrosion inhibitors.

However, the formation of the perfect protective film with corrosion inhibitors is sometimes disturbed by the adhesion of fouling materials such as mill scale and oil, and the accumulation of suspended solids in the water on carbon steel surfaces. Thus, there is some possibility of local corrosion even under the use of corrosion inhibitors. Therefore, pretreatments for removing mill scale and oil, dispersants for preventing the sedimentation of suspended solids and so on are applied to prevent the local corrosion. Slime control agents are also effective to prevent the under deposit corrosion and the microbiologically influenced corrosion.

(2) Copper and copper alloys

Copper is also attacked by the electrochemical corrosion and Cu^{2+} ions are produced at the local anodes:

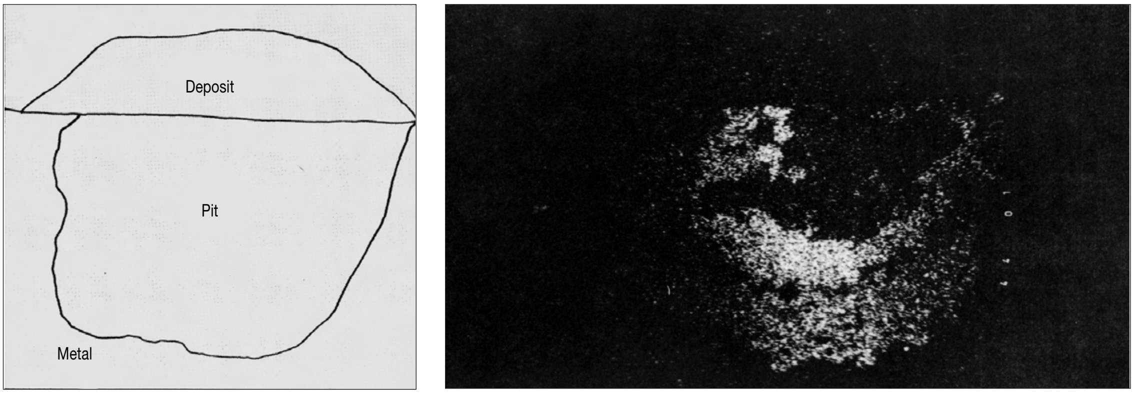
$$Cu \rightarrow Cu^{2+} + 2e^- \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots \quad (3.23)$$

The Cu^{2+} ions combine with OH^- ions, which are produced by the cathodic corrosion reaction [the equation (3.18)], and precipitate as $Cu(OH)_2$ (cupric hydroxide) on the metal surface:

$$Cu^{2+} + 2OH^- \rightarrow Cu(OH)_2 \quad \cdots\cdots\cdots\cdots\cdots \quad (3.24)$$

This $Cu(OH)_2$ is reduced on the copper surface to the final corrosion product, Cu_2O (cuprous oxide).

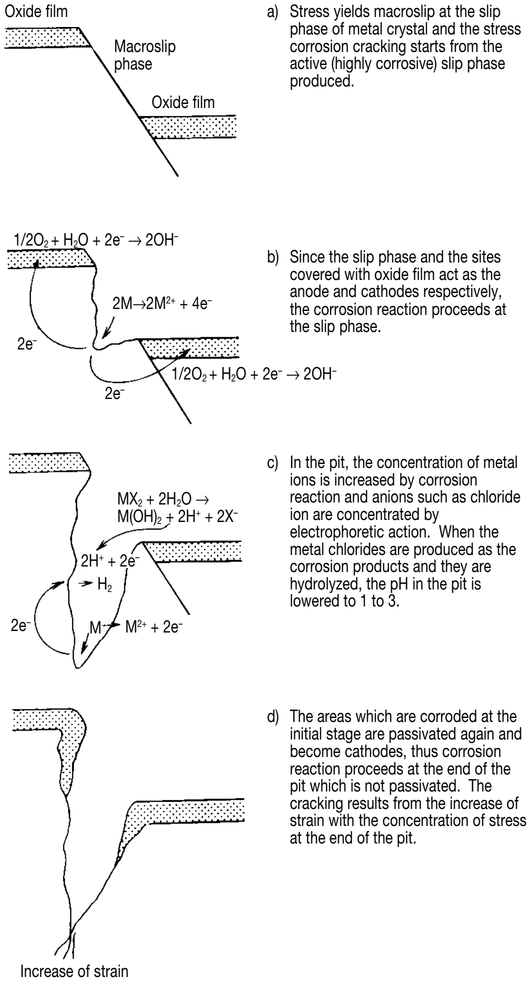
The cuprous oxide is stable in fresh water and inhibits copper corrosion. Consequently, the average corrosion rate of copper is low at 2 to 3 mg/dm²·day. However, when fouling materials, such as slime and corrosion products of carbon steel produced in the other parts of system, accumulate on copper surfaces, a pitting corrosion occurs under the fouling with the same mechanism as carbon steel shown in Figure 3.12. Such form of copper corrosion is called deposit attack and chloride ions are usually concentrated in the pit. Therefore, pitting corrosion covered with corrosion products, such as basic



a) Illustration of a pitting corrosion

b) Chloride distribution in the pit by XMA inspection

Photo 3.6 Pitting of aluminum brass and the concentration of chloride in the pit



a) Stress yields macroslip at the slip phase of metal crystal and the stress corrosion cracking starts from the active (highly corrosive) slip phase produced.

b) Since the slip phase and the sites covered with oxide film act as the anode and cathodes respectively, the corrosion reaction proceeds at the slip phase.

c) In the pit, the concentration of metal ions is increased by corrosion reaction and anions such as chloride ion are concentrated by electrophoretic action. When the metal chlorides are produced as the corrosion products and they are hydrolyzed, the pH in the pit is lowered to 1 to 3.

d) The areas which are corroded at the initial stage are passivated again and become cathodes, thus corrosion reaction proceeds at the end of the pit which is not passivated. The cracking results from the increase of strain with the concentration of stress at the end of the pit.

Fig. 3.15 Mechanism of stress corrosion cracking of stainless steel

copper sulfate with greenish blue color, are often observed on the surface of copper and copper alloys (brass, aluminum brass and so on).

Photographs 3.5 (p.3-73) and 3.6 show the local corrosion with green rust on copper tubes and the concentration condition of chloride ions within the pitting corrosion of aluminum brass respectively.

In order to prevent the local corrosion, it is effective to use copper corrosion inhibitors together with chemicals such as slime control agents and dispersants, which prevent the fouling of the metal surfaces.

(3) Stainless steels

Stainless steel surface is covered with the stable oxide film with the thickness of 10 to 30 Å and passivated in cooling water including dissolved oxygen. As the result, stainless steel shows the corrosion resistance. However, the chloride ions of high concentration partially destroy the oxide film and sometimes cause the local corrosion. The adhesion of fouling material on the surface may also cause the local corrosion of stainless steel because it disturbs the oxygen diffusion and deteriorates the oxide film stability under it.

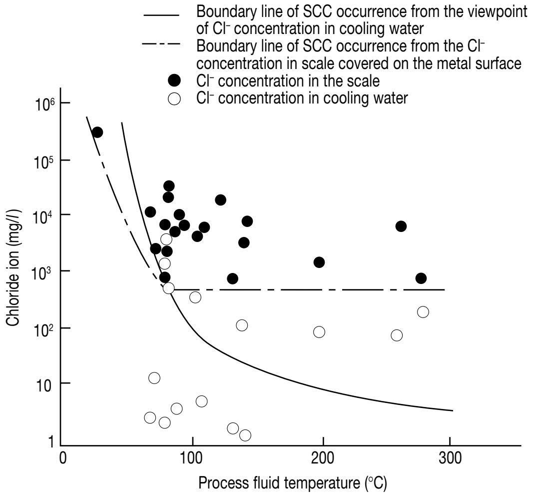


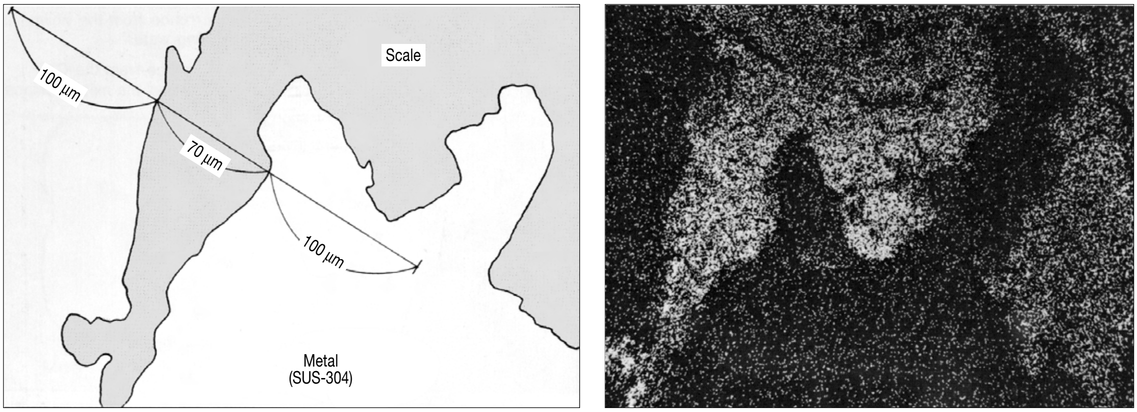
Fig. 3.16 Influnce of chloride ion concentration and process fluid temperature on the occurrence of stress corrosion cracking of stainless steels (SUS 304, 304L, 316, 316L and 405).

The typical local corrosions of stainless steel are pitting under fouling, crevice corrosion and stress corrosion cracking (SCC).

The SCC occurs when stainless steel having a tensile stress over the critical value contacts with water including chloride ions. Many mechanisms for the SCC of stainless steel have been proposed, however, the mechanism shown in Figure 3.15 is considered the most probable one. The citrical stress is 10 to 20 kg/mm^2, which causes the macroslip as shown in Figure 3.15.

Nishino[7] reported the relationship between the process fluid temperature and chloride ion concentration in cooling water on the SCC of stainless steels at the cooling water side.

However, Okubo[8] presented the relationship between the SCC and the chloride ion concentration in the scale on the metal surface. Their data are shown in Figure 3.16. These data show that the SCC tends to occur easily at higher temperature even in water of lower chloride concentration because the stainless steel surface is more fouled with scale and chloride ions is more concentrated



a) Illustration of a piting corrosion

b) Chloride distribution in the pit analyzed by XMA

Photo 3.7 Chloride concentration in the pit of a stainless steel

in the fouling compared with lower temperature condition. These data also suggest the probability of SCC prevention by applying polymer dispersants which keep the metal surface from the fouling.

The corrosion potential of stainless steel is lowered at the active region under the fouling or at the inside of a crevice because dissolved oxygen is insufficiently supplied to the metal surface.

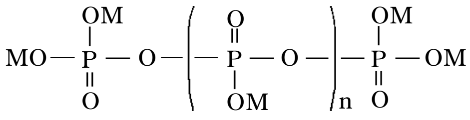
Meanwhile, the metal surface around the fouling or at the outside of the crevice acts as the cathode. Consequently, the pitting corrosion and crevice corrosion proceed under the fouling and inside the crevice respectively. In the inside of these local corrosions, chloride ions are concentrated by the same process shown in Figure 3.12. Photograph 3.7 shows such chloride ion concentration in a pit of stainless steel.

3.2.3 Types and Effects of Corrosion Inhibitors

(1) Phosphates

Phosphates are most widely used as corrosion inhibitors in open recirculating cooling water systems at present. Usually orthophosphates and polyphosphates (pyrophosphates, tripolyphosphates and hexametaphosphates) are used.

Polyphosphates are produced by a condensed polymerization reaction from a mixture of phosphoric acid, orthophosphate and alkali by heating, and have the following molecular structure:



$$\mathrm{MO-\underset{\underset{\displaystyle O}{\|}}{\overset{\overset{\displaystyle OM}{|}}{P}}-O-\left(-\underset{\underset{\displaystyle OM}{|}}{\overset{\overset{\displaystyle O}{\|}}{P}}-O-\right)_n-\underset{\underset{\displaystyle O}{\|}}{\overset{\overset{\displaystyle OM}{|}}{P}}-OM}$$

M= Na, K, NH_4, H, etc.

n = integer

The bonding forces with metal ions, the solubilities of their metal salts and the corrosion inhibition effects of the polyphosphates are different from each other depending on their degree of polymerization. In general, phosphates show good corrosion inhibition effects in the presence of divalent

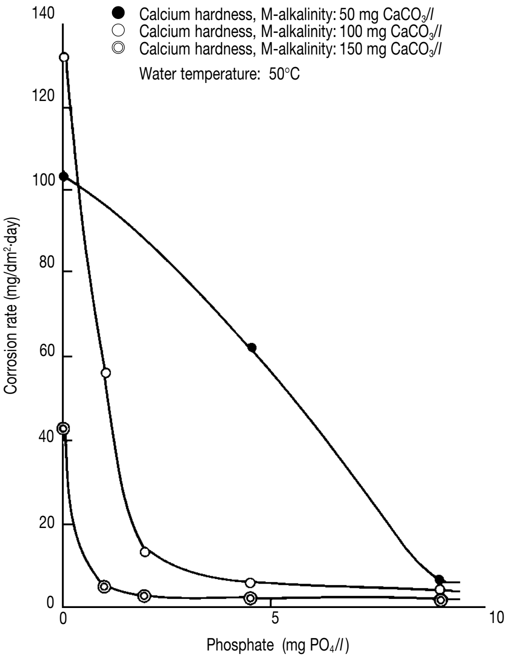


Fig. 3.17 Relationship between the corrosion inhibition effect of a polyphosphate on carbon steel and calcium hardness

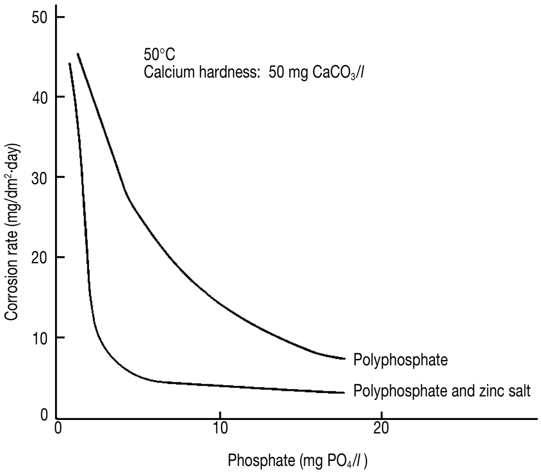


Fig. 3.18 **Improvement of the corrosion inhibition effect of a phosphate on carbon steel by using a zinc salt**

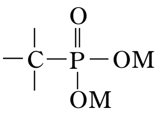
metal ions such as calcium ion.

Figure 3.17[9)] shows the relationship between the corrosion inhibition of a polyphosphate on carbon steel and calcium hardness in water. The critical concentration of the phosphate for the corrosion inhibition becomes lower as the calcium hardness increases.

Figure 3.18 shows the comparative corrosion inhibition effects of a polyphosphate and a polyphosphate-zinc treatments in water with low calcium hardness. The combined use of zinc salts together with polyphosphates improves the corrosion inhibition provided by polyphosphates especially in low calcium hardness water.

(2) Phosphonates

Phosphonates are widely applied as corrosion inhibitor in open recirculating cooling water systems as same as phosphates. Typical phosphonates used in the cooling systems are hydroxy-ethylidene-diphosphonate, 2-phosphonobutane-1,2,4-tricarboxylate, aminotrimethylene phosphonate and so on. These phosphonates have the following phosphonic group in their structure:



$$-\underset{|}{\overset{|}{\mathrm{C}}}-\underset{\underset{\mathrm{OM}}{|}}{\overset{\overset{\mathrm{O}}{\|}}{\mathrm{P}}}-\mathrm{OM}$$

M = Na, K, H, NH_4, etc.

Characteristics of phosphonates, such as the bonding forces with metal ions, the solubilities of their metal salts and the corrosion inhibition effects, are different each other depending on their chemical structures. In general, phosphonates show the sufficient corrosion inhibition on carbon steel in water including calcium ions. Figure 3.19 shows the relationship between the corrosion inhibition effect of a phosphonate and calcium hardness in water. The critical concentration of the phosphonate for corrosion inhibition lowers as the calcium hardness increases. The corrosion inhibition provided by phosphonates is improved by the combined use of zinc salts as shown in Figure 3.20. Since the hydrolysis rates of phosphonates are remarkably low comparing with polyphosphates, phosphonates are usually applied for cooling water systems of high calcium hardness and high cycles of concentration. The phosphonates are also used as scale inhibitors because they have excellent inhibition effects on calcium carbonate deposition in water.

(3) Divalent metal salts

Divalent metal salts, such as zinc and nickel salts, have the corrosion inhibition effect for carbon steel, copper and copper alloys. However, their solubilities are usually too small to keep their effective concentrations in neutral water such as cooling water. Therefore, the application of divalent metal salts alone rarely shows a good effect. Figure 3.21 shows the relationship between the corrosion

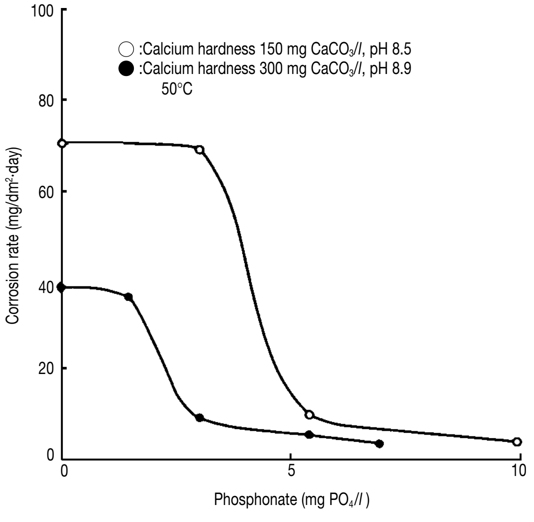


Fig. 3.19 **Relationship between the corrosion inhibition effect of a phosphonate on carbon steel and calcium hardness**

inhibition effect of a zinc salt on carbon steel and pH. The zinc salt shows the corrosion inhibition with the dosage of 50 mg Zn/*l* in the water of pH 7. However, the effect is remarkably reduced in the water of pH 8 because the zinc salt is precipitated as zinc hydroxide. On the contrary, the combined use of the zinc salt with a scale inhibitor shows the sufficient corrosion inhibition even in the water of pH 8 because the scale inhibitor controls the deposition of zinc salt.

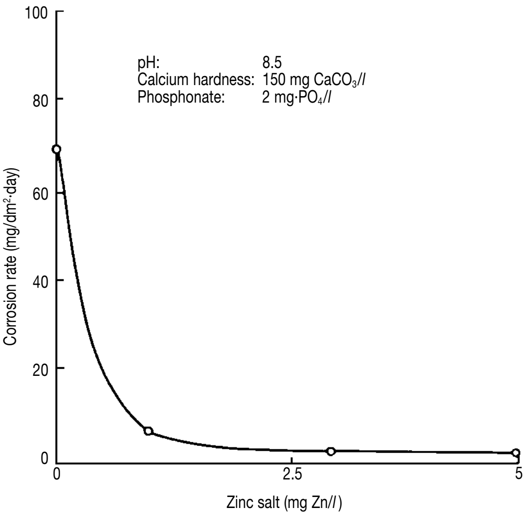


Fig. 3.20 **Improvement of the corrosion inhibition effect of a phosphonate on carbon steel by using a zinc salt**

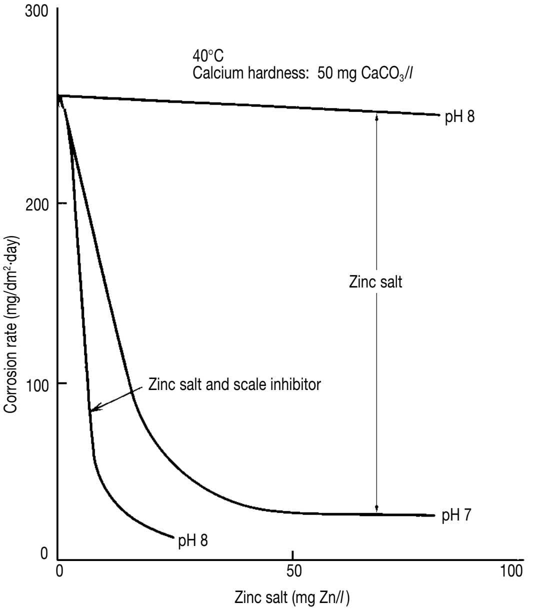


Fig. 3.21 **Influences of pH and a scale inhibitor on the corrosion inhibition effect of a zinc salt against carbon steel**

The divalent metal salts are scarcely applied alone. They are usually used in combination with phosphates or phosphonates.

(4) Low molecular weight water soluble polymers

Some low molecular weight water soluble polymers, such as polyacrylate and polymaleate, inhibit the carbon steel corrosion. Their corrosion inhibition effects are not stable in water of low hardness. However, Uchida et al.,$^{3),10)}$ reported that their effect became stable in water supersaturated with calcium carbonate. Recently, these polymers have been applied as non-metal and non-phosphorous corrosion inhibitors for open recirculating cooling water systems.

Figure 3.22 shows the typical corrosion inhibition effect of a polymer on carbon steel in a water of high calcium hardness and high M-alkalinity.

(5) Nitrite

Nitrites have the excellent corrosion inhibitions on carbon steel. Nitrites are less toxic than chromates but they are scarcely used as corrosion inhibitors in open recirculating cooling water systems because they are easily decomposed by microorganisms. However, the nitrites are widely used as corrosion inhibitors in closed recirculating cooling water systems with the application of non-oxidizing biocides.

Figure 3.23 shows the relationship between the corrosion rate of carbon steel and the dosage of a nitrite. The nitrite with the dosage of 100 mg NO_2^- /*l* sufficiently lowers the corrosion rate of carbon

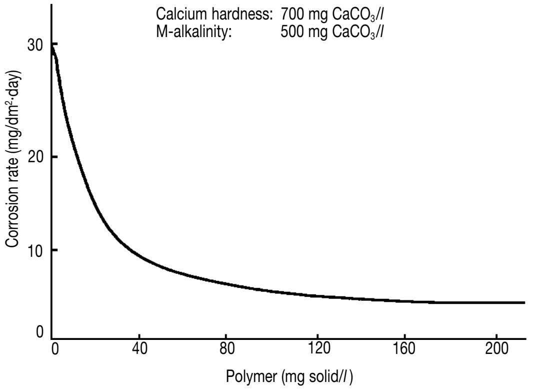


Fig. 3.22 **Corrosion inhibition effect of a low molecular weight water soluble polymer on carbon steel**

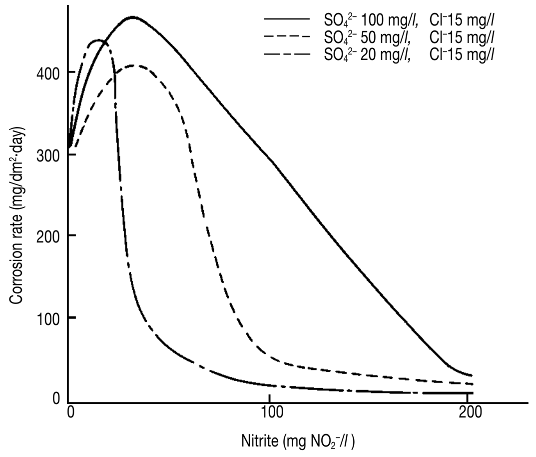


Fig. 3.23 Influence of sulfate ion on the corrosion inhibition effect of a nitrite against carbon steel

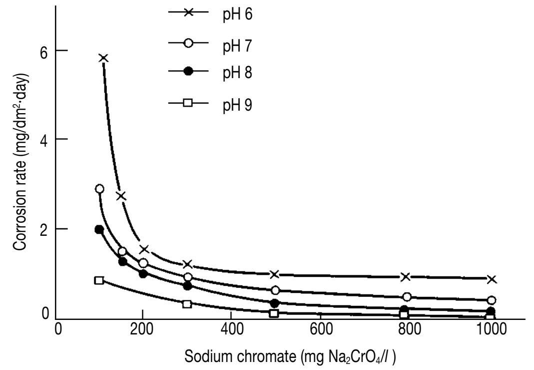


Fig. 3.24 Influence of sodium chromate concentration and pH on the corrosion rate of carbon steel

steel in water with low sulfate and chloride ion concentrations. The increase of these anion concentrations, especially sulfate ion, deteriorates the corrosion inhibition of nitrites and rises the required dosage for the sufficient corrosion inhibition.

(6) Chromates

Chromates had been used as corrosion inhibitors for a long time and showed the excellent corrosion inhibition effects on carbon steel. However, they are scarcely used in the present because of their strong toxicites.

Figure 3.24[11)] shows a typical relationship between the dosage of chromate and the corrosion rate of carbon steel. The critical concentration of chromates for corrosion inhibition depends on environmental conditions, such as water temperature, and the kinds and concentrations of dissolved salts in water, but, it is usually 30 to 500 mg CrO_4^{2-}/l for carbon steel in neutral water. Sodium chromate and sodium dichromate are generally used as corrosion inhibitors. Chromates are usually used in combination with polyphosphate and/or zinc salts because severe pitting corrosion may occur if chromate is used alone with the insufficient concentration.

(7) Amines and azoles

Amine based corrosion inhibitors are usually used for acid cleaning and boiler water treatment, however, they are not often used in open recirculating cooling water systems because of their higher cost and lower corrosion inhibition effect on carbon steel in neutral water as compared with the inorganic corrosion inhibitors.

Azoles, such as benzotriazole and tolyltriazole, are very effective for inhibiting the corrosion of copper and copper alloys with the low dosages of few mg/*l*. Figure 3.25 shows the corrosion inhibitions of benzotriazole on copper and aluminum brass.

Azoles are widely applied for cooling water systems with heat exchangers having copper or copper alloy tubes.

(8) Others

Molybdates, tungstates and some organic acid salts inhibit the carbon steel corrosion. They are more often used in closed cooling water systems than in open recirculating cooling systems because of their higher costs.

Silicates are sometimes used as corrosion inhibitors in drinking water lines because of the nontoxicity as same as phosphates. However, silicates

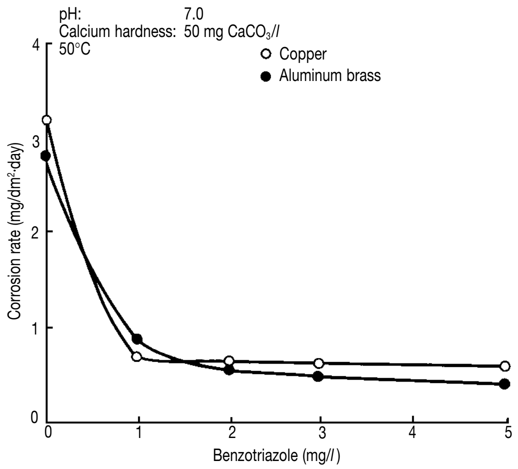


Fig. 3.25 Corrosion inhibition effect of benzotriazole on copper and aluminum brass

are scarcely applied for open recirculating cooling systems because their corrosion inhibitions on carbon steel are fluctuated depending on water quality, water temperature and so on.

3.2.4 Factors Influencing the Effects of Corrosion Inhibitors

The effects of corrosion inhibitors are widely influenced with water qualities such as pH, concentration of dissolved salts and hardness, and the operating conditions such as water temperature and water flow rate. The influences of these factors on the effects of corrosion inhibitors are discussed here.

(1) pH

Figure 3.26 shows a typical relationship between the corrosion inhibition effect of a polyphosphate based inhibitor on carbon steel and pH. The corrosion inhibition is stable within the wide pH range of 6.5 to 9.0. However, scale inhibitors should be applied together with the corrosion inhibitor in water of pH above 8.0 because calcium carbonate, calcium phosphate, etc., tend to precipitate in water of higher pH.

At present, many kinds of scale inhibitors have been developed and the scaling is sufficiently controlled under phosphate treatments even in water of high pH around 9.

(2) Calcium hardness

Phosphates and phosphonates show the stable corrosion inhibition effects in the presence of calcium ions as described in the Section 3.2.3. For obtaining the good corrosion inhibition effect, the higher dosages are required in water of lower calcium hardness, while the lower dosages are sufficient in water of higher calcium hardness as shown in Figures 3.17(p.3-16) and 3.19(p.3-17).

(3) Concentration of aggressive anions

Aggressive anions, such as chloride and sulfate ions, of high concentrations attack the protective films formed by corrosion inhibitors and deteriorate their effects.

Figure 3.27 shows the influence of chloride and sulfate ion concentration on the effects of various corrosion inhibitors. The influence of anion concentration is different depending on the types of corrosion inhibitors. In general, the inhibitors formulated with zinc salts are less influenced by the anions.

(4) Residual chlorine concentration

Chlorine compounds, sodium hypochlorite, liquid chlorine, etc., are usually used for slime control with the dosage of 0.3 to 1.0 mg $\text{R-Cl}_2/l$ in cooling water systems. However, the residual chlorine concentration sometimes reaches several mg/l in cooling water when the chlorination is poorly controlled.

Figure 3.28 shows the influence of residual chlorine concentration on the corrosion rate of copper. The corrosion of copper is accelerated in proportion to the chlorine concentration. Although this corrosion is inhibited by the addition of a inhibitor for copper, the corrosion rate tends to increase if the chlorine concentration exceeds 1 mg/l. Therefore, the residual chlorine concentration should be controlled below 1 mg Cl_2/l even when the corrosion inhibitor is used.

However, the corrosion rate of carbon steel is

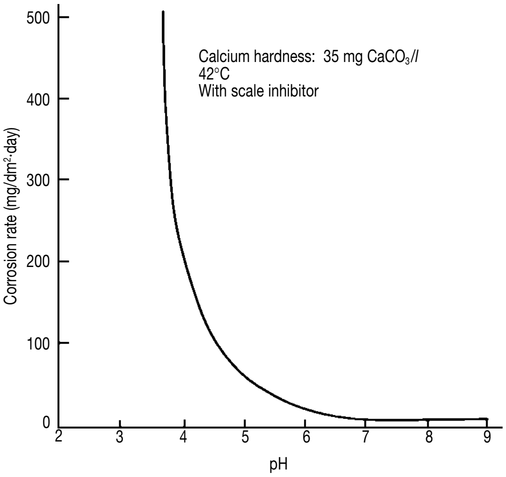


Fig. 3.26 Influence of pH on the corrosion inhibition effect of a polyphosphate against carbon steel

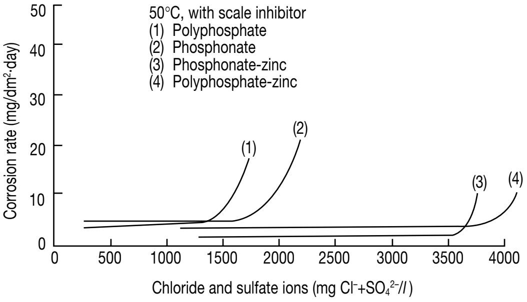


Fig. 3.27 Influence of chloride and sulfate ion concentration on the effects of various corrosion inhibitors against carbon steel

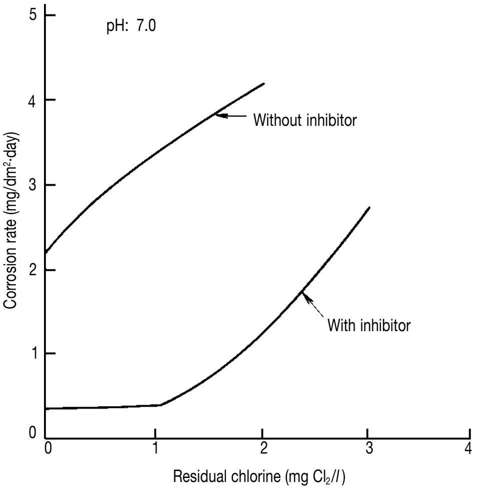


Fig. 3.28 Influence of residual chlorine on the corrosion rate of copper and the effect of a copper corrosion inhibitor

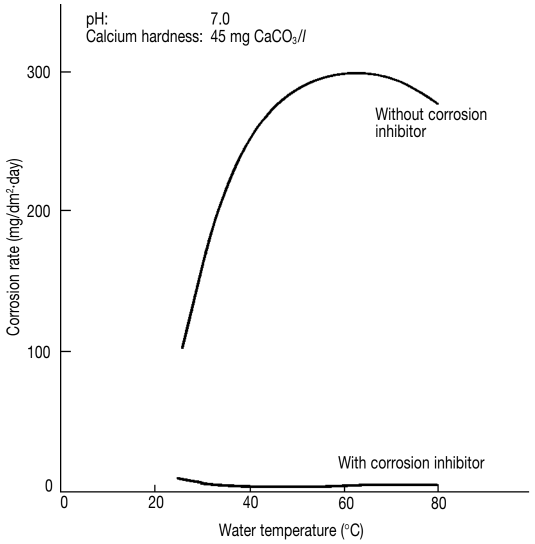


Fig. 3.29 Influence of water temperature on carbon steel corrosion rate and the inhibition effect of a polyphosphate based chemical

scarcely influenced with residual chlorine concentration up to 5 mg Cl_2/l under the suitable corrosion inhibitor treatment.

(5) Water temperature

Figure 3.29[12] shows the relationship between the corrosion inhibition effect of a polyphosphate-zinc based inhibitor on carbon steel and water temperature. In the absence of the inhibitor, the corrosion rate of carbon steel increases in proportion to the increase in water temperature in the range of 25 to 50°C. The influence of the temperature becomes not obvious in the range of 50 to 80°C. On the contrary, the polyphosphate-zinc based inhibitor shows the stable corrosion inhibition in the wide temperature range of 30 to 80°C. However, the combined use of scale inhibitor with the corrosion inhibitor is required for controlling zinc and calcium phosphate scale.

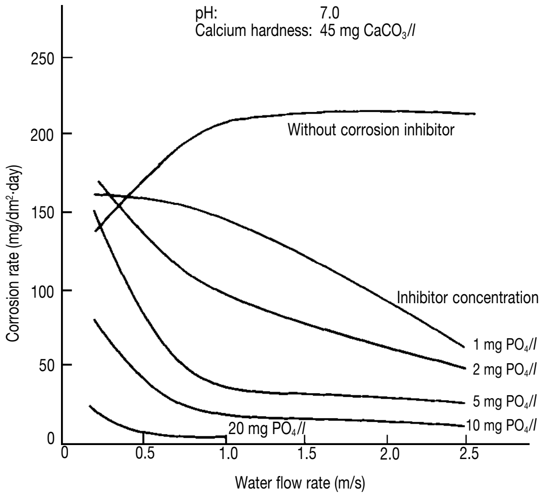


Fig. 3.30 Relationship between the effect of a polyphosphate based corrosion inhibitor on carbon steel and water flow rate

(6) Water flow rate

In cooling water, the corrosion rate of carbon steel is determined by the diffusion rate of dissolved oxygen to the steel surface. Therefore, the higher the water flow rate, the higher the corrosion rate of the steel. On the other hand, in the presence of corrosion inhibitors, the good corrosion inhibition effect is generally obtained at higher water flow rate because the diffusion rate of inhibitor increases as the flow rate is increased. Therefore, the proper water flow rate is required to obtain the maximum effect of the corrosion inhibitor.

Figure 3.30[13] shows a relationship between the corrosion inhibition effect of a polyphosphate based inhibitor on carbon steel and water flow rate. An increase in the flow rate improves the corrosion inhibition and gives the better effect even with the lower dosage. The water flow rate of 0.5 m/s or higher is desirable to obtain the sufficient effect in the presence of an adequate amount of the inhibitor.

3.2.5 Corrosion Prevention Methods Other Than Corrosion Inhibitors

(1) Cathodic protection

Some places in cooling water systems are insufficiently protected by the application of corrosion inhibitor alone. For example, channel covers and tube sheets of heat exchangers with the low water flow rate sometimes corrode. The application of cathodic protection together with corrosion inhibitors improves the inhibition effect at such places. In cooling water systems, the cathodic protection is usually applied by connecting the sacrificed anodes of magnesium or zinc alloys with the materials to be protected.

Photographs 3.8 and 3.9[14] (p.3-74) shows the effect of cathodic protection by applying magnesium based anodes to the channel cover of a heat exchanger in a cooling water system treated with a phosphonate based corrosion inhibitor. The local corrosions with corrosion products were observed in the inside of the channel cover as shown in Photograph 3.8. In the heat exchanger inspection after 1 year from the application of cathodic protection, no new corrosion was found as shown in Photograph 3.9.

(2) Linings and coatings

Recently, linings and coatings have been applied to prevent the corrosion of heat exchangers. Since various type of linings and coatings are available, the excellent durability can be attained with careful consideration of the corrosive environment.

However, the application of linings or coatings on the heat transfer surfaces of heat exchangers is not so popular because the thermal conductivity of the organic materials is remarkably less than that of metals.

(3) Corrosion resistant materials

Copper, copper alloys and stainless steels are most widely used as corrosion resistance materials for heat exchangers. High-nickel alloys, titanium and so on are used for heat exchangers where the process side fluids are highly corrosive.

3.3 Scale and Scale Prevention

Typical components of scales found in cooling water systems are as follows:

① Calcium carbonate,
② Calcium and zinc phosphates,
③ Silica and magnesium silicates,
④ Calcium sulfates.

These scale components generally tend to deposit and adhere as scales on heat transfer surfaces with higher temperature because their solubilities decrease as the pH and water temperature increase.

Since the thermal conductivities of scales are extremely low in comparison with those of tube materials, the scale adhesion remarkably lowers the thermal efficiencies of heat exchangers. Excessive scale growth in the tubes may clog them.

3.3.1 Kinds of Scales and Their Solubilities

(1) Calcium carbonate

Calcium carbonate is the most common scale in cooling water systems. The solubility product of calcium carbonate is shown in the following equation:

$$[Ca^{2+}]\ [CO_3^{2-}] = K_{sp}^* \quad \cdots\cdots (3.25)$$

where

K_{sp} = solubility product of calcium carbonate
[ ] = Volumetric molarity of ionic species

The dissociation equilibrium of hydrogen carbonate ion is as follows:

$$HCO_3^- \rightleftarrows H^+ + CO_3^{2-} \quad \cdots\cdots (3.26)$$

$$\frac{[H^+]\ [CO_3^{2-}]}{[HCO_3^-]} = K_2 \quad \cdots\cdots (3.27)$$

where

K_2 = secondary dissociation constant of carbonic acid

Equation (3.28) is derived from the equations (3.25) and (3.27).

$$\frac{K_2[Ca^{2+}]\ [HCO_3^-]}{[H^+]} = K_{sp} \quad \cdots\cdots (3.28)$$

Since the concentration of HCO_3^- is approximately equal to M-alkalinity[15] of water, the equation (3.28) is expressed as follows:

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* The solubility product is exactly defined with the following equation, $r_1 \cdot r_2[Ca^{2+}]\ [CO_3^{2-}] = K_{sp}$, however, it is approximated by the equation (3.25) in the dilute solution in which the activities, r_1 and r_2, are almost equal to 1.

$$\log [Ca^{2+}] + \log [M{\cdot}ALK] + pH = \log(K_{sp}/K_2) \quad \text{.........................} \ (3.29)$$

Table 3.10 shows the temperature dependence of $\log(K_{sp}/K_2)$. The equation (3.29) shows the saturation conditions of calcium carbonate in water and the pH satisfying the condition of this equation, which is called the saturation pH (pH_s). The relation expressed by the equation (3.29) at 25°C is shown in Figure 3.31.

The point A in the Figure 3.31 represents the quality*1 of an industrial water. As the water is not saturated with calcium carbonate, no deposition of calcium carbonate occurs. The point B shows the quality*2 of water which is concentrated to five times of the industrial water. Since this water is supersaturated solution with calcium carbonate, calcium carbonate must deposit in it. The point C shows the saturation pH (pH_s) of the industrial water. The difference between the actual pH (pH_a) of the industrial water and the pHs is called the saturation index (SI) of calcium carbonate or Langelier index[16]. The relationship between the SI and the saturation condition of calcium carbonate in water is expressed as follows:

$SI = pH_a - pH_s > 0$: Supersaturation condition of calcium carbonate ...... (3.30)

$SI = pH_a - pH_s < 0$: Unsaturation condition of calcium carbonate ...... (3.31)

The pH_s is calculated by using the equation (3.32).

$$pH_s = (9.3 + A + B) - (C + D) \quad \text{...................} \ (3.32)$$

The A, B, C and D in the equation (3.32) are determined by using Tables 3.11 to 3.14 according to the cooling water quality and the temperature.

Since calcium carbonate is more easily deposited under higher pH condition, it tends to precipitate at the cathodes on metal surface where the pH is increased by the cathodic corrosion reaction [the equation (3.18)]. The deposited calcium carbonate acts as a barrier to the diffusion of dissolved oxygen into the metal surface and inhibits the corrosion. Ryznar[17] proposed the stability index [equation (3.33)] which predicts more exactly the corrosion prevention by calcium carbonate deposition in comparison with the saturation index.

$$\text{Stability index (S)} = 2pH_s - pH_a \quad \text{.................} \ (3.33)$$

The corrosion tendency of water is predicted from the stability index as follows:

S = 6: chemical equilibrium condition ...... (3.34)
S > 6: corrosive tendency .... (3.35)
S < 6: scaling (protective) tendency .... (3.36)

(2) Calcium Phosphate

In cooling water systems, orthophosphates or polyphosphates are used as corrosion inhibitors.

Table 3.10 Temperature dependence of calcium carbonate saturation conditions

Water temperature (°C)	Secondary dissociation constant of carbonic acid, K_2	Solubility product of calcium carbonate, K_{sp}	log K_{sp}/K_2
0	2.40×10^{-11}	9.55×10^{-9}	2.60
5	2.75×10^{-11}	8.13×10^{-9}	2.47
10	3.24×10^{-11}	7.08×10^{-9}	2.34
15	3.72×10^{-11}	6.03×10^{-9}	2.21
20	4.17×10^{-11}	5.25×10^{-9}	2.10
25	4.68×10^{-11}	4.57×10^{-9}	1.99
30	5.13×10^{-11}	3.98×10^{-9}	1.89
40	6.03×10^{-11}	3.02×10^{-9}	1.70
50	6.76×10^{-11}	2.34×10^{-9}	1.54

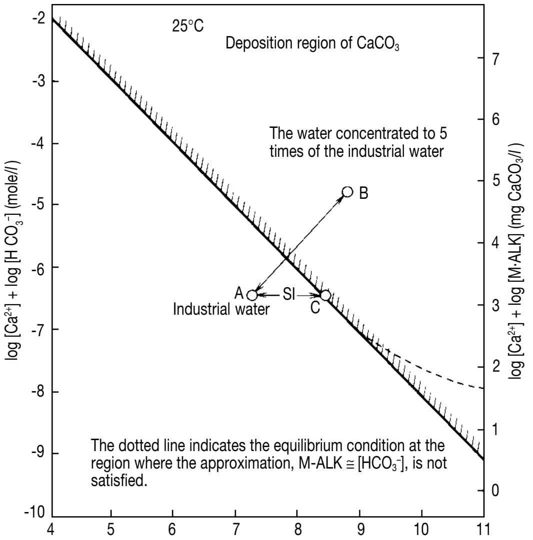

Fig. 3.31 Schematic illustration of saturation index for calcium carbonate under the precipitation equilibrium condition

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*1 Calcium hardness: 45 mg $CaCO_3/l$, M-alkalinity: 50 mg $CaCO_3/l$, pH: 7.2

*2 Calcium hardness: 225 mg $CaCO_3/l$, M-alkalinity: 250 mg $CaCO_3/l$, pH: 8.7

Polyphosphates are hydrolyzed to orthophosphates at higher temperature. The hydrolysis rate of polyphosphates in the cooling water may be 40 to 90%, though its percentage varies with the retention time of the circulating water. The orthophosphate combines with calcium ions to form calcium phosphate.

Green, et al.,[18] reported that the relationship expressed by the equation (3.37) was found in the saturation solution of calcium phosphate:

$$2\log\left[\frac{K_1K_2K_3}{K_1K_2K_3+[H^+]^3+K_1\,[H^+]^2+K_1K_2[H^+]}\right]$$

$$-\log K_{sp} = -3\log[Ca^{2+}] - 2\log\{[H_3PO_4] + [H_2PO_4^-] + [HPO_4^{2-}] + [PO_4^{3-}]\} \quad \ldots\ldots\ldots\ldots (3.37)$$

where

K_{sp} = solubility product of calcium phosphate, $Ca_3(PO_4)_2$

K_1, K_2, and K_3 = primary, secondary, and tertiary dissociation constants of phosphoric acid respectively

[ ] = volumetric molarities of phosphate and other ion species

Table 3.11 Relationship between total dissolved solids and A in the equation (3.32)

Total dissolved solids (mg/*l*)	A
0–350	0.1
351–5,000	0.2

Table 3.12 Relationship between temperature and B in the equation (3.32)

Temperature (℃)	B
0–1	2.6
2–5	2.5
6–9	2.4
10–13	2.3
14–17	2.2
18–21	2.1
22–27	2.0
28–31	1.9
32–37	1.8
38–43	1.7
44–50	1.6
51–56	1.5
57–63	1.4
64–71	1.3
72–78	1.2
79–85	1.1

Table 3.13 Relationship between Ca-hardness and C in the equation (3.32)

Ca-hardness (mg $CaCO_3$/*l*)	C
6–7	0.4
8–9	0.5
10–11	0.6
12–13	0.7
14–17	0.8
18–22	0.9
23–27	1.0
28–34	1.1
35–43	1.2
44–55	1.3
56–69	1.4
70–87	1.5
88–110	1.6
111–138	1.7
139–174	1.8
175–225	1.9
226–275	2.0
276–345	2.1
346–435	2.2
436–555	2.3
556–695	2.4
696–875	2.5
876–1,000	2.6

Table 3.14 Relationship between M-alkalinity and D in the equation (3.32)

M-alkalinity (mg $CaCO_3$/*l*)	D
6–7	0.8
8–9	0.9
10–11	1.0
12–13	1.1
14–17	1.2
18–22	1.3
23–27	1.4
28–35	1.5
36–44	1.6
45–55	1.7
56–69	1.8
70–88	1.9
89–110	2.0
111–139	2.1
140–176	2.2
177–225	2.3
226–275	2.4
276–355	2.5
356–445	2.6
446–555	2.7
556–695	2.8
696–885	2.9
886–1,000	3.0

Table 3.15 pH-temperature factor for tricalcium phosphate

pH	°C 10	20	30	40	50	60	70	80	90	100
	°F 50	68	86	104	122	140	158	176	194	212
6.0	13.64	14.00	14.32	14.64	14.86	15.04	15.30	15.42	15.58	15.68
6.1	14.02	14.38	14.69	15.02	15.44	15.56	15.69	15.81	16.02	16.04
6.2	14.40	14.76	15.07	15.38	15.90	16.04	16.05	16.20	16.46	16.42
6.3	14.78	15.13	15.45	15.74	16.30	16.46	16.44	16.57	16.89	16.81
6.4	15.14	15.51	15.82	16.14	16.68	16.84	16.81	16.94	17.32	17.19
6.5	15.52	15.87	16.18	16.50	17.04	17.20	17.18	17.32	17.73	17.59
6.6	15.90	16.24	16.53	16.88	17.38	17.56	17.54	17.70	18.13	17.94
6.7	16.24	16.61	16.88	17.24	17.70	17.88	17.91	18.06	18.50	18.30
6.8	16.58	16.95	17.22	17.60	18.00	18.18	18.25	18.40	18.87	18.68
6.9	16.94	17.29	17.57	17.92	18.31	18.49	18.60	18.73	19.20	19.02
7.0	17.30	17.61	17.92	18.24	18.59	18.78	18.92	19.06	19.52	19.38
7.1	17.62	17.92	18.25	18.56	18.88	19.08	19.25	19.40	19.83	19.70
7.2	17.94	18.23	18.57	18.86	19.18	19.36	19.57	19.70	20.12	20.02
7.3	18.24	18.53	18.86	19.14	19.44	19.66	19.87	20.00	20.39	20.34
7.4	18.54	18.81	19.13	19.42	19.72	19.94	20.16	20.30	20.65	20.64
7.5	18.83	19.08	19.40	19.70	19.96	20.20	20.44	20.56	20.90	20.93
7.6	19.10	19.35	19.66	19.96	20.22	20.46	20.71	20.84	21.14	21.20
7.7	19.38	19.60	19.92	20.20	20.46	20.70	20.96	21.10	21.36	21.47
7.8	19.62	19.84	20.17	20.44	20.69	20.94	21.20	21.34	21.59	21.72
7.9	19.86	20.08	20.40	20.68	20.92	21.18	21.43	21.58	21.82	21.96
8.0	20.10	20.32	20.64	20.92	21.16	21.40	21.67	21.80	22.04	22.20
8.1	20.32	20.54	20.86	21.14	21.37	21.64	21.89	22.03	22.26	22.44
8.2	20.54	20.76	21.08	21.36	21.58	21.86	22.12	22.24	22.47	22.66
8.3	20.76	20.98	21.29	21.58	21.81	22.06	22.33	22.46	22.69	22.88
8.4	20.97	21.19	21.50	21.78	22.02	22.28	22.54	22.68	22.90	23.10
8.5	21.18	21.41	21.72	22.00	22.23	22.50	22.75	22.90	23.11	23.32
8.6	21.38	21.62	21.94	22.22	22.44	22.70	22.96	23.10	23.31	23.52
8.7	21.60	21.83	22.15	22.42	22.66	22.90	23.17	23.31	23.52	23.72
8.8	21.80	22.04	22.36	22.62	22.86	23.10	23.36	23.51	23.73	23.94
8.9	22.00	22.25	22.56	22.83	23.08	23.30	23.57	23.72	23.93	24.15
9.0	22.20	22.46	22.76	23.02	23.28	23.52	23.76	23.93	24.13	24.36
9.1	22.43	22.66	22.96	23.26	23.48	23.71	23.97	24.12	24.35	24.56
9.2	22.64	22.86	23.17	23.46	23.69	23.92	24.17	24.32	24.54	24.76
9.3	22.84	23.06	23.37	23.66	23.90	24.12	24.36	24.53	24.74	24.97
9.4	23.04	23.27	23.57	23.86	24.10	24.32	24.56	24.74	24.93	25.18
9.5	23.24	23.47	23.77	24.06	24.30	24.54	24.75	24.93	25.13	25.38
9.6	23.45	23.67	23.97	24.26	24.51	24.74	24.95	25.12	25.32	25.58
9.7	23.65	23.87	24.17	24.45	24.71	24.94	25.14	25.32	25.52	25.78
9.8	23.86	24.07	24.37	24.65	24.91	25.14	25.33	25.52	25.71	25.98
9.9	24.06	24.27	24.56	24.85	25.10	25.34	25.52	25.71	25.91	26.18
10.0	24.26	24.46	24.76	25.04	25.30	25.53	25.70	25.91	26.09	26.37
10.1	24.45	24.66	24.96	25.23	25.50	25.73	25.89	26.10	26.28	26.57
10.2	24.65	24.86	25.14	25.42	25.70	25.92	26.07	26.29	26.47	26.76
10.3	24.84	25.05	25.35	25.62	25.89	26.12	26.25	26.48	26.66	26.94
10.4	25.03	25.24	25.54	25.82	26.09	26.32	26.44	26.66	26.85	27.15
10.5	25.22	25.44	25.73	26.01	26.28	26.50	26.62	26.85	27.03	27.35
10.6	25.42	25.64	25.93	26.21	26.46	26.69	26.80	27.04	27.23	27.55
10.7	25.62	25.84	26.12	26.40	26.64	26.88	26.98	27.23	27.41	27.74
10.8	25.82	26.03	26.32	26.59	26.83	27.06	27.16	27.42	27.60	27.94
10.9	26.00	26.23	26.51	26.78	27.01	27.24	27.34	27.61	27.79	28.14
11.0	26.20	26.43	26.70	26.98	27.19	27.44	27.51	27.80	27.96	28.35

Table 3.16 Calcium factor for tricalcium phosphate

Calcium hardness (mg $CaCO_3/l$)	Calcium factor	Calcium hardness (mg $CaCO_3/l$)	Calcium factor
1	15.00	120	8.75
2	14.10	140	8.55
4	13.19	160	8.38
6	12.66	180	8.22
8	12.28	200	8.08
10	11.99	250	7.79
12	11.75	300	7.56
14	11.55	350	7.36
16	11.37	400	7.18
18	11.22	500	6.89
20	11.08	600	6.66
30	10.55	800	6.28
40	10.18	1,000	5.99
50	9.89	1,200	5.75
60	9.65	1,400	5.55
80	9.28	1,600	5.38
100	8.99	1,800	5.23

Table 3.17 Phosphate factor for tricalcium phosphate

Orthophosphate (mg PO_4^{3-}/l)	Phosphate factor	Orthophosphate (mg PO_4^{3-}/l)	Phosphate factor
1	9.96	30	7.00
2	9.35	35	6.87
3	9.00	40	6.75
4	8.75	45	6.65
5	8.56	50	6.56
6	8.40	55	6.48
7	8.27	60	6.40
8	8.15	65	6.33
9	8.05	70	6.27
10	7.96	80	6.15
12	7.79	90	6.05
15	7.60	100	5.96
20	7.35	110	5.87
25	7.16	120	5.80

The left side of the equation (3.37) is called the pH and temperature factor, and the first and second terms on the right side are called the calcium and the phosphate factors respectively.

Tables 3.15 to 3.17[18)] show the values of these factors which were calculated under various conditions of temperature, pH, calcium hardness and phosphate concentration. Green also proposed the following relationship among those factors and the saturation conditions of calcium phosphate:

(pH-temperature factor) > [(calcium factor) + (phosphate factor)]: Supersaturation solution of calcium phosphate .... (3.38)

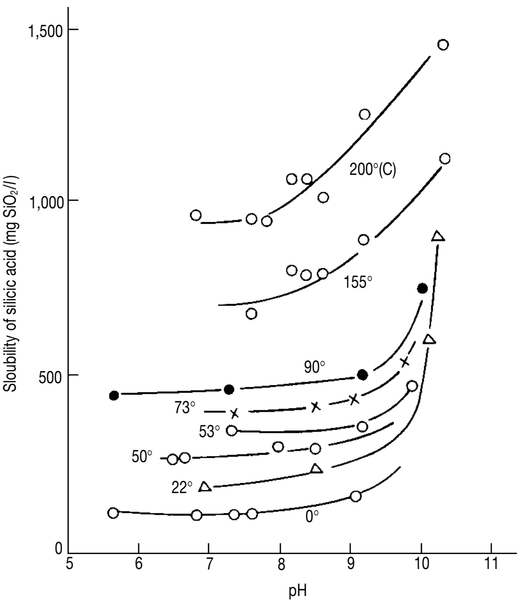


Fig. 3.32 Relationship among the solubility of silicic acid, pH and water temperature

(pH-temperature factor) < [(calcium factor) + (phosphate factor)]: Unsaturation solution of calcium phosphate .... (3.39)

The index obtained by Green, et al., is rather different from actual conditions in the field, because the index is derivated from the dissolution equilibrium condition of the pure calcium phosphate.

Hence, Kubo, et al.,[19)] determined the critical deposition pH (pH_c) of calcium phosphate by experiments and obtained the following experimental formula:

$$pH_c = \frac{11.75 - \log[CaH] - \log[PO_4] - 2\log T}{0.65} \qquad \text{.................. (3.40)}$$

where

[CaH] = calcium hardness (mg $CaCO_3/l$)
[PO_4] = phosphate concentration (mg PO_4^{3-}/l)
T = temperature (℃)

The definition of the saturation index (SI) is expressed as follows:

$$SI = pH_a - pH_c \qquad \text{....................................... (3.41)}$$

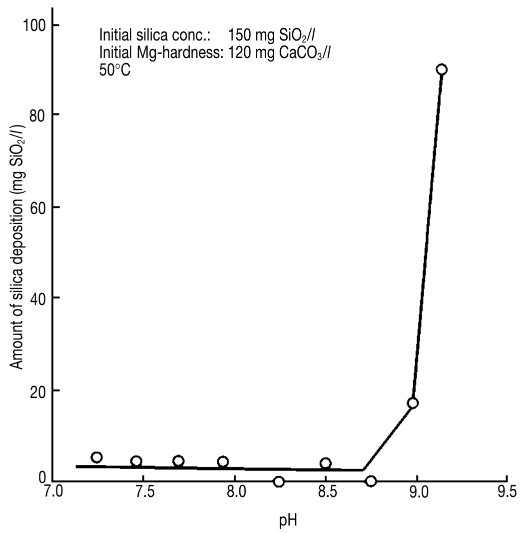


Fig. 3.33 Influence of pH on magnesium silicate deposition

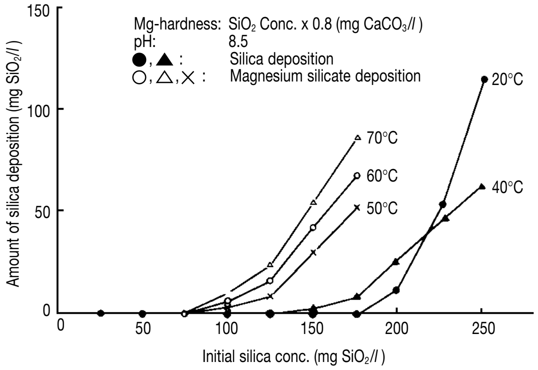


Fig. 3.34 Influence of temperature on magnesium silicate deposition

where

pH_a = actual pH

SI>0 = supersaturation condition of calcium phosphate .... (3.42)

SI<0 = unsaturation condition of calcium phosphate .... (3.43)

(3) Silica and magnesium silicates

The relationship among the solubility of silicic acid, pH and water temperature is shown in Figure 3.32[20)]. The solubility increases as the water temperature and pH increase. When the concentration of silicic acid in water exceeds the solubility, silicic acid monomers are combined together by the condensation polymerization and change to the polymers. However, silica scarcely forms the scale in heat exchangers having the higher skin temperatures than water.

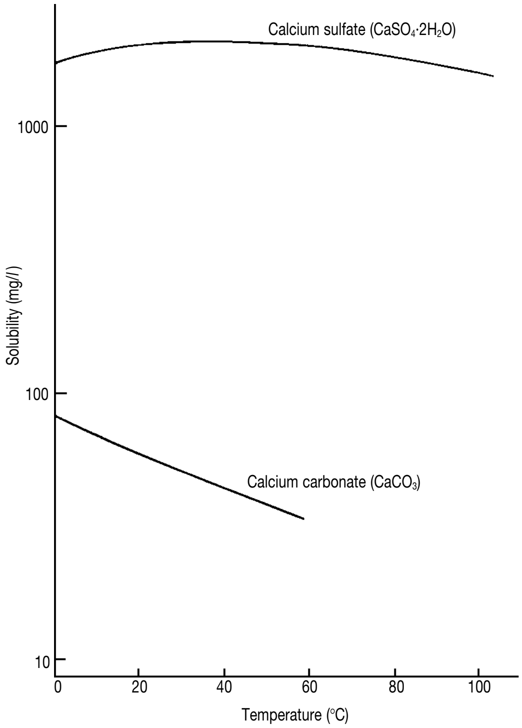
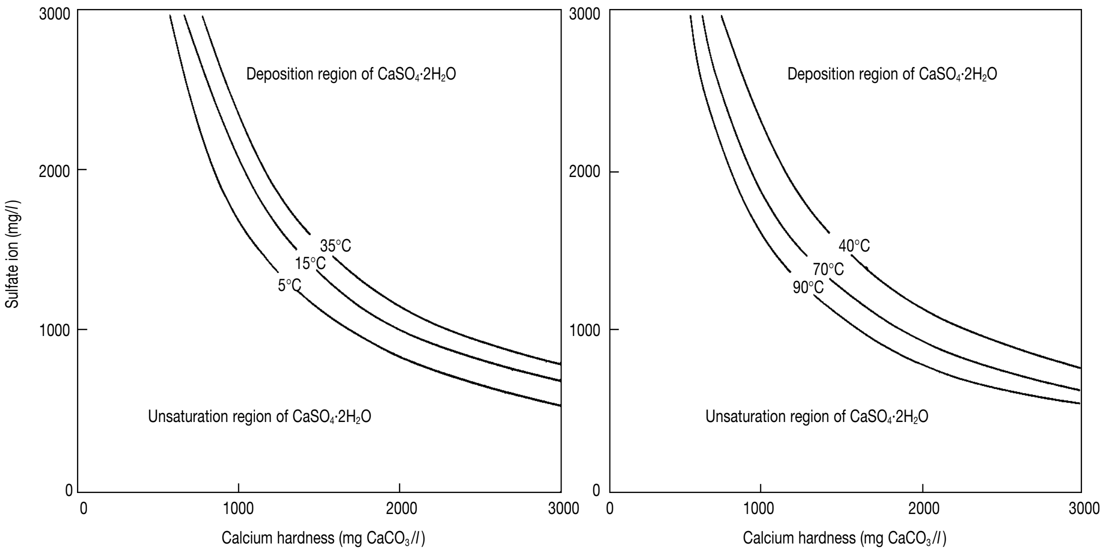


Fig. 3.35 Solubilities of calcium sulfate and carbonate

The scaling of magnesium silicates is sometimes observed in heat exchangers with high temperature in open recirculating cooling water systems including high silica and high magnesium hardness. Magnesium silicates include the four types; forsterite [Mg_2SiO_4], chrysotile [$Mg_3Si_2O_5(OH)_4$], talc [$Mg_3Si_4O_{10}(OH)_2$] and sepiolite [$Mg_2Si_3O_{7.5}OH \cdot 3H_2O$]. The talc is usually found as the magnesium silicate scale in cooling water systems.

Figure 3.33 shows a typical influence of pH on magnesium silicate deposition. Magnesium silicate tends to deposit easily at higher pH. The critical pH on magnesium silicate deposition is varied according to water temperature, magnesium hardness and silica concentration. A typical influence of temperature on magnesium silicate deposition is shown in Figure 3.34. Silica is deposited as the polymer at lower water temperature of below 40°C. On the other hand, magnesium silicate deposits at higher temperature of above 50°C. The amount of magnesium silicate deposition increases as the temperature increases. In general, there is the probability of magnesium silicate scaling under the conditions of pH above 8.5 and temperature over 50°C.



a. Water temperature: 5–35°C

b. Water temperature: 40–90°C

Fig. 3.36 Influences of water temperature, calcium hardness and sulfate ion concentration on calcium sulfate ($CaSO_4 \cdot 2H_2O$) deposition

(4) Calcium sulfates

Calcium sulfate includes three types; dihydrate ($CaSO_4 \cdot 2H_2O$) stable below 98°C, hemihydrate ($CaSO_4 \cdot 1/2H_2O$) stable between 98 and 170°C and anhydride ($CaSO_4$) stable over 170°C. Calcium sulfate scale is very hard and is hardly removed by chemical cleaning.

As shown in Figure 3.35[21)], the solubility of calcium sulfate is around 40 times more than that of calcium carbonate. So the pH control of cooling water with sulfuric acid injection is used to prevent calcium carbonate scaling.

In cooling water systems of high calcium hardness and high sulfate ion concentration, calcium sulfate ($CaSO_4 \cdot 2H_2O$) may be deposited at some temperature. Figure 3.36 shows the influences of temperature, calcium hardness and sulfate ion concentration on calcium sulfate deposition. The solubility of calcium sulfate increases as water temperature increases up to 35°C and then decreases at temperature above 40°C.

3.3.2 Process of Scale Formation and Functional Mechanisms of Scale Inhibitors

(1) Process of scale formation

The solutes exist in the form of ions, complex ions or single molecules in the dilute and unsaturated solution. However, several to dozens of them combine together and form the crystal nucleus in the supersaturated solution.

The nucleus is dissolved again when its particle size is smaller than the critical size (critical nucleus), while it grows up to the crystal when the size exceeds the critical size. It is required some induction period to form the crystal in the supersaturation solution. The induction period becomes longer in the solution of lower saturation degree* and shorter in the solution with higher saturation degree.

In the cases of calcium carbonate and calcium phosphate, the increase of water temperature shortens their induction periods and accelerates their crystal depositions because their solubilities are reduced at higher temperature.

The increase of water flow rate shortens the induction period because it increases the frequency of molecular collisions in the solution.

The crystal growth rate is determined by the diffusion rate of the solute into the crystal surface and the deposition rate of the solute on the surface. The driving force of solute diffusion is the difference of the solute concentration between the crystal surface and the bulk solution. The factors concerning the diffusion rate of solute are water flow rate,

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* The saturation degree is zero in saturated solution, positive in supersaturated solution or negative in unsaturated solution when the degree is expressed by the longarithm of the activity product or the solubility product of cations and anions composing the crystal in water.

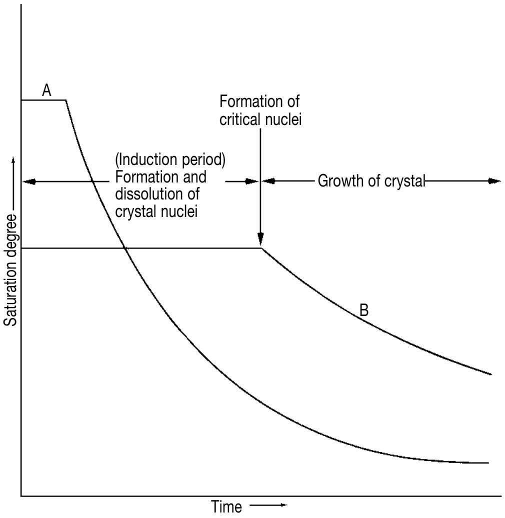


Fig. 3.37 Change in the saturation degree of a scale component through the process from the formation of crystal nuclei to the crystal growth

temperature, the viscosity of solution, etc.

Since the phenomenon of solute deposition on the crystal surface is very complicated, various mechanisms of the deposition have been proposed. Among them, Kossel proposed the following mechanism:

① Adsorption of solute on the crystal surface,
② Movement of solute adsorbed to a crystal lattice defect called "kink" by the diffusion on the crystal surface,
③ Crystallization at the kink.

Figure 3.37 illustrates the change in the saturation degree of a scale component through the process from the formation of crystal nuclei to the crystal growth. The induction period for crystal growth is shorter in the solution A which has higher saturation degree than the solution B. Once the crystal size exceeds the critical nucleus and the crystal growth begins, the saturation degree of the solution is rapidly decreased because the solute concentration is lowered.

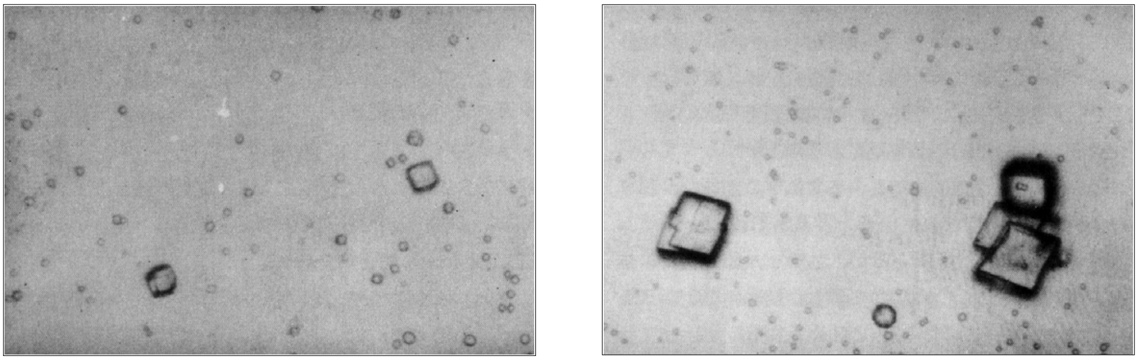
Deposited crystals tend to aggregate and form the large precipitates. This aggregation of crystals is shown in Photograph 3.10. The Photograph 3.10 a) shows the calcium carbonate crystals after two minutes from their deposition in the supersaturated solution. Some crystals become larger than the others, however, no aggregation is observed. After twelve minutes, some large crystals aggregate together as shown in Photograph 3.10 b).

(2) Functional mechanisms of scale inhibitors

In general, following three methods are applied for scale inhibition:

① Prevention of crystal nuclei formation or critical nuclei formation,
② Prevention of crystal growth,
③ Dispersion of crystals (prevention of crystal aggregation).

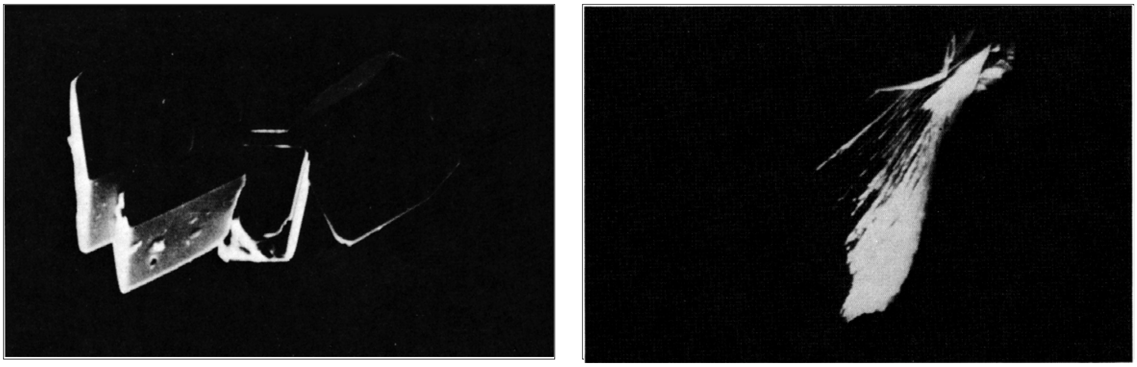
Crystal nuclei are formed only in the supersaturated solution. The formation of crystal nuclei and the resulting scaling are prevented by controlling the pH of solution with acid injection to keep the scale component in an unsaturated condition. In supersaturated solutions, scale inhibitors are used for scale prevention. The most popular scale inhibitors are polyphosphates, phosphonates and low molecular weight polyelectrolytes (polymers) which have carboxyl groups, etc.



a) After 2 minutes from crystal deposition (x 400)

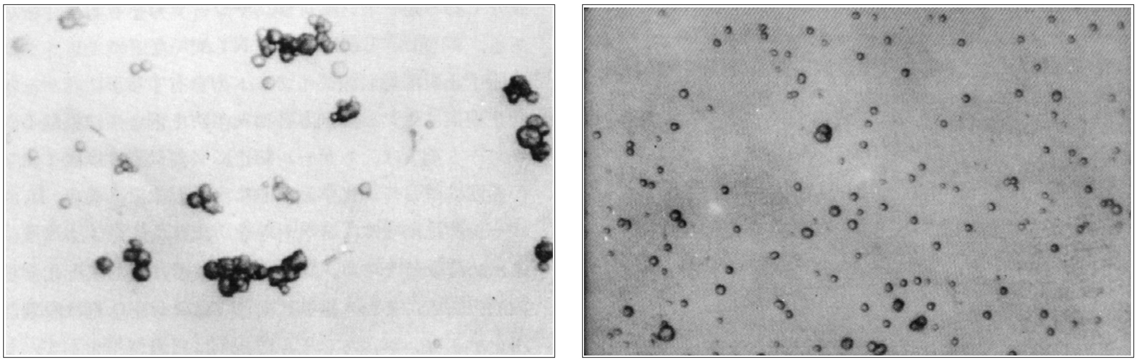
b) After 12 minutes from crystal deposition (x 400)

Photo 3.10 Growth of calcium carbonate crystals in the absence of scale inhibitor (optical microscopic photographs)



a) Normal crystal form of calcium carbonate (x 7000 electron microscopic photograph)

b) Changed crystal form of calcium carbonate by a scale inhibitor (x 7000 electron microscopic photograph)



c) Aggregation of calcium carbonate crystals in the absence of scale inhibitior (x 400 optical microscopic photograph)

d) Dispersion of calcium carbonate crystals by a scale inhibitor (x 400 optical microscopic photograph)

Photo 3.11 Crystal distortion and dispersion by sacle inhibitors

The functional groups of scale inhibitors have the ability of chelating cations which compose the scales. The required dosages of inhibitors for scale control are usually very low and non-stoichiometric against the concentration of scale components. The scale inhibitors selectively adsorb on the active growth sites of crystal nuclei or crystals and inhibit their growths. Therefore, the low and non-stoichiometric amount of inhibitors controls scale formation. Such inhibition effect of scale inhibitors with non-stoichiometric dosages is called the "threshold effect".

The typical functional mechanisms of scale inhibitors are shown in Photograph 3.11. The normal crystal of calcium carbonate is a cubic type as shown in the Photograph 3.11 a). However, the crystal form is changed (distorted) as shown in the Photograph 3.11 b) by adding a scale inhibitor. The change of crystal form is caused by the adsorption of scale inhibitors on the active growth sites on the crystal surface. Such function of scale inhibitor is called "crystal distortion effect".

Photograph 3.11 c) shows the aggregation of calcium carbonate crystals. The use of a scale inhibitor prevents the crystals from the aggregation and keeps them in a dispersion condition as shown in Photograph 3.11 d). Since scale inhibitors adsorb on the crystals by using some of functional groups, the rest of functional groups which are free from the adsorption, give the negative electrical charges to the crystals. Thus the static electrical repelling forces keep the crystals in the dispersion condition.

3.3.3 Kinds and Effects of Scale Inhibitors

(1) Kinds of scale inhibitors

Some natural organic products, such as lignins and tannins, have been known for a long time as scale inhibitors against calcium carbonate, zinc hydroxide and so on. However, these natural products usually show the insufficient and unstable scale inhibitions.

Polyphosphates have been used as scale inhibitors in cooling water systems since Rosenstein[22)] found them to be effective for inhibiting calcium carbonate deposition with their low concentrations in 1936. However, their scale inhibition effects become insufficient in cooling systems with long retention time or high water temperature because of their hydrolysis to orthophosphates.

Recently, some organic synthetic products, such as polymers, phosphonates and polyol phosphate esters, have been found effective for scale prevention of calcium carbonate, calcium phosphate, etc. They are scarcely hydrolyzed and show the stable scale inhibition effects.

The present popular scale inhibitors are as follows:

① Phosphonates;
Aminotrimethylene phosphonates, 2-phosphonobutane-1,2,4-tricarboxylates, etc.
② Polymers;
Acrylic acid homopolymers, acrylic acid based copolymers and terpolymers, maleic anhydride homopolymers, maleic anhydride based copolymers, etc.
③ Miscellaneous;
Sodium lignin sulfonate, etc.

(2) Effects of scale inhibitors

The kinds of effective inhibitors on various scale components are listed in Table 3.18. The typical effects of various inhibitors on calcium carbonate, calcium phosphate and magnesium silicate are shown in Figures 3.38 to 3.40 respectively. Figure 3.41 shows the effect of an inhibitor against calcium and zinc phosphate scaling in a heat exchanger.

As shown in those data, the kinds of effective inhibitors are different according to the composition of scale. The operational conditions of the system, such as water and skin temperatures, and water flow velocity, also give the influences on the effects of scale inhibitors.

Table 3.18 Kinds of effetive inhibitors on various scale components

Scale	Effective inhibitor
Calcium carbonate	Phosphonates Maleic anhydride homopolymers Acrylic acid homopolymers
Calcium phosphate Zinc phosphate	Acrylic acid copolymers and terpolymers Maleic anhydride copolymers
Magnesium silicate	Acrylic acid copolymers Acrylamide homopolymers Maleic anhydride copolymers
Calcium sulfate	Polyphosphates Phosphonates Acrylic acid homopolymers

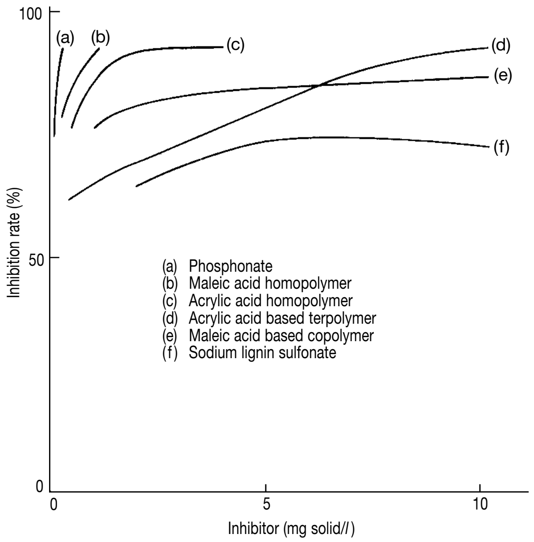


Fig. 3.38 Effects of various inhibitors for preventing calcium carbonate precipitation

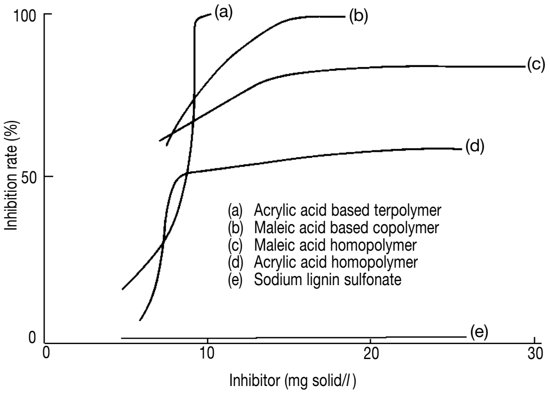


Fig. 3.39 Effects of various inhibitors for preventing calcium phosphate precipitation

3.3.4 Characteristics and Performances of Polymer Scale Inhibitors

Generally, polymers having carboxyl groups are used as scale inhibitors in cooling water systems. The carboxyl group has the ability of chelating cations[23)] which are composed of the scales, and adsorbs the surface of scale crystal. However, a

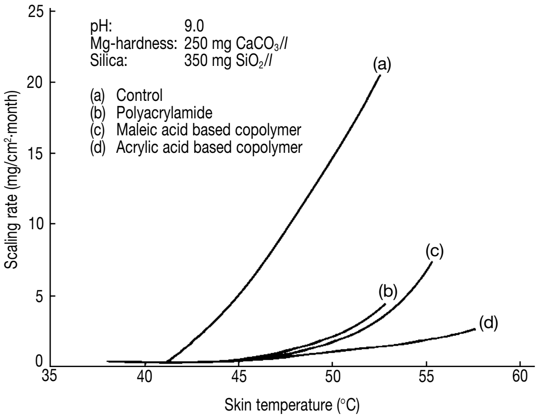


Fig. 3.40 Effects of various inhibitors against magnesium silicate scaling on a heat transfer surface

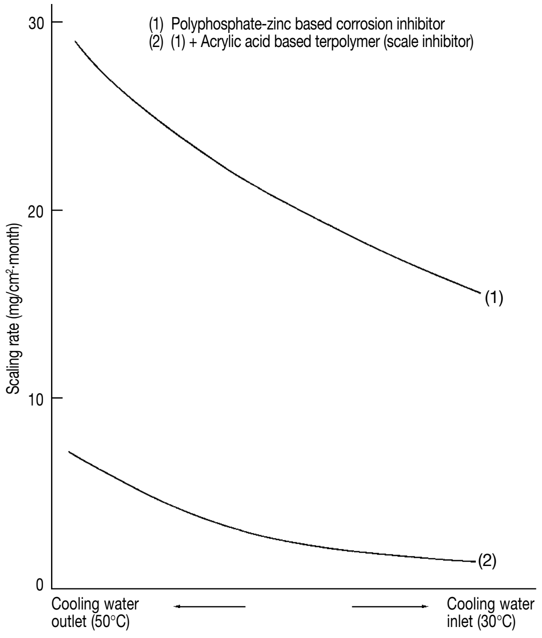


Fig. 3.41 Effect of a polymer scale inhibitor on calcium and zinc phosphate scaling in heat exchanger tubes

polymer sometimes forms the gel[23] when the excess cations combine with the polymer. The chelate bonding force of polymer increases as the molecular weight increases. On the other hand, the polymer of higher molecular weight more easily forms the gel together with cations in water. The formation of the gel reduces the effective polymer concentration in water and deteriorates the scale inhibition. Moreover, the adhesion of the gel in heat exchanger lowers the thermal efficiency.

The other hydrophilic groups, such as hydroxyl group and sulfonate group, hardly improve the chelate bonding force of polymer but they keep the polymer from the gel formation.

The control of the ratio of carboxylic group to the other hydrophilic groups in the polymer and the molecular weight is very important for producing the effective polymer scale inhibitor which has the high chelate bonding force and the low gel forming tendency.

3.3.5 Factors Influencing the Effects of Scale Inhibitors

(1) Water quality

Many factors, such as the concentrations of scale forming ions (calcium ion, phosphate ion, etc.), pH and water temperature, relate to scale formation. Various indexes concerning the relationship between these factors and scale formation have been proposed and are used to predict scale formation. Langelier's index[16] for calcium carbonate, and Green's index[18] and Kubo's equation[19] for calcium phosphate are described in detail in the Section 3.3.1.

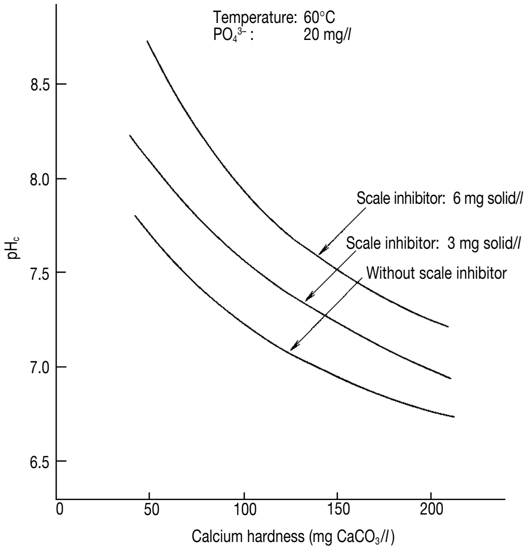


Fig. 3.42 Relationship among the critical pH of calcium phosphate deposition, calcium hardness and the dosage of a scale inhibitor (polymer)

Figure 3.42 shows a typical relationship among the critical deposition pH (pH_c) of calcium phosphate, calcium hardness and the dosage of a scale inhibitor (polymer) calculated by using Kubo's equation. The increase of calcium hardness decreases the pH_c, however, the use of scale inhibitor rises the pH_c under the specified water temperature and phosphate concentration. Therefore, scale trouble is prevented by calculating the pH_c of an aimed scale component and by keeping the pH_c higher than the actual pH (pH_a) of cooling water.

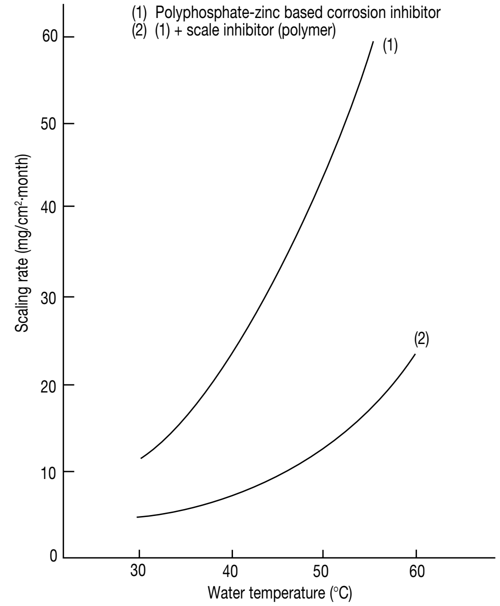


Fig. 3.43 Influence of water temperature on scaling rates

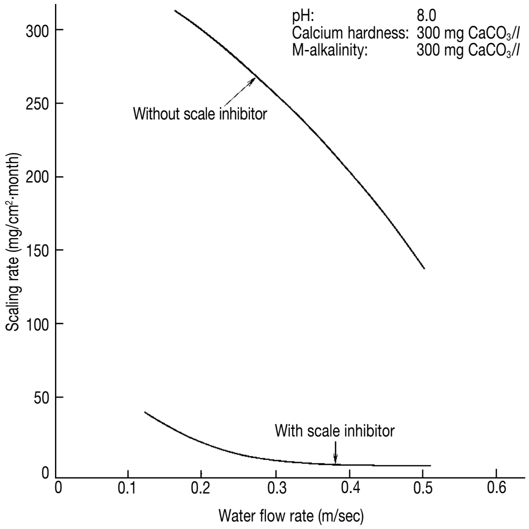


Fig. 3.44 Influence of water flow rate on the scaling rate of calcium carbonate and the effect of a scale inhibitor

(2) Water temperature

In general, the solubilities of scale components in cooling water decrease in inverse proportion to the increase of water temperature. Therefore, scaling rate begins to increase when the water temperature of heat exchanger inside exceeds 40°C and the scale problems sometimes occur at the temperature of 60°C or higher even under a scale inhibitor treatment. Figure 3.43 shows a typical relationship between scaling rates and the water temperature of heat exchanger inside.

(3) Water flow rate

Figure 3.44[12)] shows the influence of water flow rate on the scaling rate. As the flow rate increases, the scaling rate decreases. The scaling rate at a flow rate of 0.5 m/s is about half of that at a flow rate of 0.2 m/s, even without scale inhibitor. The effect of a scale inhibitor also tends to be stabilized at higher flow rate (over 0.3 m/s).

(4) Heat flux and skin temperature of heat exchanger tube

The reduction of the scaling rate by the increase of the flow rate, shown in Figure 3.44, may result from the skin temperature drop of the heat exchanger tube.

Suzuki[24)] investigated the relationship between the scale adhesion in heat exchangers and the skin temperatures calculated from the water flow rate, water temperature and heat flux. He reported that the scale troubles often occurred in heat exchangers of which skin temperature at water side exceed 90°C even though scale inhibitors were used. He also reported that the critical heat flux and the skin temperature for scale trouble occurrence were 2×10^4 to 3×10^4 kcal/m²·h and around 60°C in cooling water system treated with polyphosphate based corrosion inhibitor without scale inhibitor.

Figures 3.45 and 3.46 show the relationships among the water flow rate, water temperature and the skin temperature of heat exchanger tube. In the case of heat exchanger with the outlet water temperature of 50°C and the heat flux of 50,000 kcal/m²·h, the skin temperature at the water outlet lowers from 81°C to 69°C by increasing the water flow rate from 0.2 m/s to 0.5 m/s as shown in Figure 3.45. This skin temperature drop of 12°C is considered as one factor for the reduction of scaling rate shown in Figure 3.44.

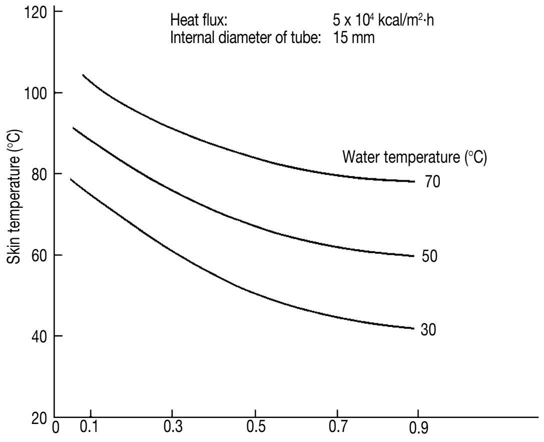


Fig. 3.45 Relationship between the water flow rate and skin temperature of heat exchanger tube

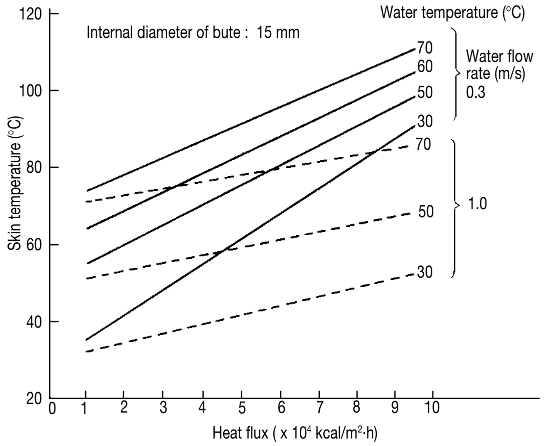


Fig. 3.46 Relationship between the heat flux and skin temperature of heat exchanger tube

(5) Retention time

Scale inhibitors reduce the scaling rate by decreasing the growth rate of scale crystals and dispersing the microcrystals of scale. Therefore, each scale inhibitor has a critical retention time of circulating cooling water for maintaining its sufficient scale inhibition. This critical retention time is varied depending on water quality, water temperature and so on, however, it is usually 150 to 300 hours under the normal operational conditions of open recirculating cooling water systems.

3.3.6 The Other Scale Control Methods

(1) pH control

The control of cooling water pH by acid injection has long been applied for preventing the scaling of calcium carbonate, calcium phosphate and so on. The solubilities of those scale components are generally increased as the pH is lowered. Therefore, the scaling rate is reduced by lowering the water pH. However, the disadvantages of the pH control method are as follows:

① Corrosion acceleration by an excess pH reduction of below 6.5,
② Narrow optimum pH control range of 7.0 to 7.5 for scale and corrosion control,
③ Danger in handling of sulfuric acid, hydrochloric acid and so on,
④ High installation cost for automatic pH control systems.

In the present, the pH control becomes not popular scale control method in the countries obtaining low hardness fresh water, like Japan, Korea, etc., because of its disadvantages. However, the combined use of scale inhibitor together with pH control is still effective and economic scale inhibition method in the case of high hardness cooling water. The use of scale inhibitor eliminates the excess pH reduction and minimizes the acid consumption because it rises the lower pH control range for scale inhibition and expands the pH control range.

(2) Control of the operational conditions of heat exchanger

The scaling rate is influenced by water flow rate, water temperature, etc. ,of heat exchanger as shown in the Figures 3.43 and 3.44. The reduction of the outlet water temperature by increasing the water flow rate of heat exchanger reduces the scaling rate by decreasing the scaling potential of water and improving the effect of scale inhibitors.

However, the change of the operational condition is limited to the range of which gives no serious influence on the process side operational condition of heat exchanger.

(3) Softening and demineralization of make-up water

It is difficult to prevent scaling when very high hardness water, such as 250 mg $CaCO_3/l$ or more, is supplied and the cooling water system is operated at high cycles of concentration, such as 5 or higher. In that case, the raw water is often treated to reduce or remove the hardness by using ion exchange resins, reverse osmosis membranes or cold lime method.

The cold lime treatment is often applied for make-up water treatment in large size open recirculating cooling water system. Lime [$Ca(OH)_2$] and soda ash (Na_2CO_3) are used for this treatment. $Ca(OH)_2$ and Na_2CO_3 react with hardness in water and form the precipitations of calcium carbonate ($CaCO_3$) and magnesium hydroxide [$Mg(OH)_2$] as shown in following equations:

$$Ca(HCO_3)_2 + Ca(OH)_2 \rightarrow 2CaCO_3\downarrow + 2H_2O \quad \text{.............................. (3.44)}$$

$$CaSO_4 + Na_2CO_3 \rightarrow CaCO_3\downarrow + Na_2SO_4 \quad \text{.............................. (3.45)}$$

$$CaCl_2 + Na_2CO_3 \rightarrow CaCO_3\downarrow + 2NaCl \quad \text{..... (3.46)}$$

$$Mg(HCO_3)_2 + 2Ca(OH)_2 \rightarrow Mg(OH)_2\downarrow + 2CaCO_3\downarrow + 2H_2O \quad \text{.............................. (3.47)}$$

$$MgSO_4 + Na_2CO_3 + Ca(OH)_2 \rightarrow Mg(OH)_2\downarrow + CaCO_3\downarrow + Na_2SO_4 \quad \text{.............................. (3.48)}$$

$$MgCl_2 + Na_2CO_3 + Ca(OH)_2 \rightarrow Mg(OH)_2\downarrow + CaCO_3\downarrow + 2NaCl \quad \text{.............................. (3.49)}$$

After the sedimentation treatment, the treated water still includes the hardness of 50 to 80 mg $CaCO_3/l$ and the pH rises to approximately 10. So the treated water is supplied after neutralizing with acid. This residual hardness level of treated water causes no scale and corrosion problem under the present phosphate-polymer treatments.

Demineralization or softening by using ion exchange resins or reverse osmosis membranes perfectly removes hardness in water and causes no scaling problems. However, the treatment costs of those methods are considerably higher than that of cold lime method. Moreover, no hardness water gives high corrosion rate of carbon steel under phosphate based treatments.

Therefore, demineralized or softened water is usually supplied into closed recirculating cooling water system which the blowdown water volume is small and phosphate based inhibitors are rarely used.

3.4 Biofouling and Its Prevention

3.4.1 Biofouling Problems

Biofouling problems are caused by the adhesion and accumulation of soft and muddy fouling (slime and sludge) composed of microorganisms, such as bacteria, algae and fungi, and inorganic matters like mud, sand, dirt, etc.

The biofouling of heat exchangers not only drops the thermal efficiency but also causes the local corrosion under it. The biofouling problems are classified into slime adhesion type and sludge accumulation type. The definitions of slime and sludge are shown in Table 3.19. Table 3.20 shows the places soiled with biofouling and the types of fouling.

Table 3.19 Definitions of biofouling

Type of fouling	Definition
Slime	Fouling including higher amount of microorganisms than inorganic matters: Slim adheres on heat exchanger tube surface, etc., with the adhesive force of the sticky organic substances produced by microorganisms even under water flow condition.
Sludge	Fouling including higher amount of inorganic matters than microorganisms: Sludge is usually accumulated at the places of low water flow rate or water stagnancy.

Table 3.20 Places soiled with biofouling and the types of fouling

Place		Type of fouling
Heat exchanger	Tube	Slime adhesion type
	Partition plate, outer surface of tube, baffle plate, etc. (in case of shell side water flow)	Slime adhesion type and sludge accumulation type
Cooling tower	Distribution deck	Slime adhesion type and sludge accumulation type
	Tower packing	Slime adhesion type
Cooling tower basin	Bottom	Sludge accumulation type
	Wall	Slime adhesion type

The troubles caused by the slime adhesion and sludge accumulation are shown in Table 3.7 (p.3-9). Among those troubles, the remarkable thermal efficiency drop of heat exchanger characterizes the biofouling problem. Since slime is mainly composed of microorganism bodies including organic matters, such as proteins and polysaccharides, its water content is 90% or higher and the volume per the dry weight becomes extremely larger than that of inorganic fouling such as scale and corrosion products. For an example, Figure 3.47[25] shows the relationship between the amount of slime as dry solid and the fouling factor of a heat exchanger as compared with calcium phosphate scaling.

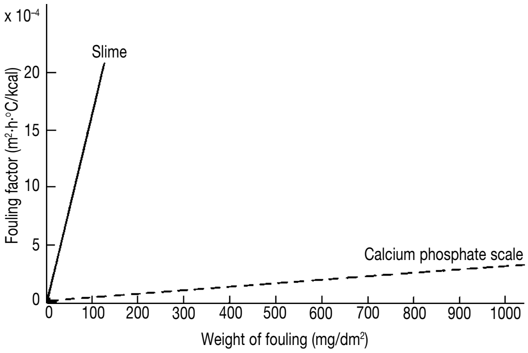


Fig. 3.47 Relationship between slime or scale adhesion, and the fouling factor of heat exchanger

3.4.2 Types of Microorganisms and Chemical Composition of Biofouling

(1) Types and characteristics of microorganisms

Table 3.21[26)] shows the types and characteristics of microorganisms producing biofouling.

In open recirculating cooling water systems, bacteria cause the most troubles, followed by algae and fungi. Among bacteria, zoogloea sp., are most often found in biofouling. The growth of sphaerotilus sp., is observed in cooling water contaminated with organic matters. Generally, aerobic bacteria dominate in open recirculating cooling water systems, however, anaerobic bacteria like sulfate reducing bacteria may grow up under the aerobic slime and cause microbiologically influenced corrosion (MIC). Nitrification bacteria sometimes grow up in cooling water contaminated with ammonia and accelerate the corrosion by reducing cooling water pH because of nitric acid formation.

Algae grow in sunny places such as distribution decks, louvers and basins of cooling towers. They never propagate in dark places like heat exchanger inside. However, their dead bodies become nutrients and will accelerate bacteria growth.

Fungi scarcely cause biofouling in cooling water systems because they require very high concentration of organic matters for their growth.

(2) Chemical composition of biofouling

Table 3.22 shows the typical examples of chemical analyses of adhered slime and accumulated sludge. Generally, the ignition loss of adhesion type slime is high, over 25%, and large quantities of organic matter (mainly microorganisms) are contained in the slime.

While the ignition loss of accumulation type sludge is less than 25% and the content of microorganisms is low. The inorganic constituents like

Table 3.21 Types and characteristics of microorganisms producing biofouling

Type of microorganisms		Characteristics
Algae	Blue-green algae	They have chlorophyll within their cells and carry out photo-synthesis by means of sun light energy. They grow in sunny places, such as cooling tower, hot water pit and cold water pit.
	Green algae	
	Diatom	
Bacteria	Zoogloea sp.	Their shape looks like a lump of agar in which bacteria are scattered. They are usually observed in cooling water systems.
	Sphaerotilus sp.	They make cottony colonies in the system contaminated with organic compounds.
	Iron bacteria	They oxidize ferrous compounds in water to precipitate ferric compounds around their own cells.
	Sulfur bacteria	They are frequently observed in filthy water and ordinarily contain sulfur grains within their bodies. They oxidize hydrogen sulfide, thiosulfate, sulfur, etc. , in water.
	Nitrification bacteria	There are two types of bacteria: one oxidizes ammonia to nitrous acid and the other oxidizes nitrous acid to nitric acid. They grow in circulating water contaminated with ammonia.
	Sulfate reducing bacteria	They are anaerobic bacteria and reduce sulfate to hydrogen sulfide.
Fungi	Phycomycetes	Spawn has no dissepiment and a whole spawn consists of one cell.
	Mycomycetes	Spawn has dissepiments.

Table 3.22 Chemical analyses of slime and sludge

Composition \ Sample	Slime in heat exchanger tube (A)	Slime in heat exchanger tube (B)	Sludge on partition plate (C)	Sludge in cooling tower basin (D)
Calcium oxide (CaO)	4.7	6.0	4.9	0.8
Magnesium oxide (MgO)	1.6	0.9	1.5	1.2
Ferric oxide (Fe_2O_3)	6.5	5.7	8.6	11.3
Aluminum oxide (Al_2O_3)	13.7	trace	7.6	10.7
Phosphoric anhydride (P_2O_5)	0.7	4.4	0.4	2.6
Acid insoluble matter	37.0	16.6	50.8	45.1
Ignition loss (600 ± 25°C)	25.4	58.9	19.6	25.0

(weight %)

Table 3.23 Energy sources and nutrients of microorganisms growing in cooling water systems

Kind of microorganisms	Energy source	Nutrient
General aerobic and anaerobic bacteria, fungi	Oxidation of organic substances	Organic substances with small amount of minerals
Iron bacteria, sulfur bacteria, nitrification bacteria	Oxidation of inorganic substances	Inorganic substances*
Algae	Solar energy	Inorganic substances (mainly carbonate)

* Some kinds of them sometimes utilize organic substances depending on the circumstances on their growth.

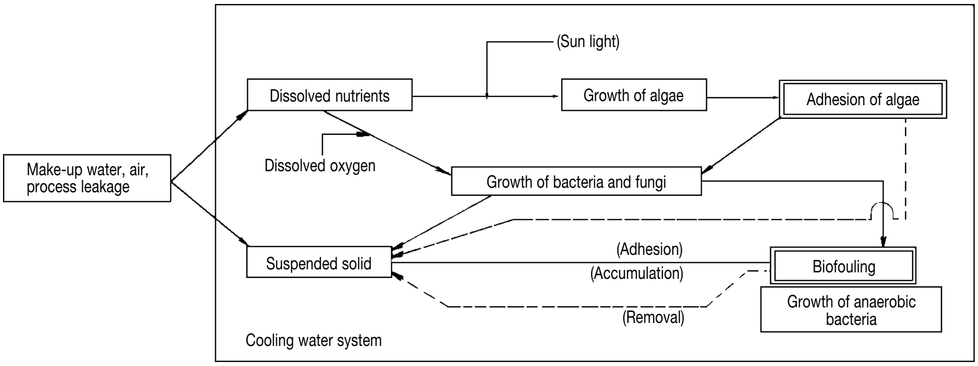


Fig. 3.48 Schematic process of biofouling formation in open recirculating cooling water systems

mud, sand, etc., increase in comparison with the slime.

As the ignition loss includes some amount of organic matter other than those of microorganisms, the quantity of protein contained in the microorganisms is measured in order to improve the accuracy of slime analysis.

3.4.3 Factors Influencing Biofouling Formation

(1) Nutrients

Microorganisms take energy sources and nutrients for their growth in different ways according to their types. Table 3.23 shows the energy sources and nutrients required for their growth. Figure 3.48 indicates a schematic process of biofouling formation. There are three ways of which nutrients come into cooling water systems, i.e., make-up water, air and the leakage of process fluids from heat exchangers.

General bacteria, zoogloea sp., etc., grow by taking and oxidizing organic substances. Therefore, the higher concentration of organic substances in cooling water causes the severer biofouling troubles by accelerating the bacteria growth. Figure 3.49 shows the relationship between the concentration of organic substances in cooling water and the frequency of biofouling troubles in heat exchangers. The Chemical Oxygen Demand by permanganate (COD_{Mn}) is used as an unit showing the concentration of organic substances. The increase of COD_{Mn} in cooling water

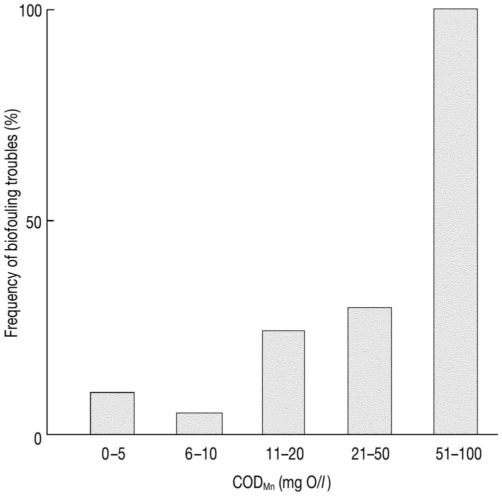


Fig. 3.49 Relationship between the COD_{Mn} of cooling water and the frequency of biofouling troubles in heat exchangers under intermittent chlorination

deteriorates the biocidal effect of chlorination and increases the frequency of biofoiling troubles. Therefore, the careful selection of biofouling control program should be required for the cooling water including the high concentration of organic substances.

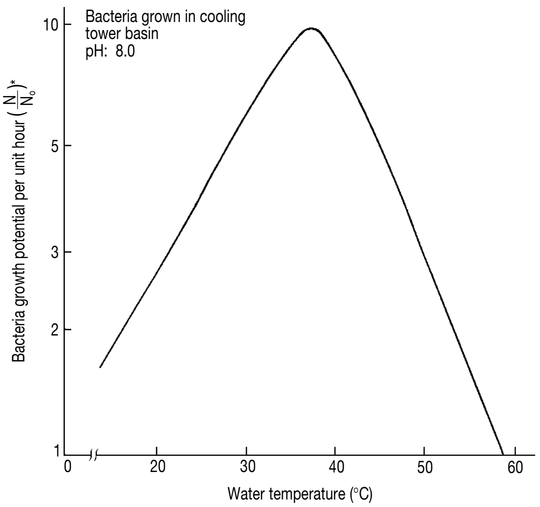
Nitrification bacteria grow in water contaminated with ammonia because they utilize the energy yielded when ammonia is oxidized to nitrous acid and nitric acid by themselves. Iron bacteria oxidize ferrous ion to ferric ion and obtain the energy.

Algae only grow under the sun light because they carry out photosynthesis and produce organic substances from carbon dioxide (CO_2) and water. Algae never grow in heat exchangers without sun light. However, the dead bodies of algae become the nutrients for the other microorganisms.

(2) Water temperature

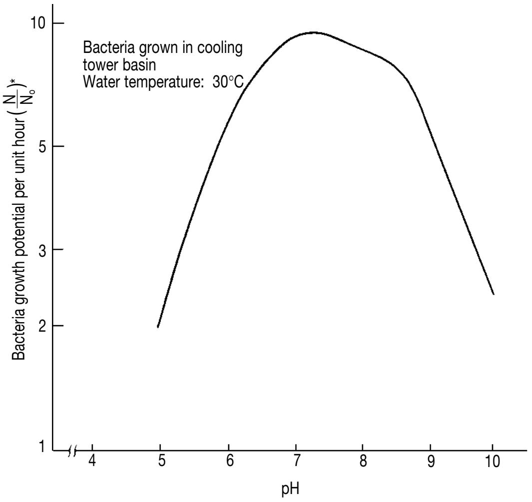
The influence of water temperature on the growth rate of microorganisms depends on the kinds of them. Each microorganisms has own optimum growth temperature. Figure 3.50 shows an example of relationship between the water temperature and the growth rate of bacteria growing in a cooling water system. In this case, the optimum growth temperature is approximately 30 to 45°C.

Therefore, biofouling troubles more frequently occur in summer because of the higher water temperature, in comparison with that in winter.



$\frac{*N}{N_o} = e^{\mu t}$
N: the number of bacteria after 1 hour
N_o: the initial number of bacteria
t: time (h)
μ: specific growth rate of bacteria

Fig. 3.50 Influence of water temperature on the growth rate of bacteria



$\frac{*N}{N_o} = e^{\mu t}$
N: the number of bacteria after 1 hour
N_o: the initial number of bacteria
t: time (h)
μ: specific growth rate of bacteria

Fig. 3.51 Influence of pH on the growth rate of bacteria

(3) pH

Generally, bacteria grow well in a pH range of neutral to weak alkaline and fungi in weakly acidic.

Figure 3.51 shows a typical relationship between the pH and growth rate of bacteria existing in a cooling water system. The optimum pH for their growth is in a range of 6 to 9. The pH of cooling water is normally controlled in the range of 6.5 to

9.0 in order to prevent corrosion and scaling. This pH range is the optimum for the microorganism growth.

(4) Dissolved oxygen

Aerobic bacteria and fungi obtain the energy required for their growth by oxidizing organic substances using dissolved oxygen. Open recirculating cooling systems provide the optimum conditions for them because the dissolved oxygen is sufficiently supplied from the cooling towers.

(5) Sun light

Most microorganisms require no sun light for their growth. Only algae carry out the photosynthesis by utilizing sun light. Therefore, algae grow at the sunny places such as cooling towers and water basins.

(6) Number of bacteria

As the biofouling is essentially caused by bacterial growth in cooling water system, the higher number of bacteria in cooling water anticipates the severer fouling in heat exchangers.

Figure 3.52 shows the relationship between the number of bacteria in cooling water and the frequency of the fouling troubles in heat exchangers. The frequency of the fouling troubles is low when the number of bacteria is less than 10^3 per m*l*, and the frequency increases when the number exceeds 10^4 per m*l*.

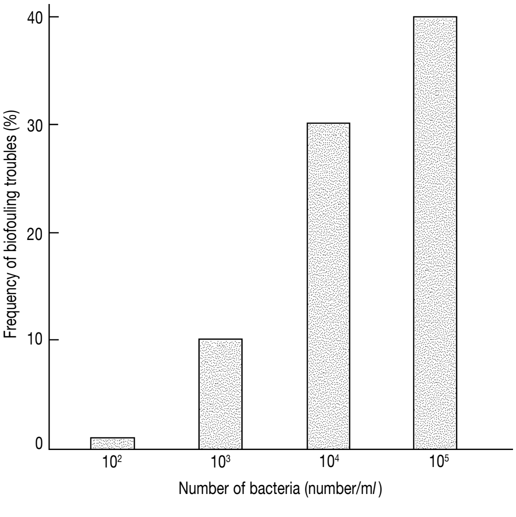


Fig. 3.52 Relationship between the number of bacteria in cooling water and the frequency of biofouling troubles in heat exchangers under intermittent chlorination

(7) Turbidity

The increase of cooling water turbidity increases the accumulation of sludge at the part of low water flow rate. Higher growth rate of microorganisms rises the turbidity by the formation of biological flocs. Therefore, the lower turbidity is better for preventing slime adhesion and sludge accumulation.

It is better to keep the turbidity of cooling water below 20 degrees for biofouling control.

(8) Slime volume

Slime volume (SV) is a volume (m*l*) of collected matter by filtering 1 m^3 of cooling water through a plankton net. In a cooling water system where the SV is more than 10 m*l*/m^3, the occurrence of slime problems increases. Generally, higher SV is observed in the system of which cooling water is contaminated with organic matters.

(9) Slime adhesion degree

The slime adhesion degree is an effective index for slime adhesion in cooling water. A glass slide is immersed into the cooling water for a certain period and the slime adhered on the surface of slide is dried. Then, in order to identify the fouling derived from microorganisms among the adhered matter, the microorganisms are dyed red and the absorbance of the glass slide is measured. The slime adhesion degree is a function of the absorbance.

Photograph 3.12 (p.3-74) shows the example of slides after dyeing the adhered slime. There is a fairly good correlation between the degree of slime problems and the slime adhesion degree.

The occurrence of biofouling troubles is rare in the cooling system where the slime adhesion degree is controlled below 10.

(10) Water flow rate

Figure 3.53 shows the relationship between water flow rate and slime adhesion rate in a carbon steel tube. The slime adhesion rate tends to be lowered inversely to the increase of water flow rate. Such tendency is explained that the increase of water shearing force by increasing the flow rate may disturb the slime adhesion.

Sludge readily accumulates in areas where the water flow rate is low, such as in vertical type heat exchangers and shell side water flow heat exchangers. Sludge also accumulates on the partition plates of the heat exchanger with the low flow rate. Figure 3.54 shows the influence of water flow rate against the sludge accumulation on a partition plate.

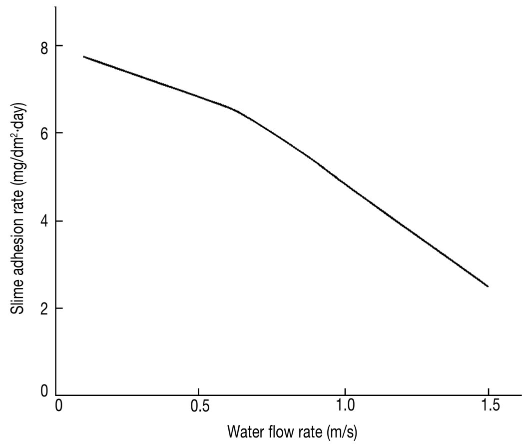


Fig. 3.53 Influence of water flow rate on slime adhesion rate in a carbon steel tube

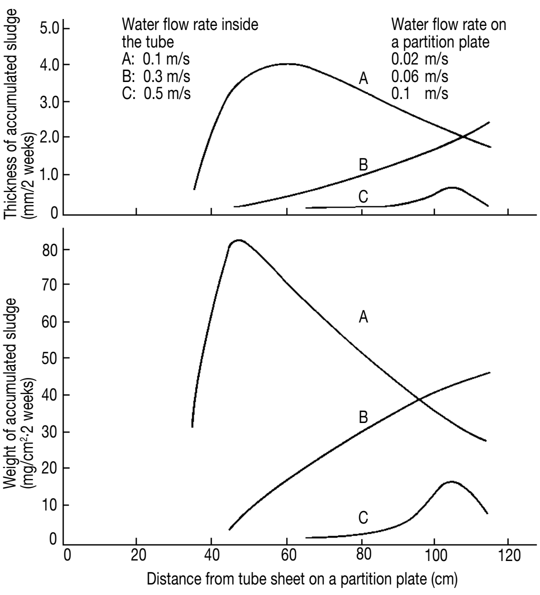
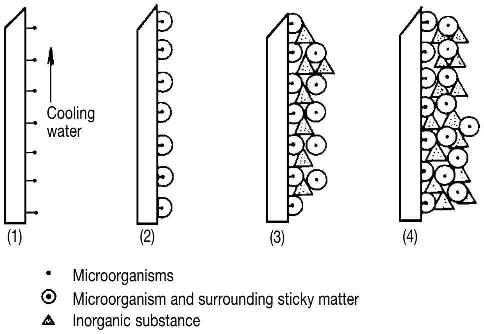


Fig. 3.54 Influence of water flow rate against sludge accumulation on a partition plate

Sludge scarcely accumulates when the water flow rate of tube inside is more than 0.5 m/s or when the horizontal flow rate on the partition plate is more than 0.1 m/s. However, when the flow rate of tube inside is less than 0.3 m/s or the flow rate on the partition plate becomes less than 0.06 m/s, the sludge accumulation increases.



(1) Microorganisms adhere to the surface of solids.
(2) Microorganisms produce sticky matter around their bodies.
(3) Inorganic suspended solids adhere due to the binding action of the sticky matter of microorganism.
(4) Slime adhesion proceeds further.

Fig. 3.55 Schematic process of slime adhesion

3.4.4 Mechanism of Biofouling

(1) Mechanism of slime adhesion

Microorganisms in water tend to adhere and grow on solid surface because it is a convenient location for utilizing nutrients necessary for their growth.

Figure 3.55 illustrates a schematic process of slime adhesion in a heat exchanger. Such adhesion also progresses on the surfaces of suspended solids and microorganism flocs in water. The adhesion of these flocs to metallic surface accelerates the slime adhesion further.

(2) Mechanism of sludge accumulation

Suspended solids (SS) in cooling water aggregate and form flocs with microorganisms having the sticky organic matters produced by their metabolism reactions. Such floc formation related to microorganisms is called bioflocculation.

Then the flocs with high sedimentation rate precipitate and form sludge at a place where the water flow rate is low. The sedimentation rate of floc is calculated by the equation of Stokes, Allen or Newton. The floc of higher specific gravity and larger diameter is more liable to be sedimented. The flocs are easily sedimented at areas of lower water flow rate. As the lowest water flow rate area in cooling water system is generally the cooling tower basin, most flocs may accumulate within the basin. However, a part of flocs are circulated with the cooling water and accumulate in the low flow rate areas and the dead spaces* in heat exchangers.

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* Area where water flow stagnates locally

3.4.5 Biofouling Control Methods and Their Functional Mechanisms

(1) Prevention of cooling water contamination with nutrients and SS

Pretreatments of make-up water, such as filtration, coagulation and sedimentation, are applied to reduce the nutrient and SS concentrations in cooling water.

The application of seal-welding of tube sheet with tubes or corrosion resistant coating of tube sheet is effective to prevent the small amount of process fluid leakage from heat exchangers.

(2) Application of biofouling control agents

(a) Sterilization

Sterilization is a treatment to lower the adhesion potential of the microorganisms in the cooling water system by killing the microorganisms. Chemicals which have the sterilization effects are chlorine compounds, bromine compounds, organic nitrogen-sulfur compounds, etc. The functional mechanisms of these chemicals are considered as follows: they have the higher reactivity with the SH radical of cysteine, which is a component of the protein in microorganisms, to kill the microorganisms by inactivating the enzyme whose active part is the -SH radical, and they kill microorganisms by destroying the cell walls of the microorganisms with their oxidizing force.

Generally, chlorination is carried out for the sterilization. However, since the chlorine is corrosive to metals, the concentration of residual chlorine in the cooling water should be controlled 1 mg Cl_2/l or less. Also, the oxidizing forces of chlorine compounds are too strong, so that they sometimes react with organic contaminants in cooling water before killing microorganisms. Accordingly, non-oxidizing biofouling control agents are generally used together with chlorination in cooling water systems having the high fouling potential.

(b) Reduction of microorganism growth rate

Some kinds of biocides reduce the biofouling rate by decreasing the growth rate of microorganisms. Organic nitrogen-sulfur compounds and some amines are used for this biostatic treatment. These chemicals inhibit the growth of microorganisms by dosing the lower concentrations than their biocidal dosages.

(c) Prevention of slime adhesion

The sticky organic matters produced by microorganisms relate to the adhesion of microorganisms on tube surfaces, etc. Some chemicals react with the sticky matters and denaturate them. Thus, the adhesion force of microorganisms is lowered.

Quaternary ammonium salts, organic bromine compounds and so on show this kind of slime control effect.

(d) Removal of adhered slime

The high concentrations of chlorine compounds, bromine compounds, peroxides and so on show the slime removal effects. These chemicals lower the adhesion force of slime by denaturating the sticky matters and remove the slime mechanically by the fine bubbles which are generated by the reaction of the chemicals and slime. Accordingly, the increase of water flow rate promotes the slime removal effect of chemicals.

(e) SS dispersion

The SS in cooling water flocculate together with microorganisms and accumulate as sludge at the place of low water flow rate. The combined use of polymer dispersants and biocides prevents the bioflocculation of SS and disperses SS. The dispersed SS are discharged from the system together with the blowdown water. As the result, the amount of sludge accumulation is decreased.

(3) Side stream filtration

The filtration of a part of circulating cooling water lowers the SS (including bioflocs) concentration in the cooling water and reduces sludge accumulation and slime adhesion troubles. The detail of side stream filtration is described in the Section 3.4.8(1).

3.4.6 Factors Influencing the Effects of Biofouling Control Agents

(1) pH

Each biofouling control agent has the optimum pH range providing the sufficient effect. Since the cooling water pH is generally controlled within the range of 6.5 to 9.0 in open recirculating cooling water systems, the chemicals effective in that pH range are applied. However, the effect of chlorine compounds is most subjected to the change of pH even in the range of 6.5 to 9.0. The influence of pH on the effect of chlorine compounds is described in the Section 3.4.7.

(2) Concentration of nutrients

The high concentration of nutrients promotes the growth of microorganisms and increases the biofouling potential of cooling water. Thus the effects of biofouling control agents are deteriorated in the water of high nutrient concentration comparing with the water of low nutrient level. The effects of oxidizing type biocides like chlorine compounds are reduced in water including the high concentration of organic matters because the biocides are consumed by reacting with organic matters.

(3) Compounds reacting with biocides

Compounds reacting with biocides are sometimes present in cooling water and deteriorate the effects of biocides by consuming them or by forming the compounds of low biocidal effects.

The typical such compounds found in cooling water systems are as follows:

① Organic compounds consuming oxidizing type biocides by the oxidation and reduction reactions,

② Ammonia reducing chlorination effect by forming chloramines with the lower biocidal effects,

③ Anionic polymer dispersants consuming cationic biocides, such as quaternary ammonium salts, by forming the precipitates through electrical neutralization reaction between the cations and anions.

(4) Water temperature

The reaction between biocides and microorganisms is a kind of chemical reaction. Therefore, the effects of biocides are usually increased as a water temperature increases.

(5) Water flow rate

The increase of water flow rate increases the diffusion rate of biocides to the surface of biofouling and strengthens the biocidal effect. Especially, in the case of slime removal treatment, the removal effect is greatly improved by the increase of shearing force accompanied with the increase of water flow rate.

(6) Resistance and succession

The deterioration in the effect of a biocide is often observed when the biocide has been almost continuously applied for a long time. This means that the microorganisms have obtained a resistance against the biocide or only strong ones against the biocide survive and grow. The former and latter phenomena of microorganisms are called the resistance and the succession respectively.

In open recirculating cooling water systems, the biofouling control agents are usually used intermittently, so microorganisms have difficulties in developing the resistance or succession. Nevertheless, the microorganisms are liable to have the resistance for some biocides like methylene bisthiocyanate, etc., when they have been used for a long time.

3.4.7 Kinds and Effects of Biofouling Control Agents

(1) Chlorine compounds

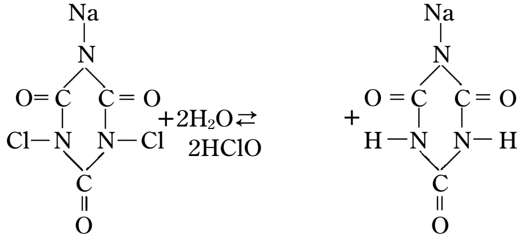
Chlorine compounds used for sterilization are liquid chlorine, calcium hypochlorite, sodium hypochlorite, chlorinated sodium isocyanuric acid, etc.

These chlorine compounds produce hypochlorous acid (HClO) and hypochlorite ion (ClO^-) in water as shown in the following reactions:

$$Cl_2 + H_2O \rightleftarrows HClO + HCl \quad \text{......} \quad (3.50)$$

$$Ca(ClO)_2 + H_2O \rightleftarrows 2HClO + Ca(OH)_2 \quad \text{......} \quad (3.51)$$

$$NaClO + H_2O \rightleftarrows HClO + NaOH \quad \text{......} \quad (3.52)$$



.... (3.53)

$$HClO \rightleftarrows H^+ + ClO^- \quad \text{......} \quad (3.54)$$

The sterilization force of ClO^- for bacteria is reported to be approximately 1/2[27] as much as that of HClO. Therefore, the HClO has the higher effect than the ClO^-. The presence ratio of HClO and ClO^- in water of various pH values is shown in Figure 3.56.

At higher pH range, as the ratio of ClO^- increases, the sterilization effect of the chlorine compounds decreases. Accordingly, countermeasures, such as an increase of chlorination frequency, are required for the system where the cooling water pH is high.

Figure 3.57 shows the relationship between the sterilization effect of chlorination and the pH of water. The chlorination time for obtaining the perfect sterilization is around 30 minutes in the water of pH 7.0, however, the increase of the pH up to 8.5 extends the time to 80 minutes or more. The application of continuous chlorination shows the sufficient biocidal effect even in the water of pH 9.

In open recirculating cooling water systems, the consumption of chlorine is considerably large and the chlorine concentration in cooling water is usually fluctuated because the chlorine is released from the water to the air in cooling towers. The use of a special chlorine keeping agent is effective to stabilize the chlorine in water and to reduce the consumption.

Figure 3.58 shows the effectiveness of the chlorine keeping agent. The use of the chemical improves the biocidal effect of chlorination and reduces the chlorine consumption because it prevents the chlorine from the release to the air and keeps the sufficient concentration of chlorine during longer time comparing with the dosing of chlorine only.

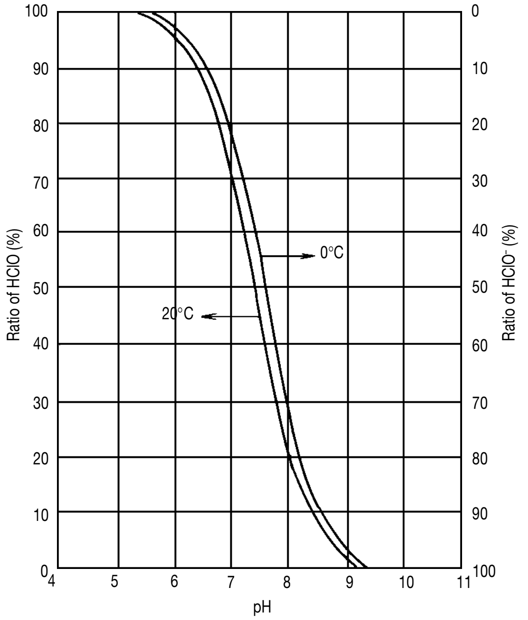


Fig. 3.56 Relationship between the presence ratio of HClO to ClO$^-$ and pH

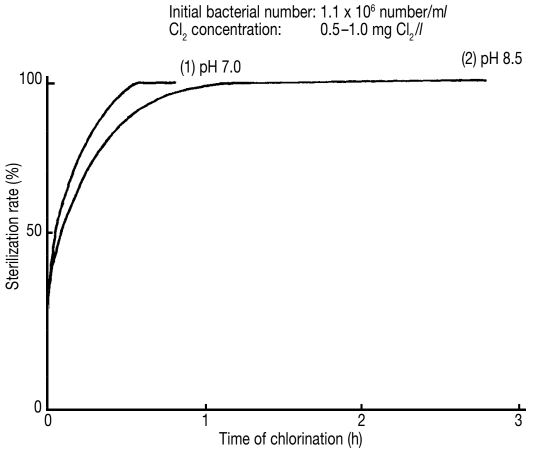


Fig. 3.57 Relationship between the sterilization effect of chlorination and pH

Since chlorine is corrosive to metals, especially copper and copper alloys, the residual chlorine concentration in cooling water should be controlled below 1 mg Cl_2/l and the period of chlorination should be shortened as much as possible. Therefore, such chlorination sometimes prevents the microorganisms growth insufficiently. In that case, the most effective control method is to use non-oxidizing biofouling control agents periodically in addition to chlorination.

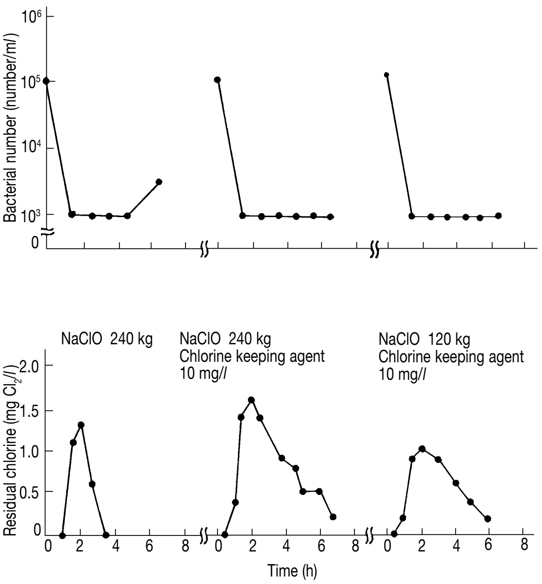


Fig. 3.58 Chlorine stabilizing effect of a chlorine keeping agent in a cooling tower system

The chlorine keeping agent mentioned above reduces the corrosivity of chlorine against copper and copper alloys as shown in Figure 3.59.

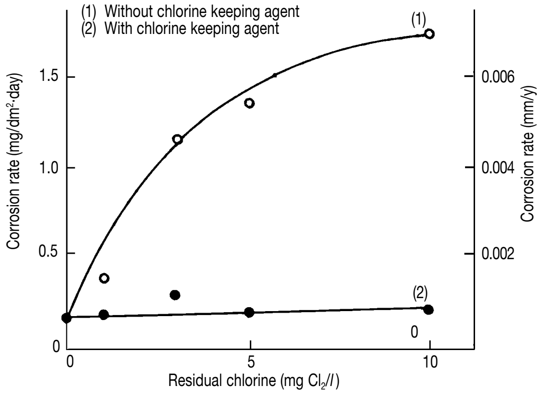
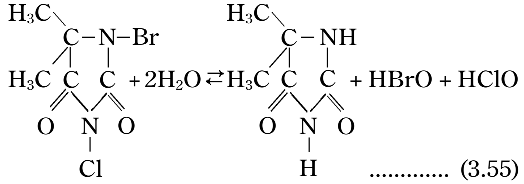


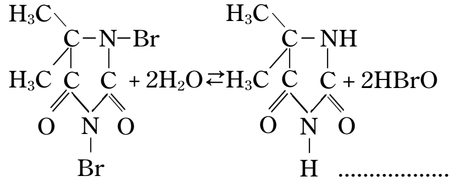
Fig. 3.59 Inhibition effect of a chlorine keeping agent against copper corrosion caused by chlorine

(2) Oxidizing bromine compounds

1-Bromo-3-chloro-dimethyl-hydantoin and 1,3-dibromo-dimethyl-hydantoin are used as the biocides for cooling water systems. These compounds release hypobromous acid (HBrO) in water as shown in the following reactions:



.... (3.55)



.... (3.56)

Sodium bromide releases hypobromous acid when it is used together with liquid chlorine, etc., as shown in the equation (3.57).

$$NaBr + HClO \rightleftarrows HBrO + NaCl \quad (3.57)$$

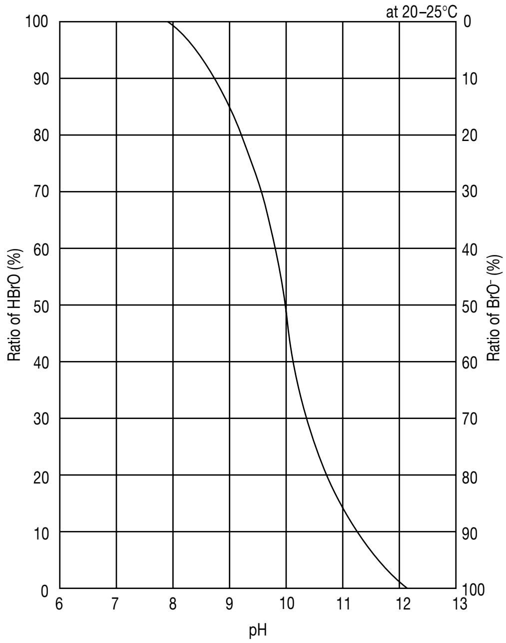


Fig. 3.60 Relationsship between the presence ratio of HBrO to BrO⁻ and pH

Hypobromous acid dessociates as shown in the equation (3.58).

$$HBrO \rightleftarrows H^+ + BrO^- \quad (3.58)$$

As same as hypochlorous acid, hypobromous acid shows the strong biocidal effect comparing with hypobromite ion (BrO^-). However, the dissociation of hypobromous acid proceeds at more alkaline side than hypochlorous acid as shown in Figure 3.60. Therefore, the bromination shows the better biocidal effect than chlorination in the case of high pH water and the short contact time as shown in Figure 3.61.

(3) Organic (nonoxidizing) bromine compounds

Organic bromine compounds, such as 2,2-dibromo-3-nitrilo-propionamide and 2-bromo-2-nitropropane-1,3-diol, are used for biofouling control in cooling water systems. These compounds show the biocidal or biostatic effects and reduce the slime adhesion rate by the continuous or intermittent dosing. Table 3.24 shows the reduction of slime adhesion rate by using an organic bromine compound in a cooling water system.

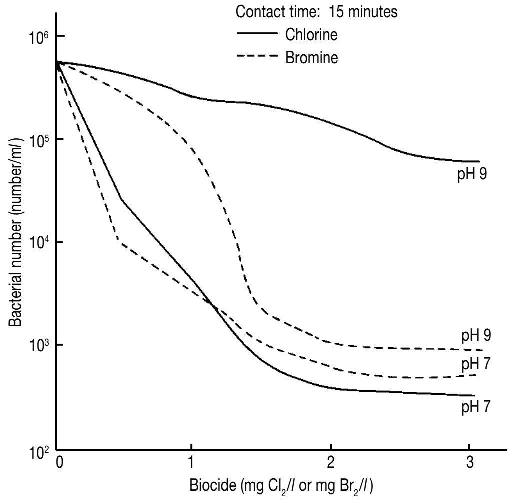


Fig. 3.61 Influence of pH on the biocidal effects of chlorination and bromination

Table 3.24 Effect of an organic bromine compound on slime adhesion (field test)

Dosage (mg/*l*)	Slime adhesion rate (mg/dm^2·day)
0	7.3, 9.0
1.5	11.0
4.5	1.3

Some kinds of organic bromine compounds are also effective to prevent the growth of nitrification bacteria.

(4) Organic nitrogen-sulfur compounds

Organic nitrogen-sulfur compounds, such as methylene bisthiocyanate, sodium dimethyl-dithiocarbamate and 5-chloro-2-methyl-4-isothiazolin-3-one, show the biocidal and biostatic effects. These compounds also show the slime removal effect by applying their high dosages.

Figure 3.62 shows the biocidal effect of an organic nitrogen-sulfur compound as compared with chlorination. In the case of chlorination, the number of bacteria increases soon after the chlorine injection is stopped. However, in the case of organic nitrogen-sulfur compound, the number of bacteria is inhibited from increasing for a long time. When the combined treatment of chlorination and the organic nitrogen-sulfur compound is applied, the number of bacteria is kept at a low level for a longer period of time.

(5) Quaternary ammonium and phosphonium salts

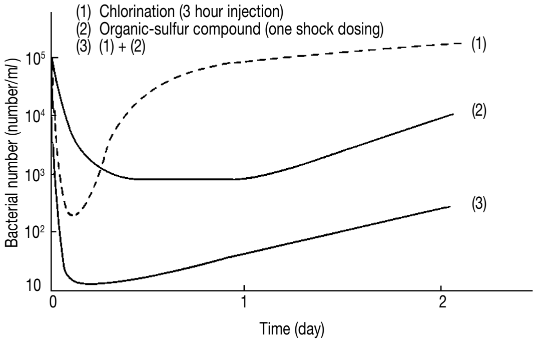


Fig. 3.62 Biocidal effects of an organic nitrogen-sulfur compound and chlorination

Table 3.25 Biostatic effect of a quaternary ammonium salt

Microorganisms	Dosage (mg/*l*)				
	0	0.4	2	4	8
E. coli IAM 1239	++	++	–	–	–
Flov. arborescens	++	++	–	–	–
Sacch. cereviceae	++	++	++	–	–
Asp. niger IAM 3001	++	++	++	++	–
Pen. citrinum	++	++	++	++	–

Note: – perfect inhibition against microorganism growth
++ growth of microorganisms

These cationic compounds are liable to adsorb on microorganisms having negative surface charges and show the biocidal or biostatic effect.

Table 3.25 shows the biostatic effect of a quaternary ammonium salt against various microorganisms. This salt shows the excellent biostatic effect with the low dosage. However, the combined use of these cationic biocides together with anionic polymer dispersants often deteriorates the effects of both kinds of chemicals because those cationic biocides react with anionic polymers and form the ineffective precipitates.

Those cationic biocides are usually applied for closed cooling water systems where polymer dispersants are scarcely applied.

(6) Peroxides

Some kinds of peroxides like hydrogen peroxide show the slime removal effects with their high dosages of above 1,000 mg/*l*. Since the peroxides generate bubbles on the surface and inside of the slime, the bubbles lift the slime from the surfaces of heat exchanger tube, etc. The slime removal treatment is usually applied when the thermal efficiency of heat exchanger becomes lower than the allowable minimum level because of the slime adhesion.

Figure 3.63 shows a recovery of heat exchanger efficiency by a slime removal treatment. Figure 3.64 shows water analyses during a slime removal treatment. Usually the turbidity and slime volume of cooling water are rapidly increased by removed slime and reach their maximum values during around 3 hours from the injection of the slime removal agent. Then water blowdown starts to discharge the removed slime from the system. However, when the insufficient slime removal effect is observed within a short time, the treatment period should be prolonged and the additional chemical dosing should be done if necessary.

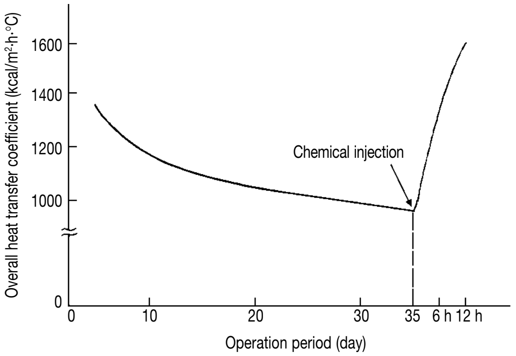


Fig. 3.63 Recovery of a heat exchanger thermal efficiency by a slime removal treatment

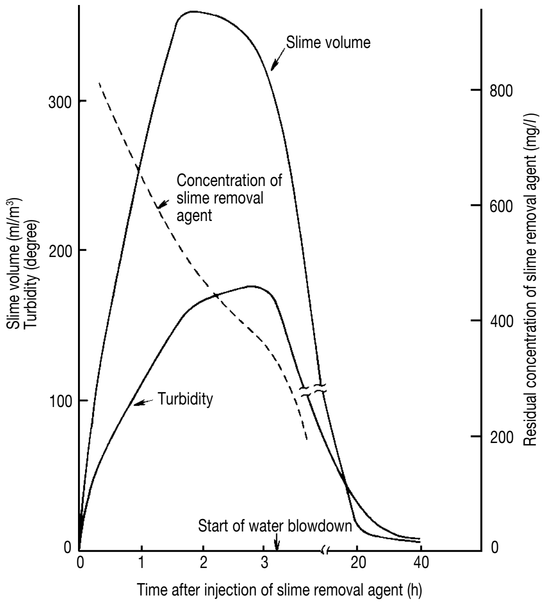


Fig. 3.64 Change of water quality during a slime removal treatment

(7) Sludge dispersants (polymers)

Ligninsulfonates and tannins were conventionally used as sludge dispersants, but recently polyelectrolytes (polymers) are being used. SS in the circulating water are prevented from the aggregation (bioflocculation) and are dispersed by the use of polymers. The dispersed SS are discharged from the system by water blowdown. Usually, anionic low molecular weight polymers are used as the dispersants. Polymers adsorb on the surface of SS and disperse them by giving the negative electrical charges to each SS. Figure 3.65 shows the SS dispersion effect of a polymer dispersant. The ratio of SS with the sedimentation rate of over 0.63 m/h, which usually cause the sludge problems in heat exchangers, is significantly lowered by applying the dispersant.

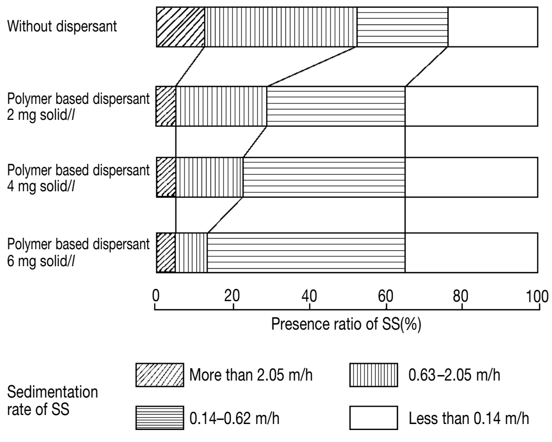


Fig. 3.65 SS dispersion effect of a polymer based dispersant

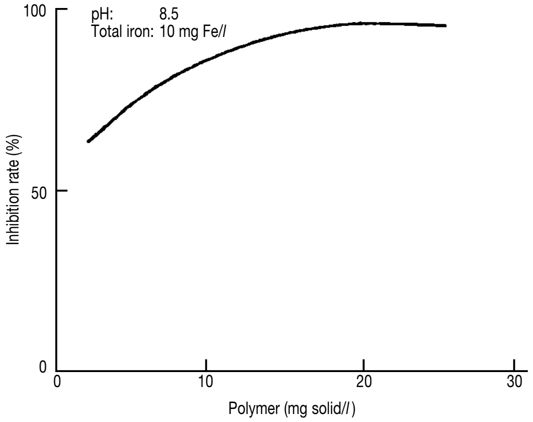


Fig. 3.66 Inhibition effect of a polymer dispersant against ferric hydroxide precipitation

Since some polymers disperse ferric hydroxide, they prevent corrosion product (ferric hydroxide) from the accumulation at the places of low water flow rate in heat exchangers, especially in the case of shell side water flow. Figure 3.66[5)] shows the dispersion effect of a polymer against ferric hydroxide.

3.4.8 The Other Biofouling Control Methods

(1) Side stream filtration

SS are discharged from the system with blowdown water, however, the discharge of SS becomes difficult in the cooling water system operated at high cycles of concentration because of the small volume of blowdown. Thus, the removal of SS from cooling water by the side stream filtration is effective to prevent biofouling troubles in that case. The combination of side stream filtration and biocide treatment economically prevents the cooling system from the slime adhesion and sludge accumulation in the case of the high cycle number operation at 3 or more.

The turbidity of circulating water in cooling systems where the side stream filtration is carried out, is calculated by equation (3.59).

$$P = \frac{R \times P_i + M \times P_m + F \times P_f}{B + W + F} \quad \text{..............} \quad (3.59)$$

where

P = turbidity of circulating water under the application of side stream filtration (degree)

R = circulating water quantity (m^3/h)

P_i = turbidity increased in the cooling water by the microorganism growth and fouling materials from air during the one circulation (degree)

M = make-up water quantity (m^3/h)

P_m = turbidity of make-up water (degree)

F = filtration rate (m^3/h)

P_f = turbidity of filtered water (degree)

B = blowdown water quantity (m^3/h)

W = windage loss (m^3/h)

Figure 3.67 shows the relationship between filtration rate and cooling water turbidity calculated by using the equation (3.59). The cooling water turbidity is kept at 15 degrees or less by applying the side stream filtration of above 2% against the circulating water quantity.

(2) Control of the operational conditions of heat exchanger

The influences of water flow rate on slime adhesion and sludge accumulation are shown in Figures 3.53 and 3.54(p.3-40). The increase of water flow rate apparently reduces the slime adhesion and sludge accumulation as shown in these figures.

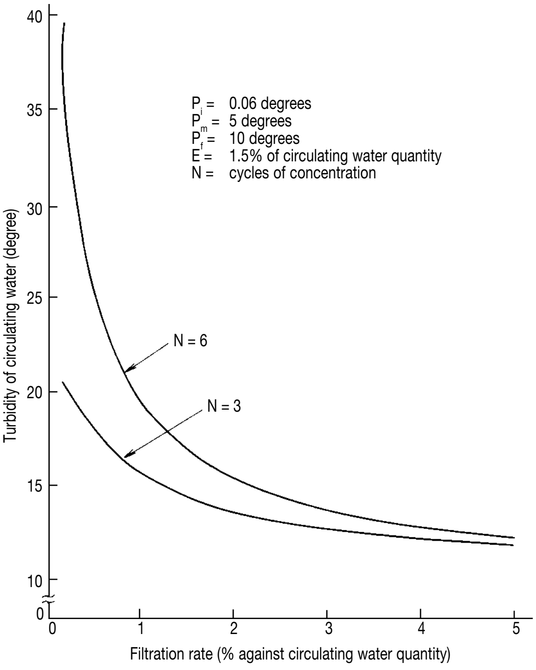


Fig. 3.67 Relationship between the turbidity of cooling water and the side stream filtration rate

Therefore, the increase of water flow rate in heat exchanger effectively reduces the biofouling when the change is possible. The desirable water flow rate for controlling the fouling of heat exchangers is generally 0.3 m/s or more.

3.5 Case Studies of Cooling Water Treatments

As mentioned in the preceding sections, the problems occurred in cooling water systems are corrosion, scale and biofouling. These problems rarely occur independently and actual troubles, such as the drop of heat exchanger efficiency, are caused as the result of a combined problems in many cases.

Table 3.7(p.3-9) lists the troubles occurred in cooling water systems and their causes. Table 3.8(p.3-9) shows the frequency of trouble occurrence in each type of cooling water systems. These tables show that those problems more or less occur in any types of cooling water systems. Accordingly, the application of suitable chemical treatments is required in order to operate the systems safely and continuously for long periods. The case studies of water treatments for each type of systems are described in this section.

3.5.1 Open Recirculating Cooling Water Systems

A suitable chemical treatment program is determined according to the make-up and cooling water qualities, and the operational conditions, such as the cycles of concentration and water temperature, in an open recirculating cooling water system. Especially, corrosion and scale control methods are varied in accordance with the cooling water quality.

Case studies of chemical treatments for typical types of cooling water qualities are described below.

(1) High hardness water

In the case of high calcium hardness (over 150 mg $CaCO_3/l$), high M-alkalinity (over 150 mg $CaCO_3/l$) and high pH (over 8) water, phosphate based corrosion inhibitors easily form the protective films on metal surfaces. Accordingly, the phosphates of low concentration, such as 3 to 6 mg $T\text{-}PO_4/l$, show the sufficient corrosion inhibitions in high hardness water as shown in Figures 3.17(p.3-16) and 3.19(p.3-17). However, the sufficient amount of scale inhibitors (polymers) should be used together with corrosion inhibitors to prevent the scaling of calcium phosphate and calcium carbonate in the heat exchangers in the case of high hardness water.

The water treatment program which uses a low concentration of corrosion inhibitors with a relatively high concentration of scale inhibitors for high hardness, high alkalinity and high pH water is called “alkaline treatment”. The good application result of an alkaline treatment is shown in Table 3.26 and the treatment result of a heat exchanger is shown in Photograph 3.13 (p.3-75).

The alkaline treatment is widely applied for high hardness cooling water in refineries, petrochemical plants, iron and steel works, electric power plants and so on.

(2) Low hardness water

The critical concentration of phosphate based corrosion inhibitors required for corrosion inhibition becomes higher in low hardness water comparing with high hardness water as shown in Figures 3.17 and 3.19. The critical concentration is 10 to 15 mg T-PO$_4$/l for the water of calcium hardness around 100 mg CaCO$_3$/l, and 15 to 20 mg T-PO$_4$/l for the water of calcium hardness around 50 mg CaCO$_3$/l. When the reduction of critical concentration is required, zinc salts are applied together with phosphates as shown in Figures 3.18 and 3.20 (p.3-17 and 3-18).

Therefore, the relatively high concentration of phosphate based or phosphate-zinc based corrosion inhibitors are usually applied for low hardness water. Scale inhibitors are used to prevent scale problems at the high temperature areas of heat exchangers even in the case of low hardness water.

The typical application result of a zinc-phosphate-polymer treatment for a low hardness water is shown in Table 3.27. Almost no corrosion, no scaling and no biofouling are observed in all heat exchangers inspected during the scheduled turnaround of the plant.

(3) High salinity water

Chloride and sulfate ions are the typical aggressive ions, and the increase of their concentrations generally lowers the corrosion inhibition provided by inhibitors. The influence of chloride and sulfate ion concentration on the effects of various corrosion inhibitors is shown in Figure 3.27 (p.3-20). Generally, zinc-phosphate based inhibitors provide the better corrosion inhibitions than phosphate based ones in the water of a high chloride and sulfate ion concentration.

Table 3.28 shows the treatment result of a zinc-

Table 3.26 Example of a high hardness water treatment (alkaline treatment)

Operational conditions of system	Circulation rate (m^3/h):	20,000	
	Holding water volume (m^3):	13,000	
	Temperature difference (°C):	8	
	Cycles of concentration:	2.5	
Chemical treatment	Corrosion and scale inhibitor (phosphonate-polymer) (mg/l):	40	
	Chlorination (mg Cl$_2$/l):	0.5–1.0, 3 h/day	
	Non-oxidizing biocide (mg/l):	50/month	
Side stream filtration	3% against circulation rate		
Water analysis		Make-up water	Cooling water
	Turbidity (degree)	2	5
	pH	8.1	9.1
	Electrical conductivity (μS/cm)	350	1,000
	M-alkalinity (mg CaCO$_3$/l)	170	430
	Ca-hardness (mg CaCO$_3$/l)	180	450
	Chloride ion (mg/l)	20	63
	Sulfate ion (mg/l)	31	79
	Silica (mg SiO$_2$/l)	7	18
Period of the chemical treatment	16 years		
Corrosion rate	Carbon steel:	3–4 mg/dm^2·day (0.014–0.019 mm/year)	
Inspection results of heat exchangers	No corrosion, no scaling and no biofouling are found in most heat exchangers. Small amount of scale and sludge is found in few heat exchangers with the low water flow rate.		

phosphonate-polymer program for a water of high chloride and sulfate ion concentration. In this factory, as the intake point of raw water is located near the mouth of a river, the water quality is widely fluctuated by the influence of the ebb and flow tides. Accordingly, the maximum chloride and sulfate ion concentrations of cooling water reach 1,394 mg/*l* and 780 mg/*l* respectively. Even though the cooling

Table 3.27 Example of a low hardness water treatment (zinc-phosphonate-phosphate-polymer treatment)

Operational conditions of system	Circulation rate (m^3/h):	5,000	
	Holding water volume (m^3):	24,000	
	Temperature difference (°C):	12	
	Cycles of concentration:	3	
Chemical treatment	Corrosion and scale inhibitor (mg/*l*) (zinc-phosphonate):	50	
	Scale inhibitor (polymer) (mg/*l*):	30	
	Chlorination (mg Cl_2/*l*):	0.3–1.0, 3h/day	
Water analysis		Make-up water	Cooling water
	Turbidity (degree)	2	7
	pH	7.2	7.9
	Electrical conductivity (μS/cm)	100	354
	M-alkalinity (mg $CaCO_3$/*l*)	23	65
	Ca-hardness (mg $CaCO_3$/*l*)	24	72
	Chloride ion (mg/*l*)	5	18
	Sulfate ion (mg/*l*)	6	15
	Silica (mg SiO_2/*l*)	6	15
Period of the chemical treatment	17 years		
Corrosion rate	Carbon steel:	3–5 mg/dm^2·day (0.014–0.024 mm/year)	
Inspection results of heat exchangers	Almost no corrosion, no scaling and no biofouling are observed in all heat exchangers.		

Table 3.28 Example of a high salinity water treatment (zinc-phosphonate-polymer treatment)

Operational conditions of system	Circulation rate (m^3/h):	2,000	
	Holding water volume (m^3):	250	
	Temperature difference (°C):	10	
	Cycles of concentration:	5	
Chemical treatment	Corrosion and scale inhibitor (mg/*l*) (zinc-phosphonate):	45	
	Scale inhibitor (polymer) (mg/*l*):	20	
	Chlorination (mg Cl_2/*l*):	0.5–1.0, 3h/day	
	Non-oxidizing biocide (mg/*l*):	50/week	
	pH control (H_2SO_4):	pH 7.5–8.5	
Water analysis		Make-up water	Cooling water
	Turbidity (degree)	1–14	14–28
	pH	7.0–10.2	7.5–8.5
	Electrical conductivity (μS/cm)	150–1,000	1,100–4,700
	M-alkalinity (mg $CaCO_3$/*l*)	16–154	80–342
	Ca-hardness (mg $CaCO_3$/*l*)	48–440	220–1,624
	Chloride ion (mg/*l*)	40–280	180–1,394
	Sulfate ion (mg/*l*)	10–76	450–780
	Silica (mg SiO_2/*l*)	18–47	60–240
Period of the chemical treatment	12 years		
Inspection results of heat exchangers	Almost no corrosion, no scaling and no biofouling are found in all heat exchangers.		

Table 3.29 Example of a non-phosphorous corrosion inhibitor treatment (1) (zinc-polymer treatment)

Operational conditions of system	Circulation rate (m^3/h):	2,000	
	Holding water volume (m^3):	700	
	Temperature difference (°C):	11	
	Cycles of concentration:	3	
Chemical treatment	Corrosion and scale inhibitor (mg/l) (zinc-polymer):	120	
	Chlorination (mg Cl_2/l):	0.5–1.0, 3h/day	
Water analysis		Make-up water	Cooling water
	pH	8.0	8.8
	Electrical conductivity (μS/cm)	116	387
	M-alkalinity (mg $CaCO_3/l$)	44	138
	Ca-hardness (mg $CaCO_3/l$)	32	108
	Chloride ion (mg/l)	7	20
	Silica (mg SiO_2/l)	12	32
Corrosion rate	Carbon steel:	3.0–3.6 mg/dm^2·day (0.014–0.017 mm/year)	
Period of the chemical treatment	15 years		
Inspection results of heat exchangers	Almost no corrosion, no scaling and no biofouling are observed in all heat exchangers.		

Table 3.30 Example of a non-phosphorous corrosion inhibitor treatment (2) (all polymer treatment)

Operational conditions of system	Circulation rate (m^3/h):	470	
	Holding water volume (m^3):	5	
	Temperature difference (°C):	5	
	Cycles of concentration:	8	
Chemical treatment	Corrosion and scale inhibitor (mg/l) (polymers):	50	
	Non-oxidizing biocide (mg/l):	7	
Water analysis		Make-up water	Cooling water
	Turbidity (degree)	Below 1	2
	pH	7.4	8.7
	Electrical conductivity (μS/cm)	180	1,400
	M-alkalinity (mg $CaCO_3/l$)	50	330
	Ca-hardness (mg $CaCO_3/l$)	50	380
	Chloride ion (mg/l)	8	60
	Silica (mg SiO_2/l)	20	180
Period of the chemical treatment	11 years		
Treatment result	No thermal efficiency drop of refrigerating machines is observed during their operation period. No corrosion, no scaling and no biofouling are found in all heat exchangers of the refrigerating machines.		

water quality is very corrosive, this program provides the good performance. Almost no corrosion, no scaling and no biofouling have been found in the heat exchangers at the scheduled turnarounds of the system.

(4) Non-phosphorous corrosion inhibitor treatment

At present, various kinds of organic and inorganic phosphates are widely used as corrosion inhibitors with good performances in open recirculating cooling water systems. However, the development of non-phosphorous corrosion inhibitors has been strongly required in Japan and the extensive researches have been carried out from the view point of environmental protection, such as the prevention of nutrification in closed water areas.

Among non-phosphorous corrosion inhibitor treatment programs, zinc-polymer treatments and all polymer treatments have been applied for many

Table 3.31 Outline of chemical treatments for closed recirculating cooling water systems

Type of corrosion inhibitor	Applicable operational conditions of system	Target corrosion rate	Remarks
Nitrite type	Make-up water; FW*1, SW*2, DW*3 Retention time*4; No limitation Water temperature; No limitation	Carbon steel; Below 1 mg/dm^2·day (Below 0.005 mm/year) Copper and its alloys; Below 1 mg/dm^2·day (Below 0.005 mm/year)	Biocides for nitrification bacteria should be used in the case of cooling water temperature of 10 to 40°C where the bacteria rapidly grow.
Molybdate-polymer type	Make-up water; FW, SW, DW Retention time; Within 50 days Water temperature; Below 60°C	Carbon steel; Below 10 mg/dm^2·day (Below 0.05 mm/year) Copper and its alloys; Below 1 mg/dm^2·day (Below 0.005 mm/year)	Polymers are used as corrosion inhibitor.
Phosphate-polymer type	Make-up water; FW Retention time; Within 10 days Water temperature; Below 50°C	Carbon steel; Below 10 mg/dm^2·day (Below 0.05 mm/year) Copper and its alloys; Below 1 mg/dm^2·day (Below 0.005 mm/year)	Polymers are used for preventing calcium phosphate scale.

*1 FW: fresh water (tap water, well water, industrial water, etc.)
*2 SW: softened water
*3 DW: demineralized water
*4 Retention time (day) $= \dfrac{\text{Holding water volume } (m^3)}{\text{Make-up water quantity } (m^3/\text{day})}$

cooling water systems in Japan. Table 3.29 shows the example of a zinc-polymer treatment. Table 3.30 shows the typical application conditions of an all polymer treatment.

Both non-phosphorous treatments show the sufficient corrosion, scale and biofouling control effects.

3.5.2 Closed Recirculating Cooling Water Systems

Troubles occurred in closed recirculating cooling water systems are mainly caused by corrosion because no concentration of dissolved salts occurs in these systems . Corrosion inhibitors applied for these systems are grouped into three types as shown in Table 3.3l.

Table 3.32 shows the types and operational conditions of closed recirculating cooling water systems, and the suitable chemical treatment methods.

In closed recirculating cooling water systems, the cooling water is scarcely discharged from the systems other than small amount of water leakage from circulating water pump, etc. Since the leakage is generally less than 0.02% against the circulation rate, the corrosion products readily accumulate in the system if corrosion is happened.

Accordingly, nitrite based corrosion inhibitors are usually applied with a high concentration in order to prevent corrosion as much as possible. However, the nitrites are changed to nitrate by nitrification bacteria and lose their corrosion inhibition effects. Figure 3.68 shows the change of nitrite ion to nitrate ion by the bacteria. Biocides for nitrification bacteria are usually used together with nitrite based inhibitors to prevent the consumption of nitrite in closed cooling water systems with the water temperature of 10 to 40°C. Table 3.33 shows the typical application results of a biocide for nitrification bacteria. The growth rate of nitrification bacteria becomes low at higher temperature than 40°C or lower temperature than 10° C.

When the nitrites are applied for already corroded systems, they are reduced to ammonia by ferrous ion and the pH of cooling water is sometimes increased. When the pH exceeds 9.0, the corrosion of copper and copper alloys is accelerated. To solve this problem, the precleaning of the system for reducing ferrous ion, the use of pH buffering agents such as borate, the use of copper corrosion inhibitors like triazole, etc., are carried out in closed cooling water systems.

In cooling water systems for marine engines, not only general corrosion problems but also cavitation corrosion of cylinder liners, etc., are often occurred. Moreover, the deterioration of mechanical strength of metallic materials caused by the corrosion fatigue is a serious problem. The use of nitrite based corrosion inhibitors is popular in this system because it is very effective to prevent the cavitation corrosion and the corrosion fatigue.

Table 3.34 shows the effect of a nitrite based corrosion inhibitor on various kinds of metals. The

Table 3.32 Types of closed recirculating cooling water systems and the suitable chemical treatment methods

Type of system		Operational condition	Chemical treatment
High water temperature system	Polymerization vessel cooling systems	Repetition of heating and cooling Max. water temperature: 90° C	Nitrite based corrosion inhibitors and biocides for nitrification bacteria
	High temperature equipment* cooling systems in iron and steel works * Hot blast valve, tuyere, lance, converter gas hood, electric arc furnace, etc.	Max. water temperature: 130° C Water flow rate: 1–10 m/s	(1) Boiler compounds, oxygen scavengers, neutralizing amines, etc. for complete closed systems (2) Nitrite based corrosion inhibitors and biocides for nitrification bacteria for general systems
	Diesel engine (for power generation) cooling systems	Max. water temperature: 90° C Intermittent operation sometimes	Nitrite based corrosion inhibitors and biocides for nitrification bacteria
	Marine engine cooling systems	Max. water temperature: 110° C Intermittent operation sometimes	Nitrite based corrosion inhibitors
Low water temperature system	Chilled water systems	Water temperature: 5–20° C Intermittent operation sometimes	(1) Nitrite based corrosion inhibitors and biocides for nitrification bacteria (2) Molybdate and polymer based corrosion inhibitors
	Bearing cooling systems in power plants	Max. water temperature: 40° C Water flow rate: 1–3 m/s	(1) Nitrite based corrosion inhibitors and biocides for nitrification bacteria (2) Molybdate and polymer based corrosion inhibitors (3) Phosphate based corrosion inhibitors and polymer based scale inhibitors
	General process and equipment cooling systems in refineries, petrochemical plants, iron and steel works, etc.	Water temperature: 20–60° C Water flow rate: 0.1–3.0 m/s	Nitrite based corrosion inhibitors and biocides for nitrification bacteria

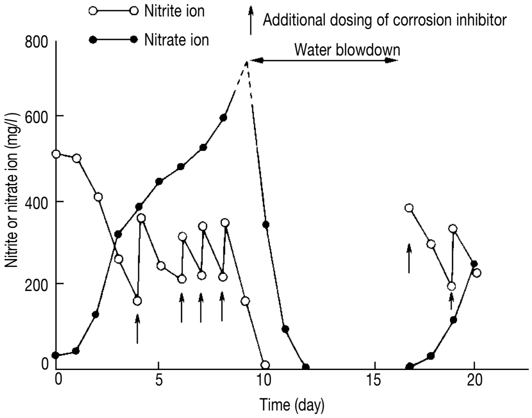


Fig. 3.68 Consumption of nitrite by nitrification bacteria in a closed cooling water system

Table 3.33 Effect of a biocide on the consumption of nitrite by nitrification bacteria

Cooling water system	Dosage (mg/l) and dosing frequency of biocide	Nitrite concentration in cooling water (mg NO_2^-/l)	Nitrate concentration in cooling water (mg NO_3^-/l)
A	0	100–350	632–677
	100/15 days	523–618	32–41
B	0	200–340	319–498
	100/15 days	201–466	10–24

corrosion inhibitor provides the sufficient corrosion inhibition even though the chloride and sulfate ion concentrations are increased in the cooling water by the contamination with seawater from the secondary cooling system. Table 3.35[28] shows the fatigue strength* of cast iron and the effect of a nitrite. The addition of nitrite increases the fatigue strength of cast iron in fresh water up to that in the

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* The fatigue strength of metal is also called the endurance limit. Metal is never destroyed by applying the stress of smaller than the fatigue strength.

Table 3.34 Effect of a nitrite based corrosion inhibitor for marine engine cooling water systems

Test solution	Chloride (mg Cl^-/l)		100	300	500	1,000
	Sulfate (mg SO_4^{2-}/l)		15	45	75	150
Corrosion rate (mg/ dm^2·day)	Carbon steel		0.5	0.9	0.4	0.4
	Aluminum brass		0.4	0.3	0.4	0.3
	Galvanic couple	Cast iron	4.1	3.3	3.3	3.7
		Copper	2.4	2.0	1.9	4.2

Dosage of inhibitor: 3,000 mg/l as product

Table 3.35 Fatigue strength of cast iron and the effect of a nitrite

Material	Tensile strength (kg/mm^2)	Fatigue strength* (kg/mm^2)		
		In air	In fresh water	In fresh water with $NaNO_2$ of 500 mg/l
Cast iron for liner	28.5	14.5	11.0	13.0
Ductile cast iron	53.6	21.0	15.0	20.5

* Measured by using Ono's rotating fatigue tester

air.

The nitrite based corrosion inhibitors are the effective and economic, however they have some possibilities of environmental pollution because of their high chemical oxygen demands and toxicities against some aquatic lives. Molybdate-polymer based corrosion inhibitors gradually become popular as the safer chemicals for the environment.

Phosphate-polymer based corrosion inhibitors are applied for the closed system for cooling bearing, etc., in electric power plants in the case of shorter retention time than 10 days. Boiler treatment chemicals are used for the complete closed cooling water systems where no oxygen enters from the circumstances.

3.5.3 Once Through Cooling Water Systems

(1) Systems using fresh water

Since the cooling water is directly discharged without the water circulation in once through cooling water systems, it is economically difficult to dose the sufficient concentrations of corrosion inhibitors. Therefore, the systems are usually operated without corrosion inhibitors.

Sometimes, polyphosphate or silicate based corrosion inhibitors are used at the low dosages of 2 to 5 mg/l as products to prevent the deposition of corrosion products and the under deposit corrosion in the systems. In that case, the water flow rate of 1 m/s or more is required for obtaining the low corrosion rate of carbon steel as shown in Figure 3.30(p.3-21).

In some electric power plants, copper corrosion inhibitors and polymer based sludge dispersants are used with the low dosages of below 1 mg/l for preventing the corrosion and fouling of steam condensers made of copper and copper alloys. Intermittent chlorination of 1 to 3 hours per day are generally carried out for the biofouling control.

(2) Systems using seawater

Seawater is often used for once through cooling water systems for steam condensers in electric power plants located near sea-coasts. Copper alloys, such as aluminum brass and cupronickel, are widely used for the steam condenser tubes.

Ferrous sulfate or ferrous ion produced by the electrolysis of iron electrodes in seawater is sometimes added into the cooling water with the dosage of 0.3 to 1.0 mg Fe^{2+}/l for 1 to 2 hours per day to prevent the local corrosion of the copper alloys.

In the case of the continuous injection, the ferrous ion of 0.1 to 0.3 mg Fe^{2+}/l shows the corrosion inhibition. Figure 3.69[29)] shows the effect of the continuous injection on aluminum brass. The protective film formed by the ferrous ion is mainly consisted of γ-FeOOH[30)].

Aquatic lives, such as marine mussels, oysters and barnacles, often adhere and grow on the walls of the seawater intake channels. When they come off the walls and flow into condensers, the condenser performances are lowered and the power plant is sometimes stopped because of the clogging of condenser tubes, the reduction of the

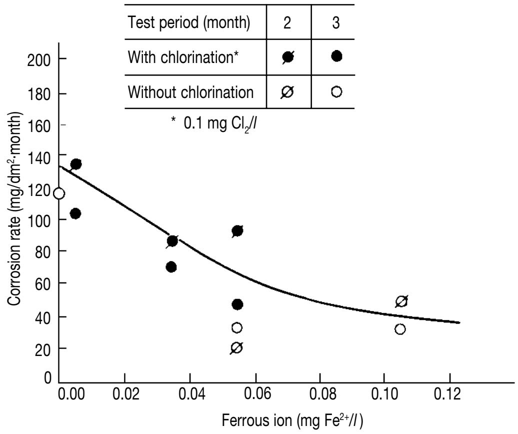

Fig. 3.69 Corrosion inhibition effect of ferrous ion on aluminum brass in seawater

water flow rate, etc. Intermittent or continuous chlorination with the dosage of 0.2 to 0.5 mg Cl_2/l, the mechanical cleaning of tubes with sponge balls and so on are carried out to prevent such troubles.

3.5.4 Brine Systems

Brines are the antifreezes using as heat transfer media in cooling or refrigerating processes. The brines are classified to inorganic brines, such as calcium chloride solution and sodium chloride solution, and organic brines like ethyleneglycol solution, propyleneglycol solution and so on.

Brine systems are widely used in beer breweries, ice plants, confectioneries, ice-skating rinks and so on.

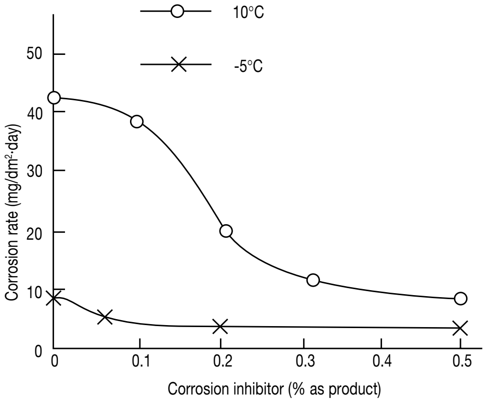

Fig. 3.70 Effect of a sugaralcohol based corrosion inhibitor on carbon steel in 20% calcium chloride brine

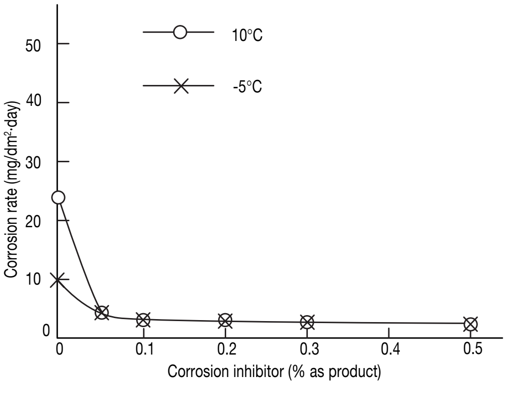

Fig. 3.71 Effect of a sugaralcohol based corrosion inhibitor on copper in 20% calcium chloride brine

(1) Calcium chloride brine

As calcium chloride brine has the high corrosivity, troubles, such as the leakage of the brine from the pipings and the shortage of service lives of the equipments, are often caused by the corrosion when no corrosion inhibitor is applied. The use of corrosion inhibitors keeps the operational efficiency of systems and saves the maintenance costs.

Although chromates were formerly used as the corrosion inhibitors, they are hardly used in the present because of severe regulation for the chromate discharge to the environment. Recently, sugaralcohol based corrosion inhibitors are successfully applied for the calcium chloride brines. Figures 3.70 and 3.71 show the effects of a sugaralcohol based inhibitor on carbon steel and copper respectively.

(2) Organic brines

Since the corrosivity of ethyleneglycol is lower than that of calcium chloride, it is widely used as brine and antifreeze for automobile engines. Propyleneglycol is used for the brine in food factories because of the extremely low toxicity and low corrosivity.

Nitrite based corrosion inhibitors are generally applied for the organic brines. Figure 3.72 shows the effect of a nitrite on carbon steel in 30% ethyleneglycol brine.

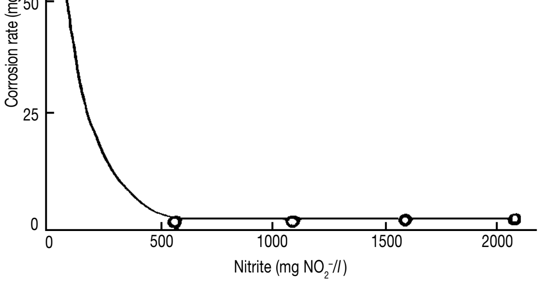

Fig. 3.72 Effect of a nitrite based corrosion inhibitor on carbon steel in 30% ethylenglycol brine

3.6 Control of Cooling Water System Operation

3.6.1 Control of Cooling Water Quality and Chemical Injection

(1) Open recirculating cooling water systems

(a) Control of cooling water quality (cycles of concentration)

In the open recirculating cooling water system, since a part of the cooling water is evaporated from the cooling tower, dissolved salts in the make-up water are concentrated in the circulating water. Therefore, the cycles of concentration should be controlled in order to maintain the cooling water quality and the concentration of chemicals, such as corrosion inhibitors and scale inhibitors, at their constant levels by adjusting the blowdown water quantity. Such quality control of cooling water is very important for obtaining the sufficient chemical treatment effects.

As an example, the blowdown water quantity is calculated for a cooling water system operating under following conditions:

①Circulating water quantity (R):	5,000 m^3/h
②Supply water temperature:	30.0°C
③Return water temperature:	41.6°C
④Windage loss (W) (0.2% of R):	10 m^3/h
⑤Calcium hardness in make-up water (CaH_M):	50 mg $CaCO_3/l$
⑥Target of calcium hardness in circulating water (CaH_R):	250 mg $CaCO_3/l$

The target cycles of concentration (N) is calculated at 5 from the CaH_M and CaH_R as shown below:

$$N = \frac{CaH_R}{CaH_M} = 5 \quad \text{.......................................} \quad (3.60)$$

The temperature difference (ΔT) between the supply and return waters across a cooling tower is calculated from ② and ③ to be 11.6°C. Evaporation loss (E) is calculated as follows:

$$E = \frac{0.01 \times R \times \Delta T}{5.8}$$

$$= \frac{0.01 \times 5000 \times 11.6}{5.8}$$

$$= 100\ (m^3/h) \quad \text{..................................} \quad (3.61)$$

The blowdown water quantity (B) is calculated by substituting the values of N, E, W in the following equation:

$$N = \frac{E + B + W}{B + W}, \ 5 = \frac{100 + B + 10}{B + 10} \quad \text{...........} \quad (3.62)$$

$$B = 15\ (m^3/h) \quad \text{.......................................} \quad (3.63)$$

Accordingly, when 15 m^3/h of blowdown is carried out in this cooling system, the circulating water quality can be kept at the target value.

At present, the cycles of concentration is usually controlled by operating the blowdown valve manually. However, the installation of automatic blowdown control systems becomes more frequently to control the cycles of concentration. Figure 3.73 shows the flow diagram of an automatic operation control system (blowdown and chemical injection control) for open recirculating cooling water systems. This system automatically controls the water blowdown and keeps the electrical conductivity of cooling water within a specified range.

(b) Control of chemical injection

Cooling water treatment chemicals, such as corrosion inhibitors and scale inhibitors, should be kept at the proper concentrations in cooling water because the fluctuation of chemical concentration in a wide range will deteriorate the treatment effect. Generally, the chemical concentration in cooling water is kept over the minimum concentration (the critical concentration) for providing the sufficient effect.

At the start-up of system operation, the concentration of corrosion inhibitor is usually increased to 3 to 10 times of the maintenance concentrations to promote the completion of the protective film on the whole surfaces of metals composed of the system. This high concentration treatment of corrosion inhibitors is called the initial treatment, passivation or pretreatment.

Figure 3.74 shows the effect of an initial treatment on carbon steel. The application of initial treatment remarkably reduces the initial corrosion after the operation start-up of system. The high concentration of scale inhibitor is sometimes dosed together with corrosion inhibitor according to the cooling water quality and the operational conditions of system at the initial treatment. In the case of initial treatment, the chemicals are often dosed into the cooling tower basin directly from tank trucks, chemical containers, etc.

The amount of chemicals required for initial treatment is calculated by using equation (3.64):

$$W_i = 10^{-3} \times C_i \times H \quad \text{................................} \quad (3.64)$$

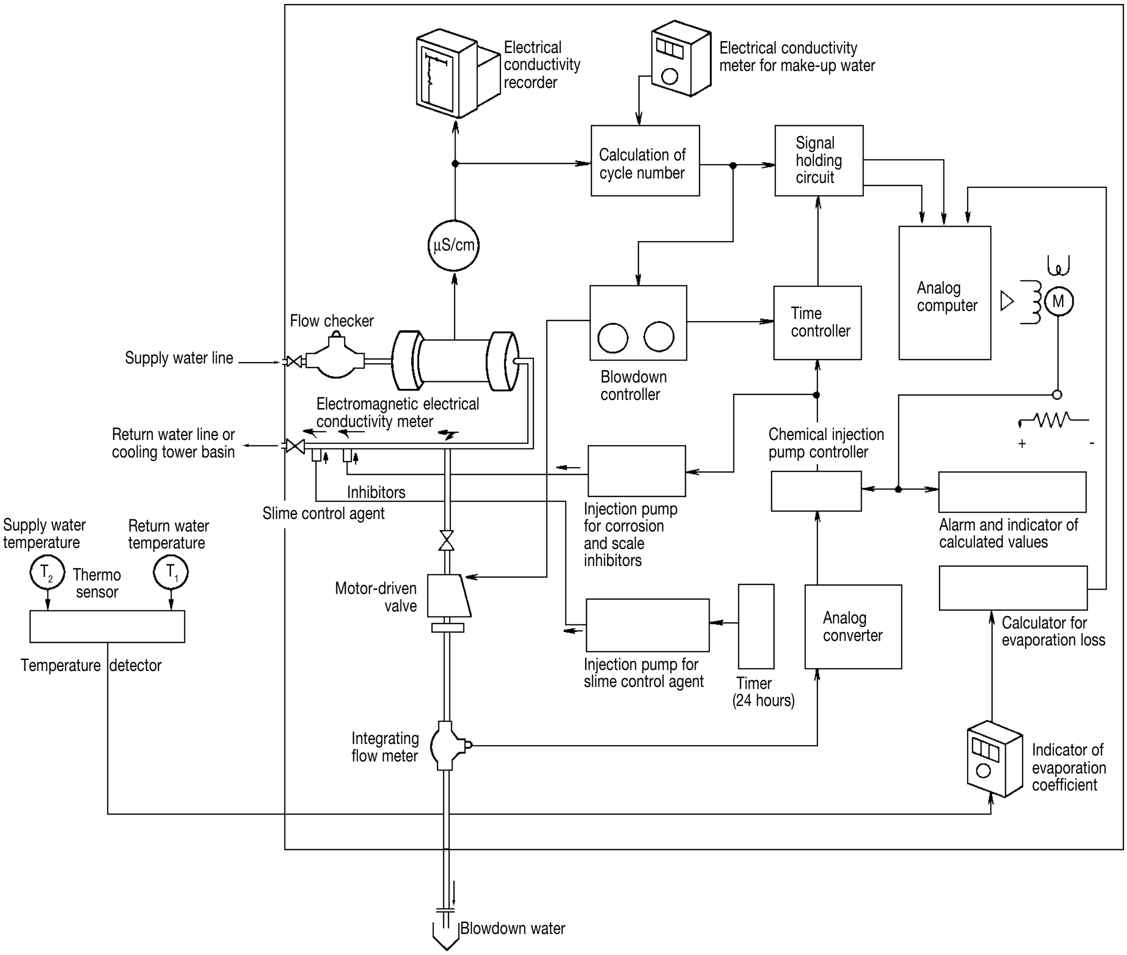

Fig. 3.73 Flow diagram of an automatic operation control system for open recirculating cooling water systems

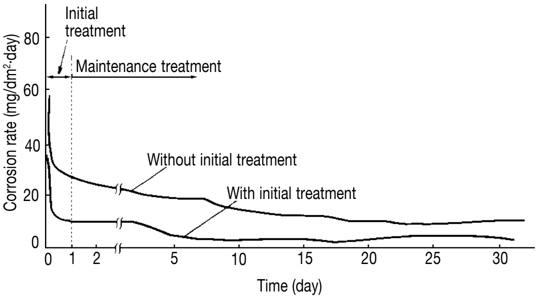

Fig. 3.74 Effect of an initial treatment with a zinc-phosphate based inhibitor on carbon steel

where

W_i = amount of chemicals required for initial treatment (kg)

C_i = required concentration of chemicals for initial treatment (mg/l)

H = holding water volume of cooling water system (m^3)

After the completion of initial treatment, the chemical concentration in the circulating water is decreased by the water blowdown. When the chemical concentration reaches the maintenance level, the continuous injection of chemicals is started to keep the maintenance concentration. The injection rate of chemicals for the maintenance treatment is calculated by the equation (3.65) or (3.66):

$$W_m = 10^{-3} \times (B + W) \times C_m \quad \text{......................... (3.65)}$$

$$W_m = \frac{10^{-3} \times C_m \times 3M}{N} \quad \text{......................... (3.66)}$$

where

W_m = injection rate of chemicals for maintenance treatment (kg/h)

B = blowdown water quantity (m^3/h)

W = windage loss (m^3/h)

C_m = maintenance concentration of chemicals (mg/l)

M = make-up water quantity (m^3/h)

N = cycles of concentration

Usually, the chemicals are continuously injected into the cooling tower basin by using metric pumps. The concentration is controlled by adjusting the injection rate of pump according to the analysis of the chemical concentration in cooling water. The installation of automatic chemical injection systems is steadily increasing year by year. The typical flow diagram of such system is shown in Figure 3.73.

Recently, KURITA developed an on-line phosphate analyzer to automatically control the injection of phosphate based chomicals.

Scale inhibitors are usually formulated with corrosion inhibitors. However, when a scale inhibitor is separately used, it is continuously injected into the cooling tower basin with a metric pump in the same manner of corrosion inhibitor injection.

Figure 3.75 shows the illustration of a chemical concentration control during from the initial to the maintenance treatment. To keep the chemical concentration at the higher level than the critical one is important to obtain the stable treatment effect.

Usually, chlorine compound is added into the cooling tower basin by using a metric pump or a chlorinator to maintain the residual concentration at 0.5 to 1.0 mg Cl_2/l for 2 to 5 hours per day. When a continuous chlorination is applied, the residual chlorine concentration is usually kept within the range of 0.2 to 0.5 mg Cl_2/l.

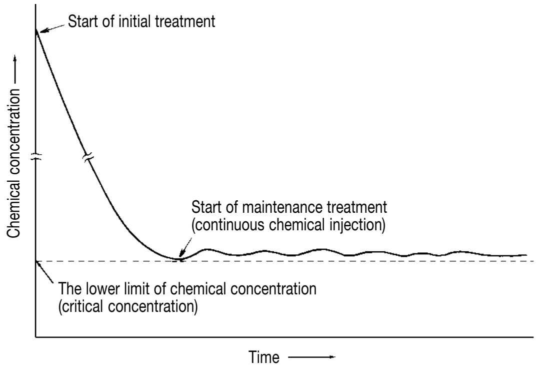

Fig. 3.75 Illustration of a chemical concentration control during from an initial to maintenance treatment period

The required dosage of chlorine compounds varies with the ratio of circulating water quantity against the holding water volume, the chlorine demand of cooling water and so on. Therefore, the appropriate injection rate of chlorine compounds should be determined according to the analysis of residual chlorine concentration in each cooling water system.

Non-oxidizing biocides are intermittently dosed into cooling tower basin at an interval of 3 to 30 days usually.

(c) Water analysis for operation control

Daily water quality control is essentially required to keep cooling water systems from corrosion, scaling and biofouling problems. For sufficient water quality control, it is important to understand the influence of each item of water quality on the occurrence of problems, and the relationship between water quality and the effects of chemicals.

Table 3.36 outlines the meaning of each water analysis item. Table 3.37 shows the items and frequencies of water analysis for the normal operation control of open recirculating cooling water systems. The frequency of analysis may be reduced in cooling water system operated stably.

(2) Closed recirculating cooling water systems

Since no evaporation of circulating water usually occurs in closed recirculating cooling water systems, the dissolved salts are scarcely concentrated in the system. Moreover, the water is rarely discharged from this system, so the circulating water quality and corrosion inhibitor concentration are scarcely changed during a short period.

Accordingly, corrosion inhibitors are applied with the high concentration and they are intermittently dosed into the system usually. When a large volume of cooling water leaks or is discharged continuously, the corrosion inhibitor should be continuously dosed by using a metric pump even in the closed system.

Biocides effective for nitrification bacteria are usually dosed at an interval of 15 to 30 days in the system treated with nitrite based corrosion inhibitors. Since the cooling water quality hardly fluctuates in the closed recirculating cooling water system, the frequencies and items of analysis for water quality control can be reduced in comparison

Table 3.36 Items of water analysis and their meanings

Item	Meaning
pH	pH is measured to confirm the corrosivity and scaling tendency of cooling water.
Electrical conductivity	This is measured to determine dissolved solids concentration in water. Water of higher electrical conductivity tends to cause corrosion problems.
Turbidity	This is measured to examine the amount of suspended solids in water. The adhesion and accumulation of suspended solids to the heat exchanger lowers the thermal efficiency and causes the pitting corrosion under the deposits.
M-alkalinity	M-alkalinity has a fairly good correlation with the pH of water and is measured to predict the scaling of calcium carbonate.
Calcium hardness	This is important to predict the scaling of calcium carbonate, etc., and to check the cycles of concentration of cooing water.
Magnesium hardness	Magnesium ions form magnesium silicate (talc) scale combining with silicate ions in high pH water.
Chloride ion	This is usually used as an index for controlling the cycles of concentration of cooling water. Water of high chloride ion concentration shows strong corrosivity.
Sulfate ion	Water of high sulfate ion concentration shows strong corrosivity.
Silica	Silica is one of scale components.
Ammonium ion	Higher concentration of ammonium ion in water accelerates slime formation. Ammonium ion accelerates the corrosion of copper by producing copper-ammonium complex salts.
Chemical oxygen demand ($\mathrm{COD_{Mn}}$) or BOD	Biofouling is usually accelerated in water of higher $\mathrm{COD_{Mn}}$ or BOD.
Number of bacteria	This is one of indexes for predicting slime occurrence. It is usually measured to determine the effect of biocide.
Total iron	Total iron is one fouling material in water. The adhesion of iron hydroxides to heat exchanger tubes causes the local corrosion of carbon steel under the deposits.
Concentrations of corrosion inhibitor and scale inhibitor	The concentrations of corrosion and scale inhibitors should be always kept at the specified levels. The wide fluctuation of chemical concentration may deteriorate the treatment effect.

Table 3.37 Items and frequencies of water analysis for open recirculating cooling water systems

Item	Analysis frequency	
	Make-up water	Circulating water
Turbidity	once/week	once/week
pH	once/week	once/day
Electrical conductivity	once/week	once/day
M-alkalinity	once/week	once/week
Calcium hardness	once/week	once/week
Magnesium hardness	once/week	once/week
Chloride ion	once/week	once/week
Sulfate ion	once/week	once/week
Silica	once/week	once/week
Total iron	once/week	once/week
Residual chlorine	—	once/week
$\mathrm{COD_{Mn}}$	once/month	once/month
Corrosion inhibitor	—	once/day

Table 3.38 Items and frequencies of water analysis for closed recirculating cooling water systems

Item	Analysis frequency (circulating water)[*1]
pH	1–2 times/month
Electrical conductivity	1–2 times/month
Chloride ion	1–2 times/month
Sulfate ion	1–2 times/month
Ammonium ion	1–2 times/month
Nitrate ion[*2]	1 time/3 months
Concentration of corrosion inhibitor	1–2 times/month

[*1] At the start-up of system operation, the analysis frequencies should be appropriately increased.

[*2] It should be measured when nitrite based corrosion inhibitors are applied.

with the open recirculating cooling water systems.

Table 3.38 shows the items and frequencies of water analysis for closed recirculating cooling water systems.

(3) Once through cooling water systems

Most of once through cooling water systems are operated without chemicals, such as corrosion inhibitors, scale inhibitors and biocides. If the chemicals are used, they are continuously or intermittently injected by using metric pumps in proportion to the cooling water volume.

In this system, only a few items, such as pH and electrical conductivity, are usually measured around once a month in order to confirm any fluctuations in the supply water quality.

3.6.2 Monitoring of Water Treatment

(1) Open recirculating cooling water systems

(a) Monitoring of corrosion rate

Test coupons or corrosion meters utilizing the linear polarization method are usually used for measuring the metallic corrosion rate in open recirculating cooling water systems. Test heat exchangers are sometimes used for monitoring the corrosion condition and the pitting corrosion rate under the heat transfer condition.

Recently, KURITA developed a pitting corrosion monitor[31)] utilizing an artificial pit electrode and it has been successfully applied in fields.

These monitoring methods are useful to evaluate the effect of corrosion inhibitors and to improve the water treatment method if the performance is insufficient.

Since each monitoring method has its features and limitations as described below, it should be properly applied according to the purpose of monitoring.

(i) Test coupon method

Test coupons cleaned and weighed are set in a coupon column installed in a bypass line of the circulating water, and contact with the water flow for a specified period. The standard water flow rate and test duration are 0.3 to 1.0 m/s and 2 to 4 weeks respectively. However, these test conditions should be changed according to the test purpose. It is better to install the coupon columns in the both bypass lines of supply and return waters.

After passing the specified test period, the test coupons are removed from the column, derusted and weighed after drying. The corrosion rate of coupon is calculated from the weight loss during test period by using the equation (3.67).

$$V = \frac{100 \times (W_1 - W_2)}{S \times D} \quad \text{..............................} \quad (3.67)$$

where

V = corrosion rate (mg/dm^2·day) (mdd)
W_1,W_2 = weight of the test coupon before and after the test respectively (mg)
S = surface area of the test coupon (cm^2)
D = test period (day)

This method gives an average corrosion rate for a relatively long period. However, it is possible to observe the change of the corrosion condition by using a transparent coupon column.

Since this method has many advantages shown below, it is widely used for corrosion rate monitoring:

① Easy to measure the corrosion rates of many kinds of metals at the same time,
② Simple and easy testing procedure,
③ Better reproducibility,
④ Low operation and installation costs.

The disadvantages of this method are the difficulties to detect the change of corrosion rate in short time and to measurer the corrosion rate at a heat transfer surface.

(ii) Corrosion meter (electrochemical measurement)

When the electrical potential of a working electrode (test electrode) is changed (polarized) few millivolts to few tens millivolts from the natural electrode potential (corrosion potential), the minute electrical current passes through between the working and counter electrodes. This electrical current has the correlation with the corrosion rate of working electrode as shown in the equation (3.68).

$$V = K \times \frac{I}{\Delta E} \quad \text{..} \quad (3.68)$$

where

V = corrosion rate (mg/dm^2·day) (mdd)
K = corrosion rate constant (mdd·V·cm^2/A)
I = current density between counter and working electrodes (A/cm^2)
ΔE = absolute value of working electrode potential difference between the natural and the polarized conditions (V)

The K value can be experimentally determined through laboratory tests by taking the operational conditions of cooling water systems into consideration. After determining the K value, the corrosion rate is calculated from the equation (3.68) by measuring the ΔE of working electrode and the I between working and counter electrodes. Potentiostatic method or galvanostatic method is applied for measuring the ΔE and the I. In the first method, the I passing through between the working and counter electrodes is measured under the condition that the ΔE value is kept at a constant value by supplying a power between the both electrodes. In the second method, the ΔE of working electrode is measured by supplying a constant electrical current between the both electrodes. Such electrochemical measurement of corrosion rate is called the linear polarization method[32] or the polarization resistance method.

Many kinds of corrosion meters applying the linear polarization technique are marketed. Photograph 3.14 (p.3-75) shows a corrosion meter developed by KURITA.

Since the corrosion meter provides a continuous and instantaneous corrosion rate measurement, it is able to apply countermeasures quickly if the corrosion rate increases. Therefore, the corrosion rate monitoring by corrosion meters is superior to that by test coupons. However, it is still difficult to measure the corrosion rate at a heat transfer surface even though the corrosion meter is used.

Figure 3.76[33] shows a typical corrosion monitoring result with a corrosion meter in a cooling water system treated with a phosphonate-polymer program (alkaline treatment). In this case, the corrosion rate was kept at a low level of approximately 1 mg/dm^2·day because the chemical concentration and cooling water quality had been appropriately controlled during the monitoring period.

(iii) Test heat exchanger

The corrosion rate measurement by test coupon or corrosion meter is difficult to monitor the corrosion condition at a heat transfer surface. Accordingly, a test heat exchanger is used for monitoring the corrosion under heat transfer condition.

Figure 3.77 shows a flow diagram of heat exchanger test. The circulating water passes through the heat exchanger and is indirectly heated by steam. Hot water is sometimes used as the heating medium. When sufficient attention is paid in determining test conditions, such as water temperatures at the inlet and outlet of heat exchanger, the temperature of steam and the water flow rate, the corrosion condition of test heat exchanger tubes are closed to those in an actual heat exchanger. It is difficult to measure the corrosion rates of the tubes, but the depth of pitting corrosion is measured in this test. The scale thickness, the amount of fouling adhered on the tube surface, etc., are also measured.

The disadvantages of this test are the difficulty in observing the tube condition during the test period of 1 to 3 months, and the high installation and operation costs of test heat exchanger. Therefore, this method is not a general monitoring method. It is usually carried out to evaluate the effect of a new cooling water treatment program or an improved program after trouble occurrence.

(b) Monitoring of scaling

(i) Estimation of scaling tendency from water quality

As described in the sections 3.3.1 and 3.3.5, the comparison of the actual pH (pH_a) of a cooling water with the critical deposition pH (pH_c) of each scale component gives the estimation that the scaling may occur or not in the cooling water system. The effect of a scale inhibitor is also predicted by calculating the allowable pHc under the inhibitor treatment.

The comparison of two kinds of cycles of concentration calculated from the concentrations of scale forming ions (calcium ion, etc.) and non-scale forming ions (chloride ion, etc.) also gives the estima-

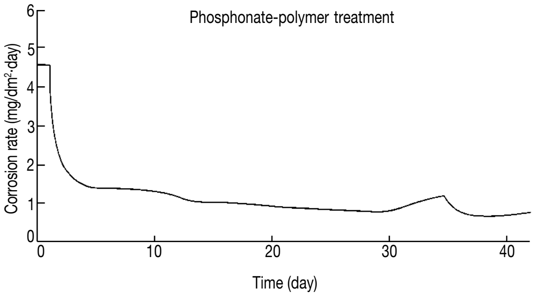

Fig. 3.76 Monitoring of carbon steel corrosion rate by a corrosion meter

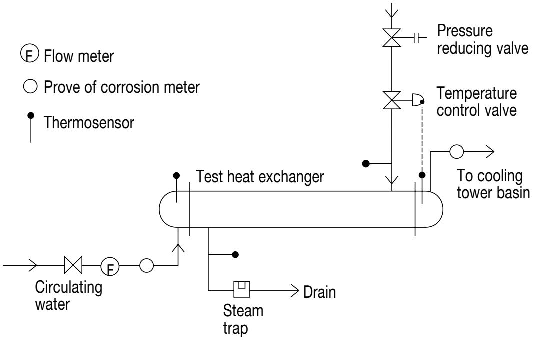

Fig. 3.77 Flow diagram of a test heat exchanger

tion that the scale deposition has occurred or not in the system.

(ii) Test heat exchanger

The scaling condition of actual heat exchanger is predicted by using a test heat exchanger. The scaling rate of test heat exchanger is calculated by using the following equations:

$$W_S = W_1 - W_2 \quad \text{.......................................} \quad (3.69)$$

$$V_S = \frac{W_S}{S} \times \frac{30}{D} \quad \text{.......................................} \quad (3.70)$$

where

W_S = amount of scale (mg)
W_1 = weight of tube with scale (mg)
W_2 = weight of tube after scale removal (mg)
V_S = scaling rate (mg/cm^2·month)
S = surface area of tube (cm^2)
D = test period (day)

Since fouling materials adhered on tube surface contain corrosion products, slime (biofouling) other than scale components, the adhesion rate of each component is usually determined from the total amount of fouling and the chemical analysis of the fouling materials.

Figures 3.43 and 3.44(p.3-33) show the typical scaling rates obtained by using test heat exchangers.

(c) Monitoring of biofouling

As mentioned in the section 3.4.3, the monitoring methods of biofouling include the analysis of circulating water, such as the measurements of the water turbidity, slime volume and bacterial number, and the measurement of the amount of biofouling adhered on glass slide or test tube.

Since the occurrence of biofouling problems is dependent on more factors in comparison with the corrosion and scale problems, only one monitoring method scarcely gives the correct result. Accordingly, the monitoring and the evaluation of biocides are usually carried out by using many kinds of tests along with experimental judgment.

(d) Total monitoring of cooling water treatment by KURITA MOBILE LABORATORY[34),35)] (KML)

The KML is composed of a vehicle loaded monitoring system, automatic water quality analyzers and computers. It is applied to monitor the corrosion, scale and biofouling conditions of open recirculating cooling water systems and to totally diagnose the chemical treatment effects.

Photographs 3.15 and 3.16 (p.3-76) show the exterior and interior views of the KML. Figure 3.78 (p.3-76) illustrates the main equipments loaded on the KML. Figure 3.79 shows the schematic diagram of monitoring and diagnosis system loaded on the KML.

Corrosion rate is monitored by using corrosion meters, test coupons and test tubes with heat loads. Scaling rate including corrosion product and biofouling is monitored by measuring the fouling factors of test tubes heated with electric heaters. The equations (3.71) and (3.72)[36)] are used for calculating the fouling factor.

$$Q = \frac{K_W \times 859.8}{S} \quad \text{.......................................} \quad (3.71)$$

$$\gamma = \frac{T_{Wf} - T_{Wc}}{Q} \quad \text{.......................................} \quad (3.72)$$

where

Q = heat flux of test tube (kcal/m^2·h)
K_W = heat duty of electric heater (kW)
S = heat transfer area of test tube (m^2)
γ = fouling factor (m^2·h·°C/kcal)
T_{Wf} = tube wall temperature with fouling (°C)
T_{Wc} = tube wall temperature without fouling (°C)

The heat duty of the electrical heater and the wall temperature of test tube are continuously measured under the steady state of bulk water temperature and water flow rate. Those data are put into the computer for calculating the fouling factor of test tube.

The diagnosis system analyzes and evaluates the data relating the operational conditions of a system, such as water quality, chemical injection rate and water balance. Then the system prints out comments and suitable countermeasures if the system conditions have some problems. The diagnosis system also selects and prints out a recommended cooling water treatment program when the operational data of the system are put into it.

(2) Closed recirculating cooling water systems

Scale and biofouling problems scarcely occur in closed recirculating cooling water systems. The probability of corrosion problems is also lower as compared with open recirculating cooling water systems.

Test coupon or corrosion meter is sometimes applied for monitoring the corrosion condition in this system.

(3) Once through cooling water systems

Since corrosion resistance materials are usually

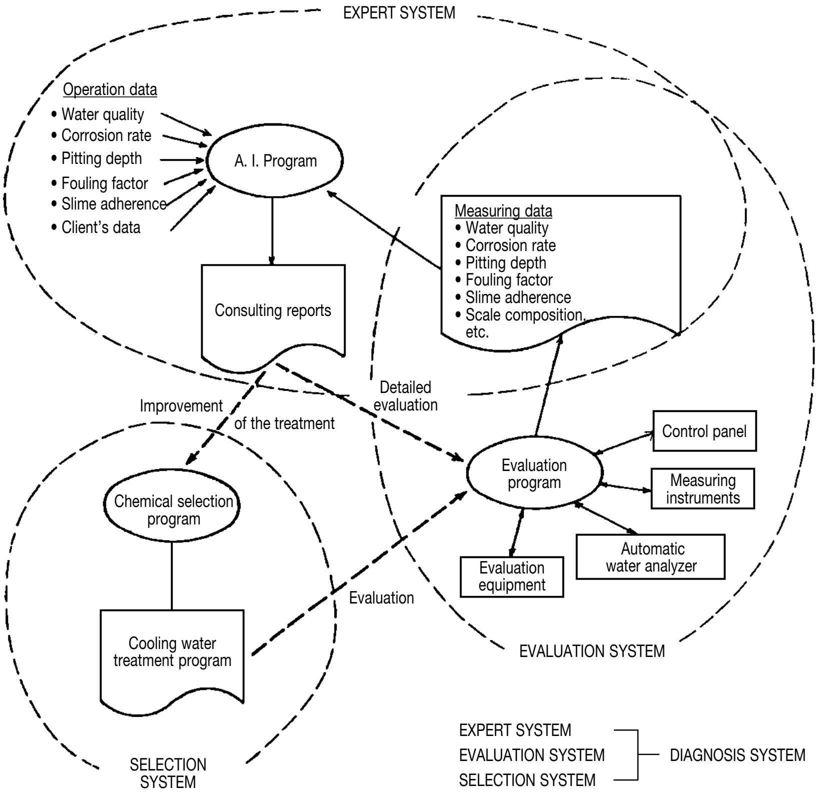

Fig. 3.79 Schematic diagram of the monitoring and diagnosing system of the KURITA MOBILE LABORATORY

used for heat exchanger tubes, corrosion problems scarcely occur in once through cooling water systems. Scale problems rarely occurs in this system because the dissolved solids in cooling water are never concentrated in the system.

Only bacterial count is usually applied for monitoring the effect of chlorination.

3.6.3 Inspection and Cleaning of Heat Exchangers

Oil refineries and petrochemical factories usually employ open recirculating cooling water systems including many heat exchangers. In these factories, the scheduled shutdown of their plants is usually carried out to inspect their equipments and to repair them if necessary. The duration and frequency of the shutdown maintenance are generally around one month and once a year to three years respectively. The frequency recently tends to reduce for increasing the production and lowering the maintenance cost.

During the shutdown maintenance period, the water cooled heat exchangers should be inspected and cleaned if necessary for their next safe and efficient operations. The inspection data are useful to evaluate the effect of chemical treatment and to improve it if necessary. The data are also utilized to determine the time for the cleaning of heat exchangers and the replacement of the tube bundles.

(1) Inspection methods of heat exchangers

(a) Visual inspection

The corrosion, scale and biofouling (slime and sludge) conditions of the tubes, tube sheets, water chambers, etc. of heat exchangers are observed and evaluated by inspectors.

The visual inspection has many merits shown as follows:

① Possible to check many items, such as the form of corrosion, the appearances and amounts of corrosion product, scale and biofouling, at many inspection points in a short period,
② Simple and easy inspection procedure,
③ Low inspection cost.

However, the visual inspection has following disadvantages:

① Limited inspection points which are visible from outside,
② Difficulty in quantifying the inspection results,
③ Different inspection results depending on each inspector.

Therefore, following measures are required for quantifying the visual inspection results:

① Determination of inspection standard,
② Quantification of inspection results by using measuring apparatus, such as a depth gauge and a scale thickness meter,
③ Extension of inspection points by using a fiberscope,
④ Recording of the conditions of inspected points by sketching or photographing.

(b) Non-destructive inspection

Recently, non-destructive inspection methods, such as ultrasonic thickness measurement and eddy current testing, are used for inspecting the corrosion condition of heat exchanger tubes and so on.

These non-destructive inspection methods are very effective to determine the corroded portions and the degrees of corrosion without tube removal from heat exchangers. The application of these inspection methods may be useful to evaluate the effect of cooling water treatment chemicals and to determine the time for the replacement of heat exchanger tube bundles more exactly.

The inspection of fouling material thickness on heat exchanger tubes is important because the fouling reduces the heat transfer efficiency. An electromagnetic film thickness meter easily measures the fouling thickness.

(c) Inspection of tubes removed from heat exchangers

The periodical inspection of tubes removed from heat exchangers is sometimes carried out to determine the time of tube cleaning or replacement.

The main items of the tube inspection are the tube wall thickness, the maximum pit depth, the amount and thickness of fouling materials and so on. In this inspection, the heat exchangers to be inspected have to be carefully selected because a large expenditure is required on the tube removal, the inspection and the installation of new tubes. Generally, following heat exchangers are selected and inspected:

① Heat exchangers tending to reduce the thermal efficiencies (heat exchangers with high outlet water temperature or high heat load),
② Heat exchangers suspecting corrosion problems (heat exchangers with low water flow rate) ,
③ Heat exchangers with the typical operation conditions in the system.

Since only several tubes are removed from a heat exchanger having the hundreds to thousands tubes and inspected, it is difficult to estimate the entire tube bundle condition from the inspection results. In the case of maximum pit depth estimation, the statistical theory with extreme values is applied for obtaining more accurate result. Table 3.39 and Figure 3.80 show an example of maximum pit depth estimation using the statistical theory.

In this case, the maximum pit depth of the sample tubes is 1.60 mm and the estimated pit depth in all the heat exchanger tubes is 2.05 mm.

(d) Chemical analyses and microscopic observation of fouling materials

The chemical analyses of fouling materials adhered on tubes give the useful information to estimate the causes of the fouling and to determine the countermeasures for reducing the fouling.

When the cause of the fouling is estimated to be biofouling, the presence of microorganisms should be confirmed with the microscopic observation.

(e) Record and utilization of inspection results

The inspection results obtained during the shutdown maintenance are recorded for each heat exchanger with reference to the specification of heat exchanger, actual operating conditions, previous inspection results, water quality, etc. Then such data should be utilized in order to enable the safety and efficient operation of the cooling water system.

(2) Cleaning of heat exchangers

Certain amounts of corrosion products, scale and biofouling accumulate in heat exchangers during the long operating period. These fouling materials cause troubles, such as the thermal efficiency drop of heat exchanger and the acceleration of corrosion under the fouling.

Therefore, the cleaning of heat exchangers is required for the safe and efficient operation of cooling water systems. Since the details of heat exchanger cleaning are discussed in the Chapter 9, the cautions for heat exchanger cleaning are briefly explained here.

Fouling materials accumulated in tubular heat exchangers are usually removed by a high pressure water-jet cleaning with the pressure of 200 to 350 kg/cm^2, except in the case of shell side of fixed

Table 3.39 Maximum pit depths of sample tubes and items relating to the statistical theory with extreme values

Rank order J	Maximum pit depth (mm) X	T	ϕ	Y
1	1.60	12	0.917	2.44
2	1.57	6	0.833	1.70
3	1.53	4	0.750	1.25
4	1.49	3	0.667	0.903
5	1.41	2.4	0.583	0.618
6	1.40	2	0.500	0.367
7	1.39	1.71	0.417	0.133
8	1.38	1.5	0.333	-0.094
9	1.30	1.33	0.250	-0.327
10	1.28	1.2	0.167	-0.583
11	1.27	1.09	0.0833	-0.910

T: ordinal number = (n+1)/J, n: number of samples (= 11)
ϕ: cumulative relative probability, Y: reduced dariate

tube sheet type heat exchangers. Table 3.40[37] shows the damages of metals due to the water-jet cleaning. The damages of the metals are very small.

Chemical cleaning is applied for the shell side of fixed tube sheet type heat exchangers, the water jacket of reactors and so on of which the application of water-jet cleaning is difficult because of their structures. However, the following measures are required for preventing problems caused by the acid cleaning:

① Perfect discharge of removed sludge from the heat exchangers by applying higher flow rate of cleaning solution, sufficient water flushing after cleaning, etc. ,
② Application of suitable neutralizing and passivation procedures after cleaning to prevent the corrosion caused by the residual acid and sludge ,
③ Storage of heat exchangers in the dry conditions to prevent the corrosion after cleaning until the operation start-up .

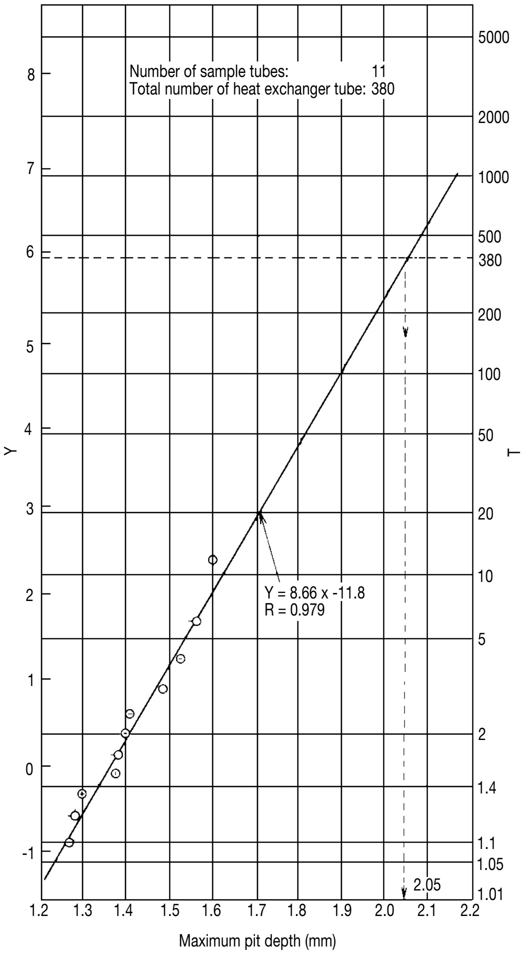

Fig. 3.80 Estimated maximum pit depth in whole tube bundle by the statistical theory with extreme values

Table 3.40 Damage of metals by a high pressure water-jet cleaning*

Material	Damage of metal (mg/cm^2)
Stainless steel (SUS-304)	0.00
Carbon steel (SS-41)	0.06
Cast iron (FC-20)	0.05
Cupronickel	0.04
Aluminum	0.63

* Water pressure: 300 kg/cm^2
Cleaning period: 30 seconds

3.6.4 Cautions for the Cooling Water Treatment of New Plants

In a new plant, unexpected severe corrosions are sometimes observed when the carbon steel heat exchangers are inspected in the first shutdown maintenance.

The following causes of these corrosions are generally considered:

① Operation of hydraulic test and water flushing of heat exchangers, and test run of the system without adequate water treatment corrode the new heat exchangers before the application of cooling water treatment chemicals.
② Fluctuation of cooling water quality, unexpected stoppage of water circulation caused by system load fluctuation, troubles in process

plant and so on deteriorate the effect of chemical water treatment and cause the corrosion of heat exchangers during the test run. ,

③ Fouling materials on new heat exchanger tubes, such as mill scale formed during the manufacturer, rust-proof oils and greases applied for the heat exchanger manufacture, and mud, sand, welding scraps, etc., adhered on tubes during construction, deteriorate the effect of water treatment chemicals and cause the local corrosion of heat exchanger tubes.

(1) Corrosion prevention of new plants

The countermeasures for the corrosion problems occurred in new plants are described here.

(a) Reconfirmation of the system operation conditions before the start-up of plant operation

As the designed conditions of plants are sometimes modified immediately before or during construction, the final designed conditions of heat exchangers (materials and operational conditions of heat exchangers, etc.) and the entire system are reconfirmed before the operation begins.

(b) Corrosion inhibition of heat exchangers during the hydraulic test

When the hydraulic test of each carbon steel heat exchanger is carried out, a sufficient concentration of nitrite or polyphosphate based corrosion inhibitor should be dosed into the test water to prevent the corrosion at the stagnant condition.

(c) Corrosion inhibition during water flushing of cooling water system

The water flushing of heat exchangers is usually carried out after the completion of the flushing of water pipings.

Even during the flushing of pipings, the use of corrosion inhibitor and dispersant is recommended for preventing the corrosion of pipings and for promoting the removal of foreign materials from pipings.

At the flushing of heat exchangers, a polyphosphate based corrosion inhibitor should be dosed into the flushing water with the initial treatment concentration to prevent the corrosion. During the water flushing, the fouling materials, such as oil, welding scraps, mud, sand and rust within the system, are suspended and increase the turbidity in the circulation water. The use of polymer based dispersants and surfactants promotes the removal of fouling materials and keeps the system from their resedimentation.

Figure 3.81 shows the effect of a chemical flushing using a polyphosphate, polymer and surfactant.

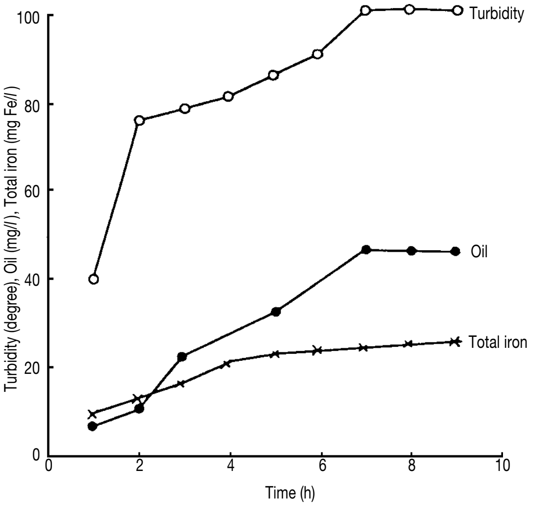

Fig. 3.81 Effect of a chemical flushing with a polyphosphate, polymer and surfactant based chemical in a new cooling tower system

It shows the excellent removal effect against fouling materials including oil and rust.

After reaching the turbidity of flushing water to the maximum value, the flushing water is discharged from the system by supplying fresh water. When the turbidity of circulation water is decreased to below 20 degrees, the water flushing is usually completed. During the flushing water discharge, the concentration of polyphosphate based inhibitor should be kept at higher than the minimum inhibition concentration to prevent the corrosion.

(d) Corrosion inhibition during test run

The initial treatment by using a high concentration of corrosion inhibitor is carried out to form the protective film on the whole metal surfaces constructed the system for preventing the initial corrosion after the completion of the flushing.

When the system is stopped for a long period after test run until the normal operation, the heat exchangers should be filled up with water including a corrosion inhibitor of the initial treatment concentration or should be dried up after discharging all the water.

When the cooling water quality fluctuates because of the fluctuation of the process operational condition during the test run, it is desirable that a polyphosphate or a polyphosphate-zinc based corrosion inhibitor is used at the higher dosage than the normal dosage to obtain the stable corrosion inhibition.

(2) Pretreatment of new carbon steel heat exchanger tubes

(a) Pitting corrosion of new tubes and its causes

Even if an appropriate cooling water treatment is applied, new carbon steel heat exchanger tubes tend to be attacked by pitting corrosion, and the maximum pit depth sometimes becomes 0.2 to 0.3 mm for the first month and approximately 0.5 mm for one year. Such pitting corrosion rate is usually lowered to 0.1 to 0.2 mm per year after the cleaning of heat exchangers with water-jet during the first shutdown maintenance as shown in Figure 3.82$^{38)}$.

The cause of initial pitting corrosion of new tubes is mainly the fouling of new tubes with mill scale, oils, greases, welding scraps, sand, mud etc., as described above.

(b) Inhibition of the pitting corrosion of new tubes by applying a pretreatment

As described in the section 3.6.4 (1), the application of suitable measures for the hydraulic test of heat exchangers, the water flushing and initial treatment of systems and so on effectively reduces the pitting corrosion rate of new heat exchanger tubes. However, when further reduction of the initial pitting corrosion is required, the application of a special pretreatment for new tubes is effective. Table 3.41 shows the effect of a pretreatment on new carbon steel tubes.

The pretreatment with a polyphosphate and surfactant completely prevents the initial pitting corrosion of new tubes because the pretreatment removes mill scale, rust-proof oil and so on from the tubes.

(c) Application method of pretreatment

This method is usually applied for new heat exchangers made of carbon steel. A temporary piping for the pretreatment is installed as shown in Figure 3.83 and the specified concentration of chemicals is dosed into the tank.

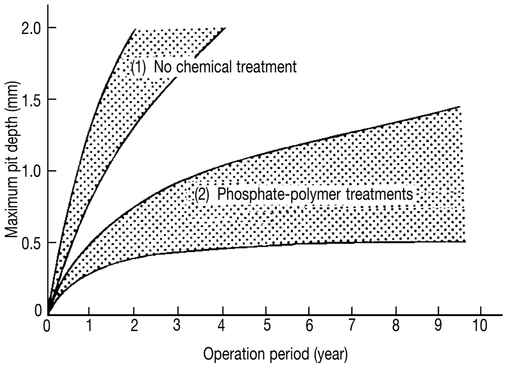

Fig. 3.82 Relationship between the maximum pit depths of carbon steel heat exchanger tubes and the operation periods

Table 3.41 Inhibition effect of a pretreatment on the pitting corrosion of new carbon steel tubes

Pretreatment	Tube manu-facturer	Number of pitting (number/dm^2)	Maximum pit depth (mm)*
No	A	120	0.41
	B	140	0.31
Polyphosphate 2.0% Surfactant 0.1%	A	0	0
	B	0	0

* Test period: 1 month

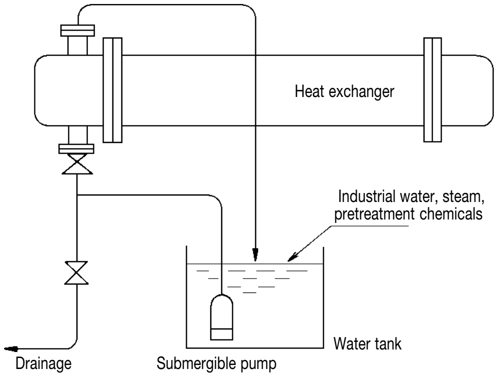

Fig. 3.83 An example of temporary piping for a pretreatment of new heat exchanger

The pretreatment solution is circulated at the temperature of 50 to 60° C during 3 to 5 hours. After the pretreatment, water flushing and initial treatment with a polyphosphate based corrosion inhibitor are carried out. Then, the temporary piping is removed and the heat exchanger is connected with the cooling water line.

3.7 Energy and Water Saving Operation of Cooling Water Systems

The operation costs of open recirculating cooling water system are summarized as follows:

①Power cost,
②Water cost,
③Cleaning cost of heat exchangers,
④Cost for cooling water treatment chemicals,
⑤Replacement cost of heat exchanger tubes.

The investment cost and the depreciation of fa-

Table 3.42 Operational conditions and specifications of a model cooling water system

Items	Operational conditions and specifications
Type of cooling tower	Induced draft cross flow type
Circulating water quantity (m^3/h)	3,000
Water temperature at inlet and outlet of cooling tower (℃)	43.6 and 32 (wet bulb temperature: 27℃)
Electric power of cooling tower fan	53 kW X 3 units
Electric power of water circulating pump	150 kW X 3 units
Evaporation loss (m^3/h)	60 (2% against circulating water quantity)
Windage loss (m^3/h)	3 (0.1% against circulating water quantity)
Holding water volume (m^3)	1,000
Duration of operation (h/year)	8,000
Heat exchanger	Tubular heat exchangers (4 paths) X 20 units
Heat transfer surface area	100 m^2/one unit X 20
Heat exchanger tube	Outer diameter: 19 mm Wall thickness: 2.2 mm Length: 5 m Material: Carbon steel
Water flow rate inside the tube (m/s)	1.0
Water temperature at the outlet of heat exchanger (℃)	50 or less
Designed fouling factor (cooling water side) (m^2·h·℃/kcal)	5 X 10^{-4}
Overall heat transfer coefficient (average) (kcal/m^2·h·℃)	500

Quality of make-up water

Turbidity (degree)	pH	Electrical conductivity (μS/cm)	M-alkalinity (mg $CaCO_3/l$)	Calcium hardness (mg $CaCO_3/l$)	Silica (mg SiO_2/l)
5	6.8–7.8	200	50	50	30

Table 3.43 Estimated operational cost of the model cooling water system (without chemical treatment)

Item		Operational cost		
		Cost (thousand yen/year)	Ratio against total cost (%)	
(1) Power cost	(a) Power cost for cooling tower fan	12,720	17	66
	(b) Power cost for water circulating pump	36,000	49	
(2) Make-up water cost		14,400	19	
(3) Cleaning cost of heat exchangers (water-jet cleaning)		3,000	4	
(4) Replacement cost of heat exchanger tubes		8,000	11	
Total cost		74,120	100	
Basis of cost estimation	Electric power cost (yen/kW)	10		
	Cycles of concentration	1.5		
	Make-up water cost (yen/m^3)	10 (Industrial water)		
	Cleaning cost of heat exchanger	1,500 thousands yen/20 units of heat exchangers for 2 times per year		
	Replacement cost of heat exchanger tubes	1,200 thousands yen/100 m^2 of heat transfer area Heat exchanger tubes and baffle plates are changed every 3 years.		

cilities, and the interest are excluded from the consideration here.

Table 3.42 shows the operational conditions and specifications of a model cooling water system in a petrochemical plant for discussing the energy and water saving effect by applying a suitable chemical water treatment.

When this cooling system is operated without chemical water treatment at the cycles of concentration of 1.5, the operation cost is calculated as shown in Table 3.43. In this cooling water system, the power cost occupies approximate 66% of the total cost. Therefore, the saving of power cost for the cooling tower fans and the circulating pumps is a very important in the total cost saving.

3.7.1 Power Cost Saving by Chemical Water Treatment

When cooling water system is operated without chemical water treatment, the efficiencies of heat exchangers and cooling tower are lowered by adhering of fouling materials such as corrosion product, scale and biofouling (slime) with them. When the circulation rate of water and the quantity of airflow in the tower are increased to recover their efficiency drops, the power cost of circulating pumps and cooling tower fans must be increased.

For keeping their efficiencies and saving their power costs, the application of suitable chemical water treatment is essential to keep them from all kinds of fouling materials. In this section, the thermal efficiency drop of heat exchangers with fouling materials and the prevention methods are summarized.

(1) Thermal efficiency drop with corrosion product

Heat exchanger tubes made of carbon steel are corroded at the high rate of 50 to 150 mg/dm^2·day (0.25 to 0.75 mm/year) in cooling water of no chemical treatment. The most of corrosion product (90% or more) adheres on the tube surface and reduces the thermal efficiency.

Figure 3.84[24)] shows an example of the change in the overall heat transfer coefficient (U value) of a heat exchanger by the adhesion of corrosion products. The thermal conductivity of corrosion product of carbon steel is calculated at around 0.5 kcal/m·h·°C from the change of U value and the thickness of corrosion product.

The allowable thickness of corrosion product to satisfy the designed fouling factor of heat exchanger is calculated by using this thermal conductivity as shown in Table 3.44. In the case of normal heat exchangers with the designed fouling factor of 5 X 10^{-4} m^2·h·°C/kcal, the corrosion rate of the carbon steel tube has to be controlled below 10 mg/dm^2·day (below 0.05 mm/year) by using a corrosion inhibitor to keep the thickness of corrosion product 0.25 mm or less during the one year continuous operation.

In other words, the use of appropriate corrosion inhibitor can reduce the water flow rate in heat exchanger without the efficiency drop and will realize the power cost saving for the circulating pumps. For example, in the cooling water system shown in Table 3.42, the use of corrosion inhibitor enables the stoppage of one among the three pumps for the power cost saving. In this case, the water flow rate of heat exchanger tube inside is lowered from 1.0 m/s to 0.67 m/s with the stoppage of one pump.

(2) Thermal efficiency drop with scale

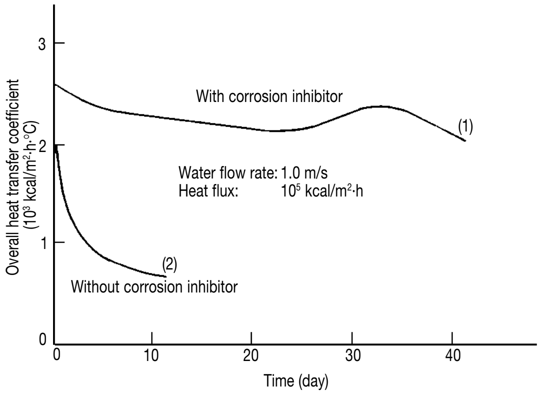

Fig. 3.84 Change of the overall heat transfer coefficient of a heat exchanger by the adhesion of corrosion products

Table 3.44 Relationship between the designed fouling factor of heat exchanger and the allowable thickness of corrosion product

Designed fouling factor*1 (m^2·h·°C/kcal)	1X10^{-4}	2X10^{-4}	3X10^{-4}	5X10^{-4}	1X10^{-3}
Allowable thickness of corrosion product*2 (mm)	0.05	0.10	0.15	0.25	0.50

*1 Cooling water side

*2 Thermal conductivity of corrosion product: 0.5 kcal/m·h·°C

The increases of water temperature and the cycles of concentration may cause a reduction in the thermal efficiency of heat exchanger due to the scale adhesion of calcium carbonate, calcium phosphate and so on.

Figure 3.85 shows the thermal efficiency drop of a heat exchanger with calcium phosphate scale and the inhibition effect of a scale inhibitor. As the thermal conductivity of calcium phosphate scale is around 0.8 kcal/m·h·°C, relationship between the allowable scale thickness and the designed fouling factor of heat exchanger is calculated as shown in Table 3.45.

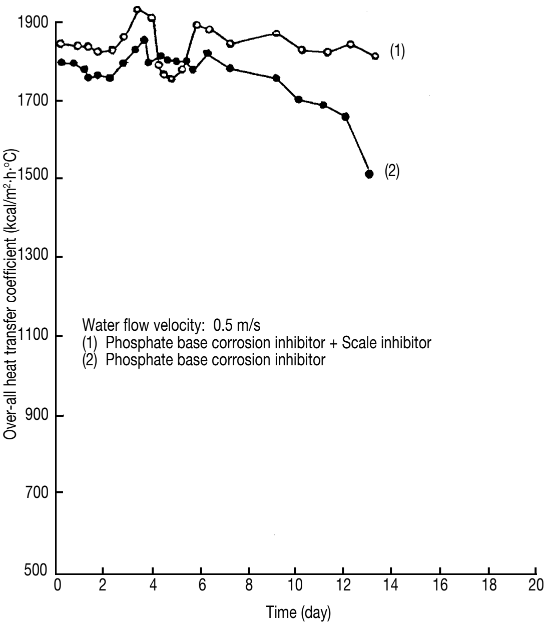

Fig. 3.85 Thermal efficiency drop of a heat exchanger by calcium phosphate scaling and the scale prevention effect of a polymer based scale inhibitor

Table 3.45 Relationship between the designed fouling factor of heat exchanger and the allowable scale thickness (calcium phosphate)

Designed fouling factor[*1] (m^2·h·°C/kcal)	$1X10^{-4}$	$2X10^{-4}$	$3X10^{-4}$	$5X10^{-4}$	$1X10^{-3}$
Allowable scale thickness[*2] (mm)	0.08	0.16	0.24	0.40	0.80

[*1] Cooling water side

[*2] Thermal conductivity of calcium phosphate: 0.8 kcal/m·h·°C

Under the treatment with phosphate based corrosion inhibitors, the application of scale inhibitors is inevitable to prevent the heat exchanger from the efficiency drop by scaling.

In the case of heat exchanger with the designed fouling factor of 5 X 10^{-4} m^2·h·°C/kcal, the scale adhesion of 0.4 mm or more causes the efficiency drop and requires the heat exchanger cleaning to recover the efficiency.

When polyphosphate based corrosion inhibitors are used without scale inhibitors, the permissible water temperature for scale adhesion is 40 to 45°C, however, the temperature limit increases to 60 to 70°C when phosphonate based corrosion inhibitors and scale inhibitors are used together.

In the cooling water system shown in Table 3.42, when one circulating pump is stopped, the water temperature at the outlet of heat exchanger is raised from 50 to 59°C with the reduction of water flow. However, the application of suitable chemicals, such as a phosphonate and polymer combination, keeps the efficiencies of heat exchangers in their designed allowances by preventing corrosion and scaling even under the elevated water temperature.

(3) Thermal efficiency drop with biofouling (slime)

Supply water and return water temperatures in

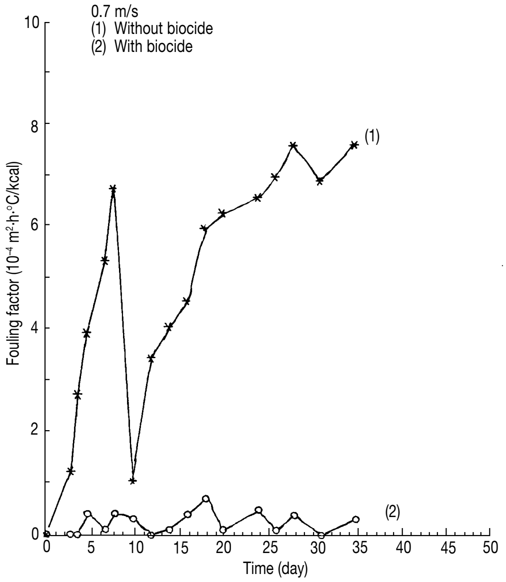

Fig. 3.86 Increase in the fouling factor of a heat exchanger with slime adhesion and the effect of a biocide

cooling water systems are generally around 30°C and around 40°C respectively. This temperature range is the optimum condition for microorganism growth as shown in Figure 3.50(p.3-38). Therefore, slime rapidly adheres to the heat exchangers and reduces their efficiencies under no chemical treatment condition. Figure 3.86[39] shows the increase in the fouling factor of a heat exchanger with the biofouling and the prevention effect of a biocide.

The reduction of water flow velocity for power cost saving may increase the slime adhesion and sludge accumulation rates as shown in Figures 3.53 and 3.54(p.3-40). However, the application of suitable biocide sufficiently prevents the increase of fouling factor as shown in Figure 3.86.

As the thermal conductivity of slime is measured at around 0.4 kcal/m·h·°C, the relationship between allowable slime thickness and the designed fouling factor of heat exchanger is calculated as shown in Table 3.46. Since the thermal conductivity of slime is the smallest among those of all fouling materials, the slime adhesion gives the biggest influence against the thermal efficiency of heat exchanger.

Therefore, the sufficient care should be paid for the biofouling control under the power cost saving operation of cooling water system.

3.7.2 Power Cost Saving for Cooling Tower Fans

The drop of air temperature increases the efficiency of cooling tower. Therefore, when cooling tower fans are constantly operated at the designed rotating speed regardless of air temperature, the supply water is overcooled and the some part of electric power for the fans is wasted in cold seasons.

This electric power loss is saved by controlling the rotating speed of fans or the partial stoppage of fan operation according to the change of air temperature.

Table 3.46 Relationship between the designed fouling factor of heat exchanger and the allowable slime thickness

Designed fouling factor*1 (m^2·h·°C/kcal)	$1X10^{-4}$	$2X10^{-4}$	$3X10^{-4}$	$5X10^{-4}$	$1X10^{-3}$
Allowable slime thickness*2 (mm)	0.04	0.08	0.12	0.20	0.40

*1 Cooling water side

*2 Thermal conductivity of slime: 0.4 kcal/m·h·°C

In our experiences in Japan, the electric power consumption by tower fans is saved around 20% by the partial operation stoppage in winter or around 74% by controlling the rotating speed of fans automatically during the one year operation.

3.7.3 Water Cost Saving by Chemical Water Treatment

As shown in Table 3.43, the allowable maximum cycles of concentration is generally 1.5 in the case of cooling water system operated without chemical water treatment. The application of suitable chemical treatment enables to increase the cycles of concentration around 5.0 or higher generally. Table 3.47 shows an example of water cost saving in the cooling water system when the cycles of concentration is increased from 1.5 to 6.0 by applying suitable water treatment chemicals.

Around 60% of water cost is saved by applying chemical water treatment comparing with that of no chemical treatment condition.

3.7.4 Saving of Maintenance Cost of Heat Exchangers

The application of suitable water treatment chemicals keeps heat exchangers from their fouling and extends the service lives by reducing the corrosion rate. As the results, the frequency of heat exchanger cleaning reduced at least from twice per year to once per year and extends the service lives of heat

Table 3.47 Water cost saving by applying a chemical water treatment in the model cooling water system

Chemical treatment	No	Yes
Circulating rate (m^3/h)	3,000	
Evaporation loss (m^3/h)	60	
Cycles of concentration	1.5	6.0
Total blowdown (m^3/h)	120	12
Make-up water (m^3/h)	180	72
Make-up water consumption*1 (m^3/year)	1,440,000	576,000
Water cost*2 (10^3 yen/year)	14,400	5,760
Water cost saved (10^3 yen/year)	—	8,640

*1 Operation period: 8,000 h/year

*2 Water cost: 10 yen/m^3

exchanger tube bundles from three years to ten years generally.

3.7.5 Total Cost Saving in the Operation of Cooling Water System by Chemical Treatment

The application of suitable water treatment chemicals keeps the heat exchangers from the fouling and extends the operation lives even under higher water temperature and lower water flow rate conditions because of the electrical power energy saving operation.

Table 3.48 shows the cost of cooling water treatment chemicals in the cooling water system when the system is operated at the cycles of concentration of 6.0. The cost of water treatment chemicals is around 9 million yen per year.

On the other hand, the saving in the operation cost by the application of water treatment chemicals

Table 3.48 Cost of cooling water treatment chemicals

Cycles of concentration			6.0
Total blowdown (m^3/h)			12
Cost of corrosion and scale inhibitor (10^3 yen/year)			5,760
Cost of chlorination (10^3 yen/year)			400
Cost of non-oxidizing biocide (10^3 yen/year)			2,640
Total cost (10^3 yen/year)			8,800
Basis of cost estimation	Corrosion and scale inhibitor	Type	Phosphonate-polymer
		Unit price (yen/kg)	800
		Dosage (mg/*l*)	75*[1]
	Chlorine compound	Type	Sodium hypochlorite
		Unit price (yen/kg)	30
		Dosage (kg/day)	40
	Non-oxidizing biocide	Type	Organic bromine compound
		Unit price (yen/kg)	1,100
		Dosage (kg)	100/2 weeks

*[1] Dosage against total blowdown

Table 3.49 An example of the operational cost saving of the model cooling water system by applying water treatment chemicals (comparison with the case of no chemical treatment)

Item	Cost saving method	Saving ratio (%)	Amount of cost saving (10^3 yen/year)
(1) Power cost	(a) Control of fan rotating speed	74	9,400
	(b) Stoppage of one circulating pump	33	12,000
(2) Make-up water cost	(c) Application of chemicals (Increase of cycles of concentration: from 1.5 to 6.0)	60	8,640
(3) Cleaning cost of heat exchangers	(d) Application of chemicals (Reduction of cleaning frequency: from 2 times/year to once/year)	50	1,500
(4) Replacement cost of tube bundles	(e) Application of chemicals (Reduction of replacement frequency: from once/3 years to once/10 years)	70	5,600
(5) Cost saving	(a)+(b)+(c)+(d)+(e)	50	37,140
(6) Chemical cost (10^3 yen/year)	—	—	8,800
(7) Total cost saving	(5)−(6)	36	28,340

and the other measures is significant as shown in Table 3.49.

In this case, around 38% (28 millions yen/year) of total operation cost is saved by applying water treatment chemicals without any trouble occurrence comparing with no chemical water treatment conditions.

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4. Coagulants, Flocculants and Sludge Dewatering Agents

4.1 Outline of Water, Wastewater and Sludge Treatments

In water and wastewater treatment processes, substances which cause troubles in the systems utilizing water and pollute the environment are removed from water.

Removed suspended solids (SS) through water and wastewater treatment processes are discharged as sludge with high water content. Sludge treatment is carried out to prevent the sludge from causing the environmental pollution and the other problems again.

As water includes many kinds of dissolved solids and SS, suitable water treatment methods have to be selected according to the water quality to be treated. Water treatment methods are generally classified into three categories of mechanical, chemical and biological treatments.

In this section, those three treatment methods are outlined. The detail should be referred to the other books.

4.1.1 Mechanical Treatments

Mechanical water and sludge treatment methods are classified as shown in Figure 4.1.

(1) Screening

Screening is the first step of water and wastewater treatment to remove large matter by using screening bars or net to protect downstream structures, such as pumps, pipings and filters. Generally, the screening effectively removes the matter of large size and low specific gravity such as pieces of wood, plastics and papers.

(2) Settling

SS having larger densities than that of water are settled to separate from water. Factors which determine the settling velocity of SS are mainly the diameter and density of particles, and the viscosity of solution. The relationship among those factors is expressed in the Stokes' equation (refer to the section 4.2.2). The SS of small size and colloids which are hardly settled under natural conditions, are settled after forming their flocs through coagulation and flocculation treatment by using coagulants and flocculants.

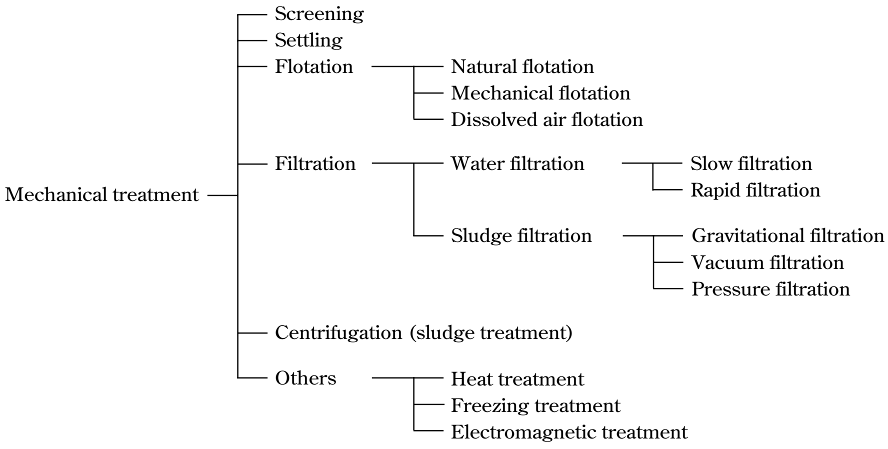


Fig. 4.1 Classification of mechanical water and sludge treatment methods

(3) Flotation

Substances having the almost same or lower densities than that of water, such as oils and fats, are separated from water by flotation. The flotating velocity of particles is also expressed in the Stokes' equation. Therefore, particles which have the large size and small density are easily floated under natural conditions. Mechanical flotation and dissolved air flotation are applied to increase the flotating velocity of particles. In those processes, fine air-bubbles are generated in water. Then the adhesion of bubbles with particles and the upward-flow of bubbles improve the flotation efficiency. Generally, the pressurizing of water and its releasing are applied to generate microbubbles efficiently.

(4) Filtration

Slow filtration applies to purify surface waters without prior coagulation or settling. The filtration rate is generally lower than 1 $m^3/m^2 \cdot day$.

Rapid filtration uses to treat drinking water, industrial water and wastewater. Generally, it applies after coagulation or flotation process. It is also used for the filtration of in-line coagulated water. The filtration rate is in the range of 4 to 50 $m^3/m^2 \cdot day$.

For sludge filtration, many kinds of vacuum filters and pressure filters are applied.

(5) Centrifugation

Centrifugation is a separation method which utilizes centrifugal force to accelerate the settling of particles in a liquid-solid mixture. This method usually uses for dewatering of sludges or for treating wastewater including high concentration of SS.

4.1.2 Chemical Treatment

Chemical treatment is generally applied to carry out mechanical treatment, such as settling, flotation and filtration, more efficiently. It is also used for treating waters which are difficult to treat sufficiently by mechanical treatment only.

Figure 4.2 shows the classification of chemical treatment methods and the kinds of typical chemicals to be applied.

(1) pH control

The solubilities of some substances in water are remarkably changed by the pH change. For example, the solubility of ferric ion or aluminum ion is sufficiently reduced to form the hydroxide precipitate in a specified pH range.

This method often applies to separate metallic ions from water and wastewater. The pH control of water is also an important measure to carry out coagulation, flocculation, oxidation, reduction treatments and so on efficiently.

(2) Coagulation and flocculation

Coagulation and flocculation treatment is a method to aggregate fine particles and colloids dispersed stably in water and to make their large flocs which are easily separated from water through settling, flotating processes and so on.

Ferric salts and aluminum salts are usually used as coagulants. High molecular weight synthetic polymers are used as flocculants. Coagulants neutralize the surface electrical charges of particles and break their stable dispersion in water. Flocculants combine with neutralized particles and form large flocs.

Thickeners, flotators, filters, etc. are used for separating those flocs from water.

(3) Oxidation and reduction

Oxidation treatment is applied to decompose cyanides, nitrites and various organic substances to harmless substances. It is also used for oxidizing ferrous ion in underground water to ferric ion which is easily precipitated as the ferric hydroxide.

The pH and temperature of water should be

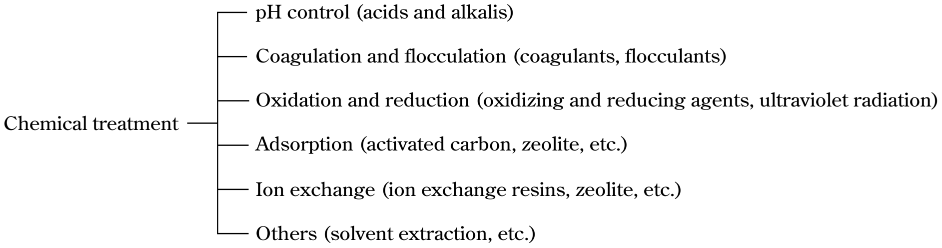


Fig. 4.2 Classification of chemical water and wastewater treatment methods

adjusted within the suitable ranges for proceeding the oxidation and reduction processes efficiently.

(4) Adsorption

Activated carbon adsorbs various organic substances in water.

Recently, special adsorbents which selectively adsorb specified heavy metal ions, etc., are also used for water and wastewater treatment.

Usually, adsorbants are filled in fixed-bed or fluidized-bed, and water to be treated passes through the bed. In a batch treatment, adsorbants are added into water and are separated by settling or filtration after the completion of adsorption.

The adsorbants after used are regenerated or disposed after making them harmless by solidification, etc.

(5) Ion exchange

In ion exchange process, ions in solution are exchanged with those of ion exchanger such as ion exchange resin. The ion exchanger approaching the full capacity is regenerated and reused.

In water treatment, ion exchangers are largely utilized for removing hardness from water (softening) and producing demineralized water. In wastewater treatment, they are applied for removing toxic substances, such as heavy metals, and recovering valuable materials from wastewater.

4.1.3 Biological Treatment

Biological treatment is a means of decomposing organic substances in wastewater by utilizing the functions of microorganisms.

Biological treatment is largely divided into aerobic and anaerobic treatments as shown in Figure 4.3.

(1) Aerobic treatment

Aerobic treatment is a way of oxidizing and decomposing organic substances in wastewater by using aerobic or facultative anaerobic bacteria. It is also called biological oxidation.

Organic substances are oxidized and decomposed by enzyme reactions of microorganisms and produce energy. Microorganisms multiply using a portion of the energy and organic substances. The excess of microorganisms grown must be separated and disposed as the excess sludge.

In activated sludge system, wastewater is mixed with microbial flocs (activated sludge) in the aeration tank to decompose the organic substances by supplying air (oxygen) to the mixed liquor.

The mixed liquor is separated in the sedimentation tank and the precipitated activated sludge is returned to the aeration tank. The supernatant water is discharged as treated water.

In activated sludge treatment, it is the most important thing to maintain a suitable environment for the activity of microorganisms. When the environment becomes an improper and the microbial activity is decreased, the efficiency of removing organic substances is reduced or an insufficient separation of sludge from water (bulking) may occur.

The suitable operation conditions of activated sludge system are generally as follows;

pH = 6–8
Temperature = 15–30℃
Dissolved oxygen = more than 0.5 mg/*l*
BOD load = 0.2–0.6 kg BOD/kg MLSS·day

(2) Anaerobic treatment

This treatment method is also called anaerobic digestion or methane fermentation, and utilizes anaerobic bacteria to decompose organic substances. Wastewater or sludges are introduced into

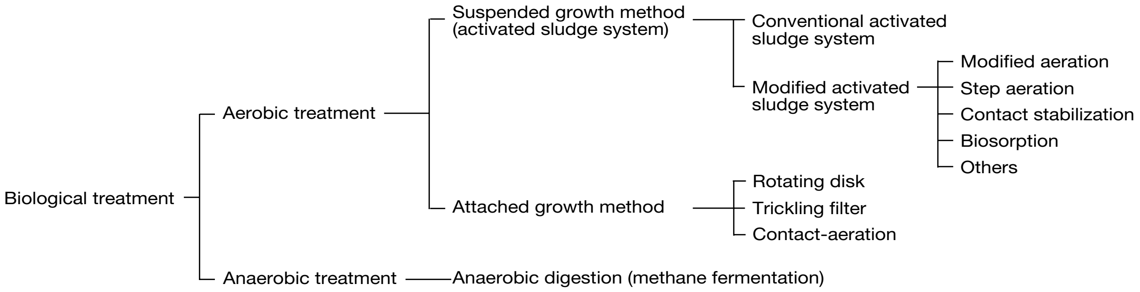


Fig. 4.3 Classification of biological wastewater treatment methods

a closed tank which is kept under anaerobic conditions and sometimes warmed to enhance the digestion. The retention time in the tank is from several days to several tens of days.

Anaerobic treatment is generally suitable for the treatment of wastes containing high concentrations of organic substances.

4.1.4 Flowsheet of Wastewater and Sludge Treatments

Various pollutants are contained in wastewaters. Therefore, mechanical, chemical and biological treatment methods are usually combined to treat them depending on the quality and quantity of the water.

Figure 4.4 shows a typical flowsheet of wastewater and sludge treatments including the applicable chemicals.

4.2 Coagulation and Flocculation

4.2.1 Outline of Coagulation and Flocculation Treatment

Coagulation and flocculation treatment is applied for removing inorganic suspended solids from water and wastewater. In the case of sewage and wastewater including organic SS, such as effluents from pulp and paper mills, and petrochemical plants, the coagulation and flocculation treatment is used for pre- or post-treatment of the activated sludge processes.

Coagulation and flocculation treatment is a process to bring SS together, which are stably dispersed as the fine and/or colloidal particles in water, and to make the large flocs by using coagulants and/or flocculants. To separate these flocs from the water, sedimentation (clarification), flotation or coagulation filtration treatment is applied.

Fine or colloidal particles in water have electrical charges on their surfaces or are covered with hydrophilic substances. Thus, they are stably dispersed because of their repellent forces.

Coagulants adsorb or react with these particles, and neutralize their electrical charges on the surfaces. As the result, their repellent forces are weakened and the particles are brought together. This function of coagulants is called coagulation or the electrical charge neutralization.

Furthermore, flocculants collect the coagulated particles to form large flocs. This action is called flocculation or bridging.

In the SS removal treatment of water and waste-

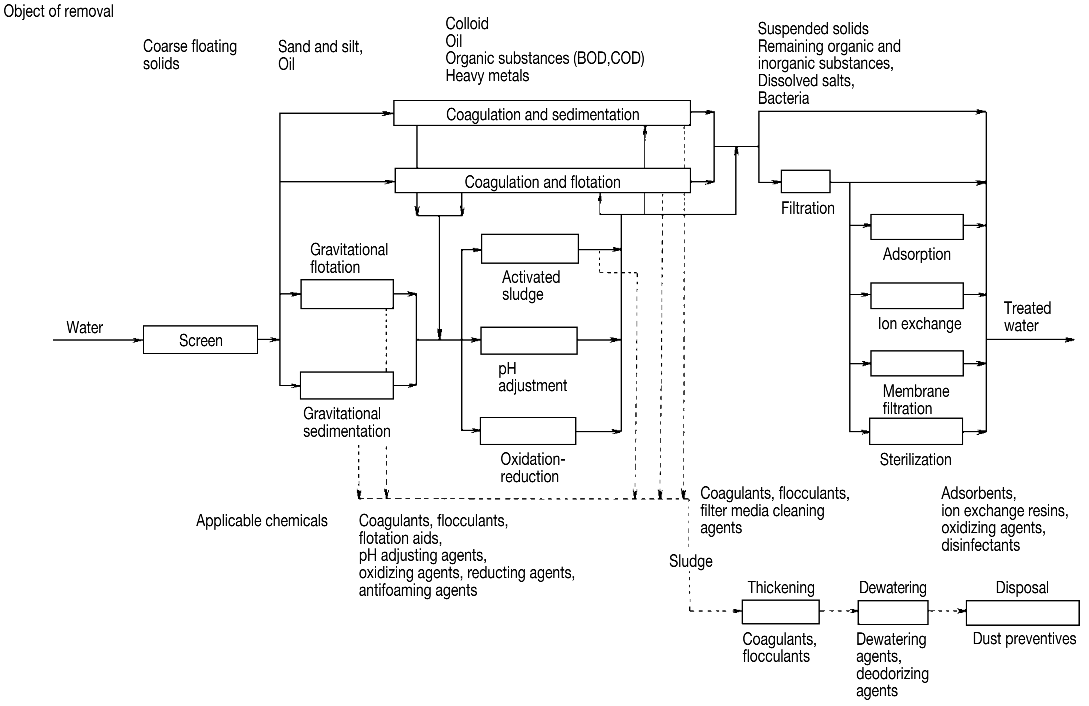


Fig. 4.4 Example of wastewater treatment processes and chemicals to be applied

water, both of coagulants and flocculants are generally used. In general, inorganic substances, such as aluminum salts and iron salts, are used as coagulants and high molecular weight organic polymers are used as flocculants.

4.2.2 Equipments for Floc Separation

After floc formation through coagulation and flocculation treatment, the flocs are separated from water by using clarifiers, flotation equipments or filters according to the concentration and characteristics of the flocs, the target SS concentration of treated water and so on.

Separated sludge is often concentrated by using thickeners before the dewatering treatment.

In this section, the structures, features and so on of these equipments are briefly described.

(1) Clarifiers

In sedimentation treatment, factors which determine the settling velocity of particles are mainly the diameter and density of particles, and the viscosity of solution. These relations are expressed in Allen's equation, Newton's equation, Stokes' equation, etc. However, the following Stokes' equation is generally used in the case of water and wastewater treatments.

$$V = \frac{g \cdot D_p^2 (d_p - d_w)}{18\mu} \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots (4.1)$$

where

V = settling velocity of particle (m/s)

g = gravitational constant (m/s^2)

D_p = diameter of particle (m)

d_p = density of particle (kg/m^3)

d_w = density of water (kg/m^3)

μ = viscosity of water (kg/m·s)

The use of coagulants and flocculants increases the settling velocity by forming flocs with large diameters. Thus, the use of coagulants and flocculants realizes the employment of compact and economical upflow clarifiers for SS separation.

Typical types of upflow clarifiers are sludge blanket type and solid-contact type. In the both units, the incoming water passes through the suspended layer of previously formed flocs, and the charge neutralization and the floc formation are efficiently done.

Figure 4.5 shows the structure of a solid-contact type clarifier.

In the case of upflow clarifiers, coagulants are dosed into the feedwater and flocculants are added into the mixing zone of clarifiers generally.

(2) Flotation equipments

In sedimentation treatment, flocs are sedimentated by utilizing the larger density of flocs than water. Therefore, when the density of flocs is similar to or lower than water density, no flocs is separated from water by sedimentation treatment. In that case, flotation equipments are used for floc separation.

When the density of flocs is sufficiently smaller than water one, flocs are naturally floated and separated. As the natural flotation separation is difficult when the floc density is similar to the water one, flocs are forcedly separated by attaching fine air bubbles with the flocs. Dissolved air flotation equipment (DAF) shown in Figure 4.6 is widely

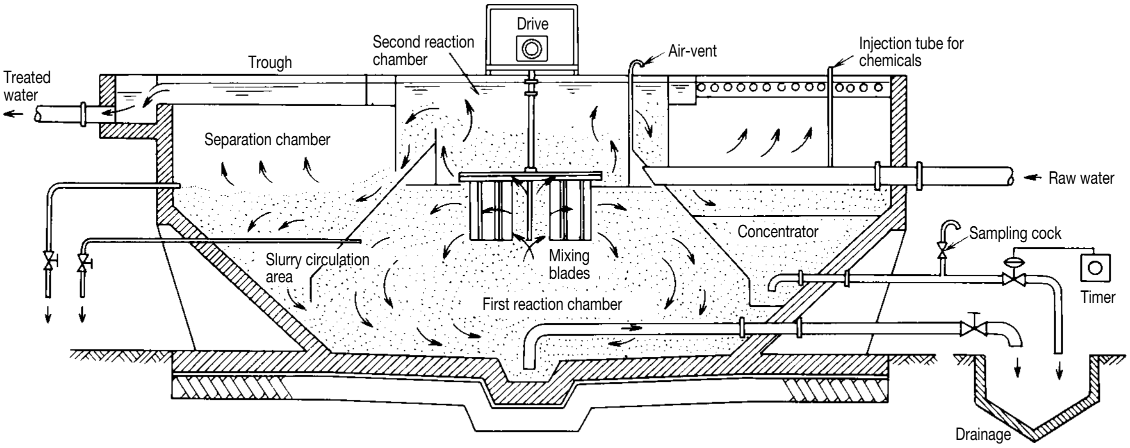


Fig. 4.5 Structure of a solid-contact type clarifier

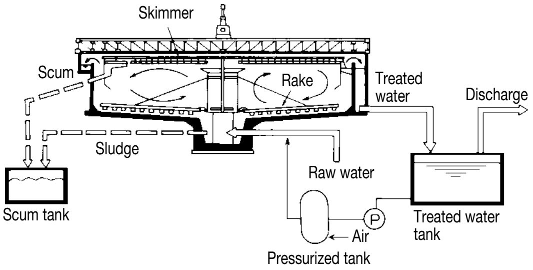


Fig. 4.6 Structure of a dissolved-air flotation equipment

used for separating oils, fats, organic flocs, etc, from water. This method is also applied for ore dressing.

In DAF, raw water or recycled treated water is sent to the pressurized tank and air from a compressor is dissolved into the water in the tank under the pressure of 2 to 5 kg/cm^2. The pressurized water is mixed with flocculated raw water with the volume of 3 to 4 times of the pressurized one and enters into the flotation clarifier through the pressure reducing valve. Thus, fine air bubbles are released from the water by the pressure reduction. The air bubbles attach with flocs and the flocs are floated.

Coagulants and flocculants are dosed into raw water and form large flocs in the flocculation tank, etc., before the mixing with pressurized water.

(3) Coagulation filtration equipments

When coagulants are added into raw water just before filtration, the electrical charges of particles in the water are neutralized and the micro-flocs are formed. By filtering this water, the filtrated water with very low SS concentration is stably obtained. This filtration method is called coagulation filtration. Pressure filter with double filter media of sand and anthracite is usually used for the coagulation filtration. Inorganic coagulants, such as aluminum salts and iron salts, are used for this treatment.

4.2.3 Mechanism of Coagulation and Flocculation

Since fine particles in water have the negative electrical charges on their surfaces generally, they repel each other and stably disperse in the water. Therefore, to sedimentate these particles, it is required to bring them together and to make large flocs.

As the first step of treatment, the charges of particles are neutralized by using chemicals and the micro-flocs are formed. This step is called coagulation and the chemicals using the charge neutralization are called coagulants.

Then, the micro-flocs are brought together to make the macro-flocs by adding another types of chemicals. This step is called flocculation (bridging) and the chemicals to be used are called flocculants.

Aluminum salts, iron salts, low molecular weight cationic polymers and so on are generally used as coagulants. High molecular weight organic polymers are used as flocculants.

A schematic model of coagulation and flocculation process is shown in Figure 4.7.

(1) Coagulation

Fine suspended particles in water generally have negative electrical charges on their surfaces because of the dissociation of substances composed of those particles, adsorption of metallic hydroxides, etc. This negative charges on the surface pull cations to the surface and repel anions. As the result, an electrical double layer is formed at the surround of the particle as shown in Figure 4.8.

The amount of cations becomes maximum near

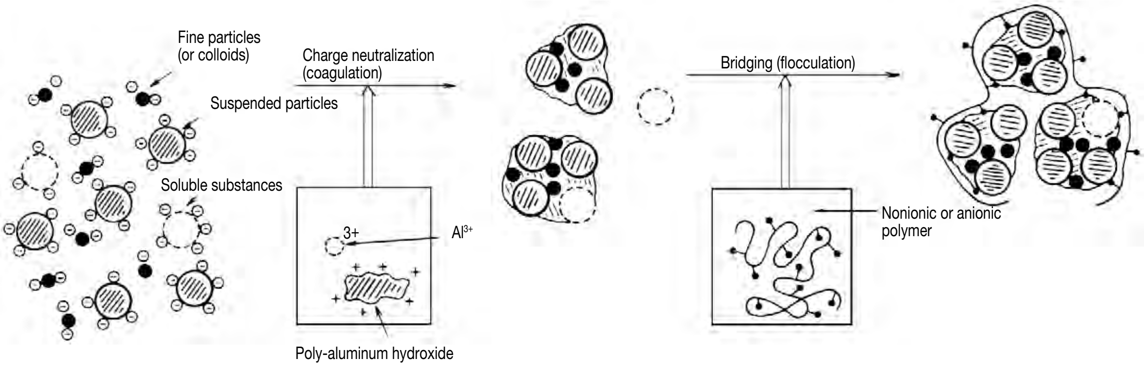


Fig. 4.7 Schematic model of coagulation and flocculation process

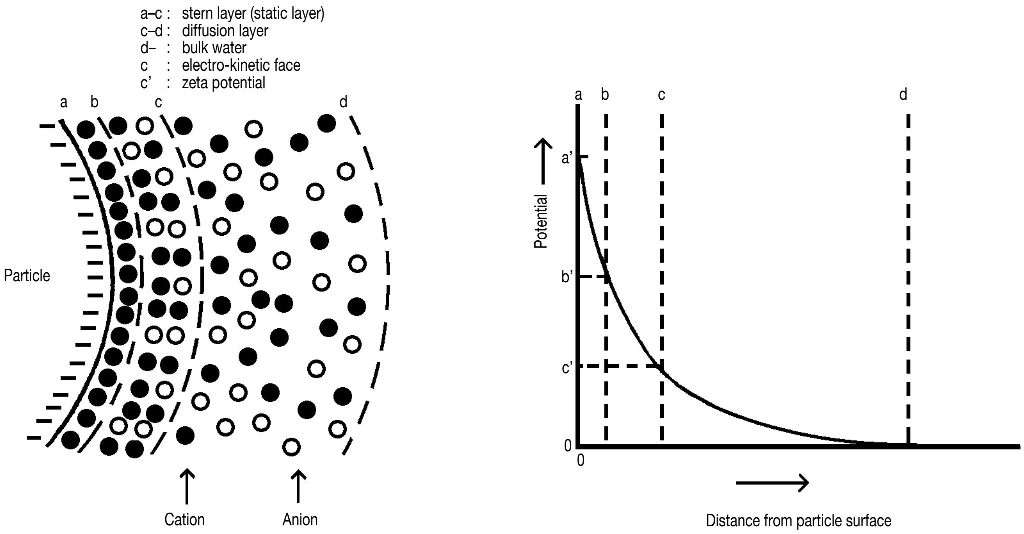


Fig. 4.8 Structure of the electrical double layer on a particle surface with negative charges in water

the particle surface (Stern layer) and the ratio of cations against anions gradually reduces for the bulk water. Thus, the ratio becomes the same to the bulk water at the interface between the diffusion layer and the bulk water. Accordingly, the electrical potential sharply drops in the Stern layer and becomes almost zero at the interface.

When a particle moves in water, a part of water moves together with the particle. The outer surface of this water moving with the particle is called the electro-kinetic face. The potential at the electro-kinetic face is called the zeta potential (c' of Figure 4.8).

The zeta potential is the remained potential of the particle, which can not be neutralized with cations in the inside of electro-kinetic face. As the measurement of the real surface potential or Stern layer potential of particle is impossible, the zeta potential is used an index showing the condition of electrical charge of particle. When two particles having the negative zeta potentials come near and the electrical repellent force between them is larger than the van der Waals force, the both particles repel each other.

When the sufficient amount of aluminum ions, ferric ions, low molecular weight cationic polymers and so on is added into water, the cations enter the inside of the electro-kinetic face of particle and reduce the zeta potential to near zero as shown in Figure 4.9.

As the result, the electrical repellent force between particles becomes almost zero and they combine together by the van der Waals force. At the same time, the deposition of metal hydroxide formed by the coagulant accelerates the floc formation.

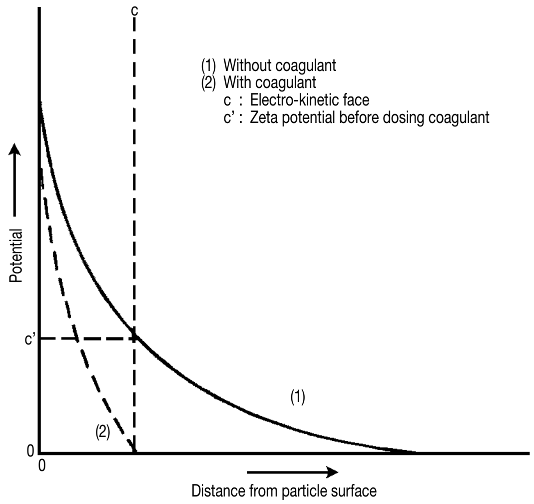


Fig. 4.9 Change of a zeta potential by coagulant dosing

The effect of inorganic coagulants becomes more effective as the valency of the metallic ion increases. The relationship between the valency of metallic ion and the minimum required concentration of coagulant for obtaining the sufficient coagulation effect is expressed in Schulze-Hardy's law, [equation (4.2)].

$$C \propto \frac{1}{U^6} \quad \cdots\cdots\cdots\cdots\cdots\cdots \tag{4.2}$$

where

C = minimum required concentration of coagulant (m mol/l)

U = valency of metallic ion

Accordingly, the C values of mono-, di- and trivalent metallic ions become the following ratio:

$$1:(\frac{1}{2^6}):(\frac{1}{3^6}) = 1:\frac{1}{64}:\frac{1}{729}$$

Table 4.1 shows the relationship between them for the coagulation of a suspended aqueous solution of coal examined by Noda1).

The effectivenesses of NaCl, $BaCl_2$ and $AlCl_3$ almost satisfy the Schulze-Hardy's law. The C values of organic cationic polymers which have the higher cationic valencies than inorganic ones are apparently lower than the C values of inorganic coagulants.

(2) Flocculation

Coagulants neutralize the charges of fine particles and form the micro-flocs by bringing them together. Further, flocculants are used to make macro-flocs by bridging the micro-flocs together.

High molecular weight anionic or nonionic polymers are usually used as flocculants. Typical functional groups of them are carboxyl group (-COOH) and amide group ($-CONH_2$).

These flocculants adsorb on the micro-flocs by using their functional groups. Carboxyl groups adsorb on the micro-floc by the electrostatic attractive force and the ionic bonding force with the metallic atoms, such as aluminum and iron, on the floc surface. The adsorption of nonionic polymer may be occurred by the hydrogen bonding force between the amide groups and hydroxy groups of metal hydroxide on the floc surface.

As flocculants adsorb on the floc by using a part of the functional groups, the free functional groups remain at the loop part separated from the floc surface as shown in Figure 4.102). Thus, when the micro-flocs come near, the free functional groups adsorb on the other floc surface and the flocs are combined as shown in Figure 4.113).

This function of flocculant making macro-flocs is called bridging.

Optimum dosage of flocculants is closely related

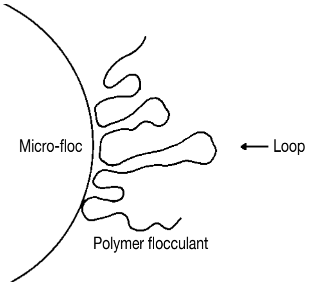


Fig. 4.10 Adsorption of a polymer flocculant on a micro-floc (formation of loop)

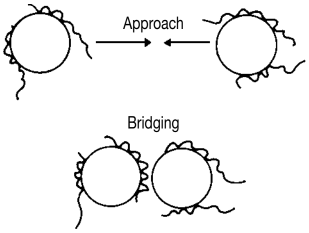


Fig. 4.11 Formation of a macro-floc by polymer flocculants (bridging)

Table 4.1 C values of various coagulants for the coagulation of a suspended aqueous solution of coal

Coagulant		C value	
Type	Chemicals	(mg/l)	(m mol/l)
Inorganic	NaCl	3750	64.2
	$BaCl_2$	250	1.20
	$AlCl_3$	40	0.30
Cationic surfactant	Aniline hydrochloride	750	5.79
	Dodecylamine hydrochloride	125	0.56
	Dodecylpyridiniumchloride	150	0.53
Organic cationic coagulant	Aniline-formaldehyde condensed polymer hydrochloride	2.0	—
	Polyhexamethylene-thiourea acetate	1.2	—
	Polyvinyl-benzyl-trimethyl-ammonium chloride	1.6	—

to the covering rate of floc surface with the flocculants. Of course, the insufficient dosage of flocculant causes the poor flocculation. The excess dosing brings the difficulty in bridging between flocs because the whole surfaces of flocs are covered with flocculants.

LaMer, et al.,[3] reported that the optimum covering rate with polymer flocculants is 0.5.

4.2.4 Inorganic Coagulants

(1) Kinds and features

In general, aluminum salts and iron salts are used as coagulants. The kinds and features of coagulants often used for raw water and wastewater treatments are summarized in Table 4.2.

(2) Application method

Since the effect of coagulant is considerably influenced by the application conditions, such as water pH and stirring condition, the sufficient attention should be paid to following conditions.

(a) pH

Each inorganic coagulant has the optimum pH range showing the excellent coagulation effect as shown in Table 4.2. This optimum pH range is the same to the pH range which the metallic ion composed of the coagulant stably precipitates as the hydroxide. For example, aluminum ion stably precipitates as the hydroxide in the pH range of 5.0 to 7.5 as shown in Figure 4.12[4], and the optimum pH range of alum or PAC is also 5.0 to 7.5.

This fact shows that not only electrical charge neutralization but also formation of metal hydroxide floc play the important role for the better coagulation of particles with inorganic coagulants.

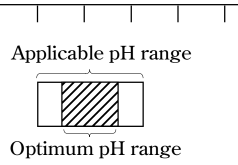
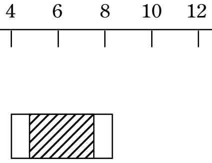
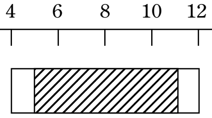
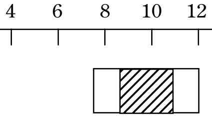
(b) Stirring strength and retention time

Strong stirring is required to increase the frequency which coagulants meet suspended particles to neutralize their electrical charges. Stirring also accelerates the floc formation by colliding the neutralized particles.

In the case of mixing tank for coagulation, the blade tip velocity of stirrer and the retention time are generally designed in the range of 1.5 to 3.0 m/s and 5 to 10 minutes respectively.

In general, the probability which neutralized particles collide and combine together with to form

Table 4.2 Kinds and features of inorganic coagulants

Kind	Effective pH range	Features	
	pH 4 6 8 10 12	Advantage	Disadvantage
Aluminum sulfate (Alum) Liquid type: Al_2O_3 8% Powder type: Al_2O_3 16%		Low corrosivity, Low skin irritation, Inexpensive	Not effective above pH 8.5
Polyaluminum chloride (PAC) Liquid type: Al_2O_3 10–11% Powder type: Al_2O_3 30%		Better coagulation than alum, Low or non-alkali consumption for neutralization, Stable effect at low water temperature (10–15°C)	Not effective above pH 8.5, More expensive than alum
Ferric chloride Liquid type: $FeCl_3$ 38%		Effective in wide pH range	High alkali consumption for neutralization
Ferrous sulfate ($FeSO_4{\cdot}7H_2O$)		Inexpensive	Narrow effective pH range

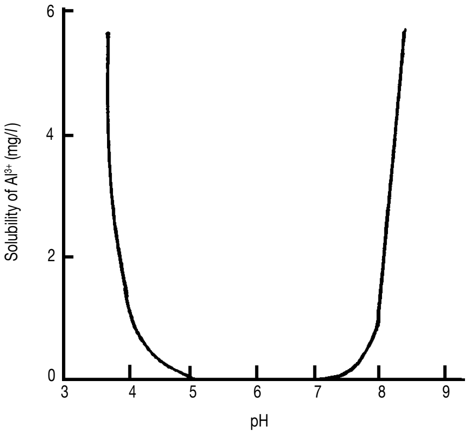


Fig. 4.12 Relationship between the solubility of aluminum ion and water pH

the micro-floc, is in proportion to the sequence of SS concentration. Therefore, when SS concentration is low, the retention time has to be extended.

In case that water to be treated includes stable emulsifying particles, etc., the stirring strength and retention time should be strengthened and extended.

(c) Order of chemical injection

Chemicals using for coagulation and flocculation treatment should be injected into the water in the order of inorganic coagulant, pH control agent (alkali) and polymer flocculant.

If alkali is added prior to coagulant, the charge neutralization ability of coagulant may be deteriorated because the coagulant will deposited as the metal hydroxide in water soon after the injection.

4.2.5 Organic Coagulants

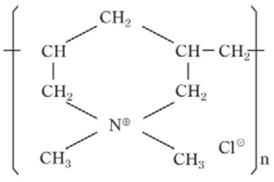
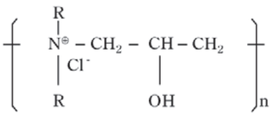
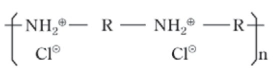
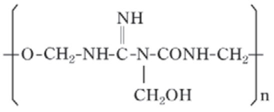
(1) Kinds and features

Organic coagulants are used for neutralizing the electrical charges of SS as same as inorganic coagulants.

The coagulation effect of organic coagulants is superior to the inorganic coagulants because of the higher ionic valencies as shown in the Table 4.1. Some organic coagulants not only neutralize the charge of SS but also react with dissolved anionic organic compounds, such as lignin-sulfonate, anionic-surfactant, arginic acid and humic acid, and form the water insoluble salts. The kinds and the structures of typical organic coagulants are shown in Table 4.3.

Most organic coagulants are cationic low molecular weight polymers and their molecular weights are generally few thousands to few hundred thousands. Their cationic functional groups are essentially amine-groups including primary, secondary and tertiary amine-groups, and quaternary ammonium chloride groups.

Table 4.3 Kinds and structures of typical organic coagulants

Chemical name	Structure
Poly-dimethyl-diallyl-ammonium chloride	
Condensed polymer of alkylamine and epichlorohydrin	 $\left(\overset{R}{\underset{R}{N^{\oplus}}}\,Cl^{-} - CH_2 - \underset{OH}{CH} - CH_2 \right)_n$
Polyethylene-imine	$\left(CH_2 - CH_2 - NH \right)_n$
Condensed polymer of alkylene-dichloride and alkylene-polyamine	 $\left(\underset{Cl^{\ominus}}{NH_2^{\oplus}} - R - \underset{Cl^{\ominus}}{NH_2^{\oplus}} - R \right)_n$
Condensed polymer of dicyandiamide and formalin	 $\left(O-CH_2-NH-\overset{NH}{\overset{\|}{C}}-\underset{CH_2OH}{N}-CONH-CH_2 \right)_n$

Comparative schematic models of coagulation processes with inorganic and organic coagulants are shown in Figure 4.13.

Organic coagulants show the excellent charge neutralizing abilities, however, they hardly form flocs by themselves. Generally, the combined use of organic coagulants together with inorganic coagulants shows the better coagulation effect.

Figure 4.14[5)] shows the comparison of zeta potentials of SS and the turbidities of treated water under an inorganic coagulant treatment and the combined treatment with an organic one.

The combined use of an organic coagulant, ZETA ACE®, with the low dosage of 5 mg/*l*, sharply reduces the zeta potential and improves the turbidity of treated water. In this case, the use of ZETA ACE could reduce the dosage of liquid aluminum sulfate from 500 mg/*l* to 200 mg/*l* for the wastewater treatment in an automobile factory.

(2) Case studies and advantages of organic coagulants

Case studies of KURITA's organic coagulants, ZETA ACE C-301 and C-302, are shown in Figures

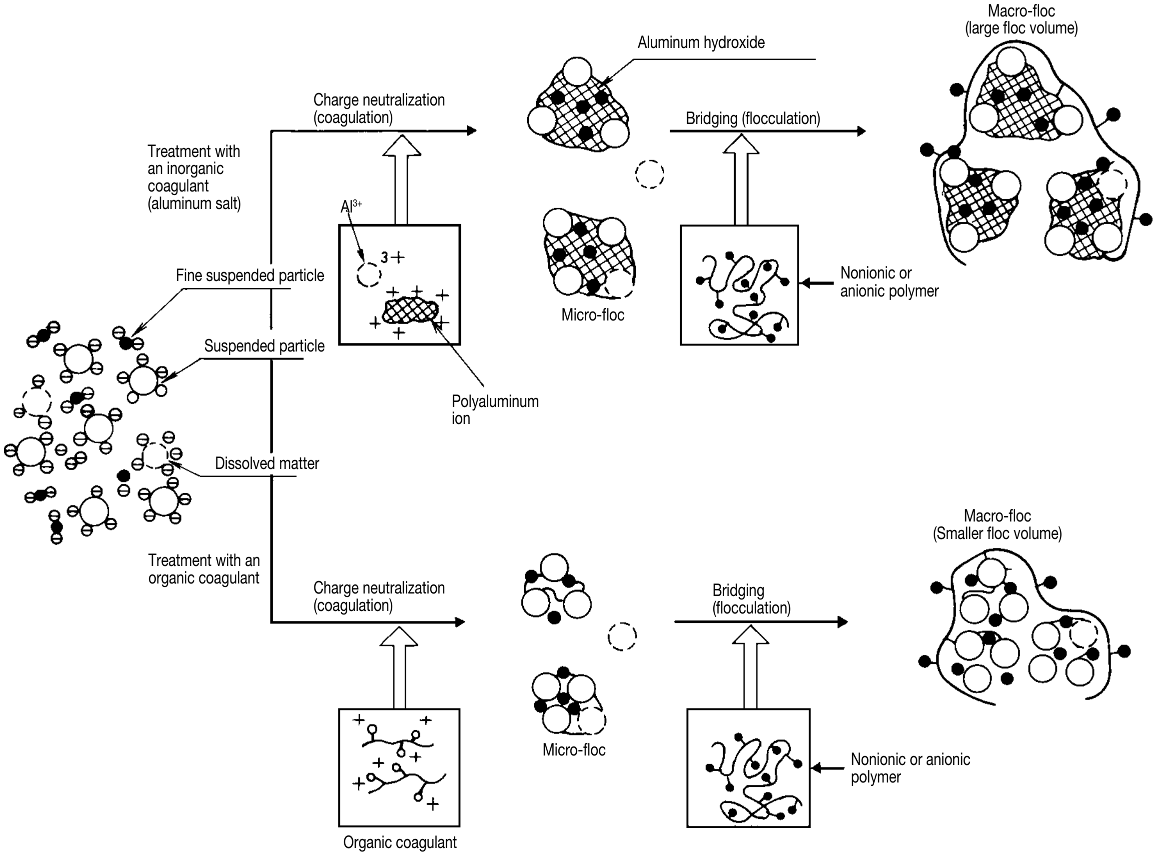


Fig. 4.13 Comparative models of coagulation processes with inorganic and organic coagulants

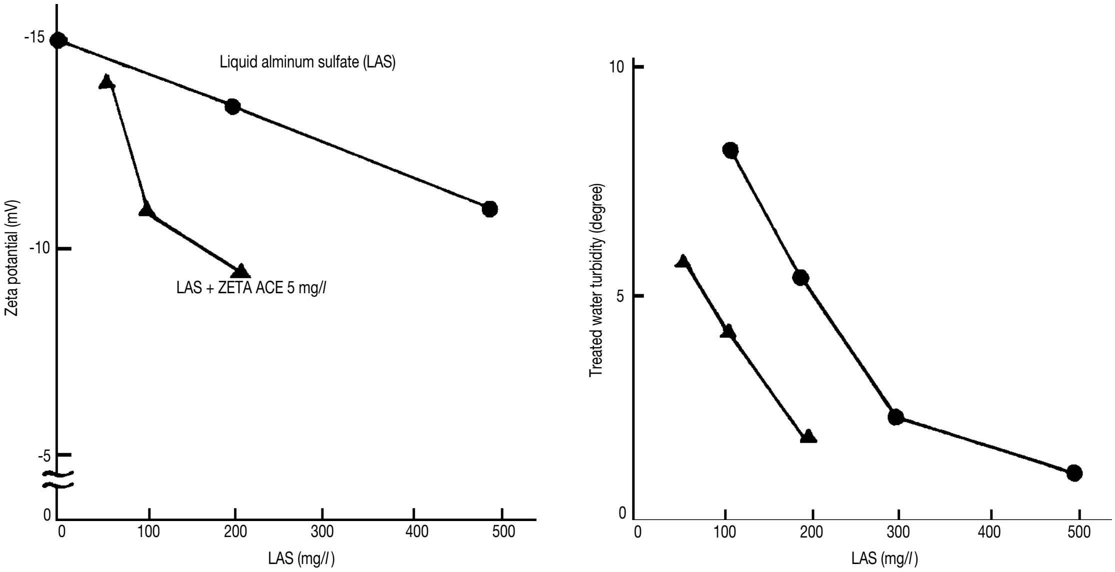


Fig. 4.14 Comparative effects of an inorganic coagulant and the combined use with an organic coagulant for a wastewater treatment in an automobile factory

4.15 and 4.16.

Case 1 (Figure 4.15) is a case study of ZETA ACE C-301 treatment for a wastewater from an automobile factory. The application of ZETA ACE C-301 with 10 mg/*l* reduced the dosage of aluminum sulfate from 1,000 mg/*l* to 160 mg/*l* and stopped the lime milk injection for neutralization.

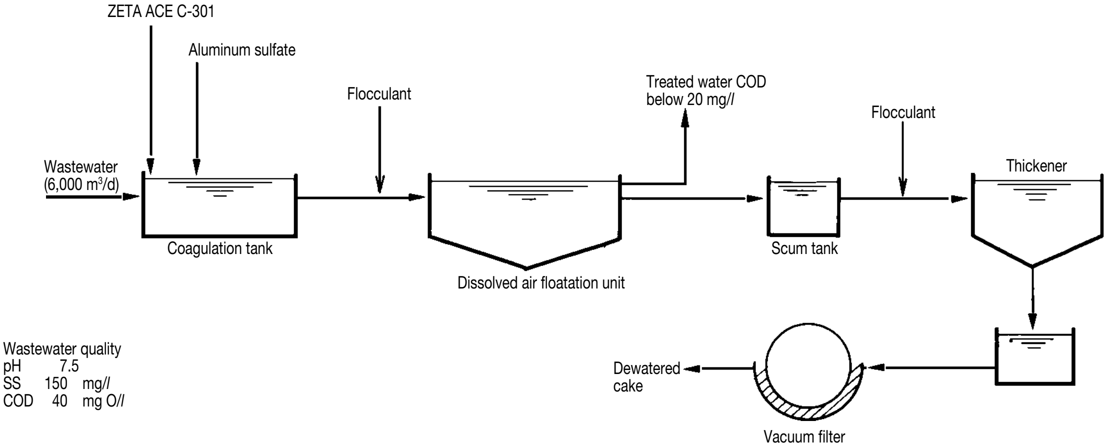
As the result, sludge volume discharged from the system was remarkably reduced, and the total treatment cost for wastewater and sludge treatment became around the half of the alum treatment without the ZETA ACE.

Case 2 (Figure 4.16) is an application of ZETA ACE C-302 for a wastewater from a toilet paper factory. The use of ZETA ACE C-302 with 2 mg/*l* reduced the dosage of alum from 400 mg/*l* to 250 mg/*l* and improved the dewatering effect against sludge from the clarifier. The total treatment cost was saved around 20%.

In this way, the combined use of organic coagulants with the low dosage remarkably reduces the required dosage of inorganic coagulants. Accordingly, the combined use improves the disadvantages of inorganic coagulant treatment as follows:

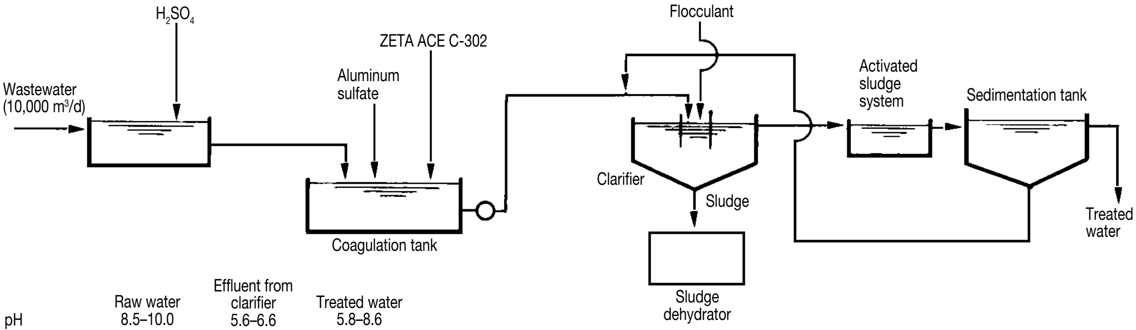
① Reduction of sludge volume including metal hydroxide originated from inorganic coagulants,
② Reduction or elimination of alkali injection for neutralization,
③ Reduction of corrosive ions (Cl^- and SO_4^{2-}) concentration in treated water, which are come from the inorganic coagulants.

When organic coagulants are used together with inorganic coagulants, it is recommended to carry out the jar test for determining their dosages, the order of their injections, a kind of suitable flocculants, etc. Normally, inorganic coagulants are added into water prior to organic ones, however, the reverse injection order sometimes shows the



Wastewater quality
pH 7.5
SS 150 mg/l
COD 40 mg O/l

Fig. 4.15 Case 1, wastewater treatment of an automobile factory



	Raw water	Effluent from clarifier	Treated water
pH	8.5–10.0	5.6–6.6	5.8–8.6
SS (mg/l)	1000–1700	30–40	40
COD (mg O/l)	300–400	100–120	80

Fig. 4.16 Case 2, wastewater treatment of a toilet paper factory

better effect.

(3) Removal of organic compounds by using special organic coagulants

There are special compounds among organic coagulants, which are soluble in acidic water and become insoluble to form their flocs in neutral to alkaline water. The effective utilization of these special organic coagulants enables to remove water soluble organic compounds and reduce the COD of treated water.

KURIDECODE® are KURITA's special organic coagulants for removing soluble COD from wastewater. Comparative removing effects of KURIDECODE L-101, a general cationic polymer coagulant and aluminum sulfate against various organic compounds are shown in Table 4.4.

Though the inorganic coagulant and conventional cationic polymer coagulant show the coagulation effects against only anionic organic compounds, KURIDECODE L-101 shows the excellent removal effect against not only anionic but also nonionic organic compounds.

Generally, starch, PEG, PVA, etc., are treated by using activated sludge systems, however, the development of KURIDECODE enables the chemical removal of these organic compounds.

Figures 4.17 and 4.18 show the PEG and PVA

Table 4.4 Removal effects of various coagulants against organic compounds (COD) in water

Organic compound / Coagulant	Anionic			Nonionic			
	Sodium lignin-sulfonate	Partially hydrolyzed polyacryl-amide[*1]	Oxidized starch	Starch	Polyethylene glycol[*2] (PEG)	Polyvinyl alcohol[*3] (PVA)	Nonionic surfactant[*4]
KURIDECODE L-101	○	○	○	○	○	○	○ – △
A conventional cationic polymer coagulant	○	○	△ – ×	×	×	×	×
Aluminum sulfate	○	○	○	×	×	×	×

COD removal rate (%): ○ above 70, △ 70–30, × below 30

*1 Paper strength agent with the molecular weight of around 100,000

*2 Molecular weight: 6,000

*3 Molecular weight: 90,000

*4 Nonyl-phenyl-ether type

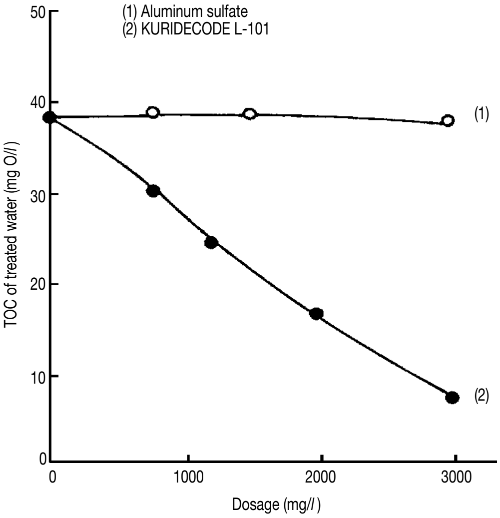


Fig. 4.17 Removal effect of KURIDECODE L-101 against PEG 6000*

* Molecular weight: 6,000

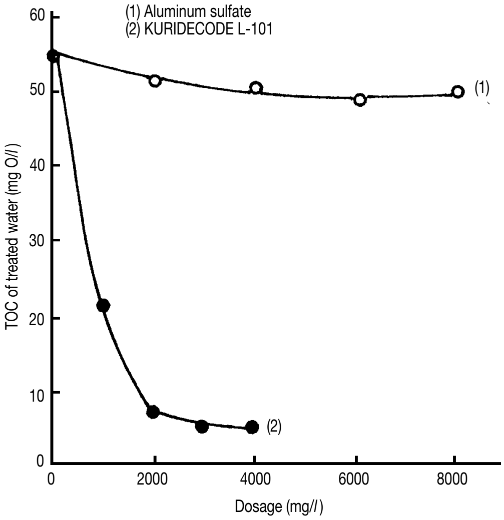


Fig. 4.18 Removal effect of KURIDECODE L-101 against PVA 2000*

* Molecular weight: 90,000

removal effects of KURIDECODE L-101 respectively. KURIDECODE L-101 sufficiently removes PEG and PVA which are not removed by coagulation treatment with aluminum sulfate.

Figure 4.19 and Table 4.5 show the field application results of KURIDECODE L-101 for the wastewater treatment in a toilet-paper factory and a dye work.

As the wastewater from the toilet-paper factory included high concentration of nonionic organic compounds, such as starch and PVA, a conventional PAC treatment only reduced the COD from around 160 to 110 mg O/*l*, although the target COD of treated water was 80 mg O/*l*. The combined use of KURIDECODE L-101 of 400 mg/*l* and PAC of 500 mg/*l* reduced the COD up to 70 mg O/*l* which satisfied the target value.

The combined treatment also shows the excellent COD removal effect in the case of the dye work.

An important advantage of KURIDECODE treatment is that it enables to reduce COD and BOD of treated water easily by removing the dissolved organic compounds together with SS without any improvement of existing wastewater treatment system.

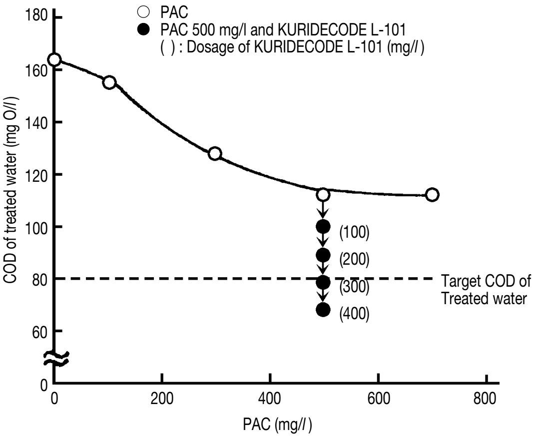


Fig. 4.19 COD removal effect of KURIDECODE L-101 against a wastewater from a toilet-paper factory

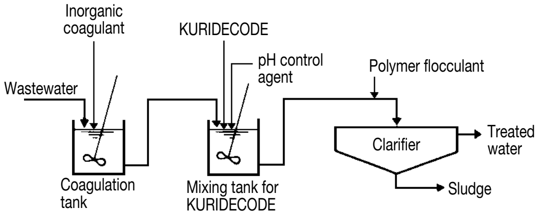


Fig. 4.20 Application method of KURIDECODE

The application method of KURIDECODE for actual system is shown in Figure 4.20.

The blade tip velocity of stirrer and the retention time in the mixing tank for KURIDECODE have to be controlled almost the same to those in the coagulation tank.

4.2.6 Nonionic and Anionic Polymer Flocculants

(1) Kinds and features of flocculants

In coagulation and flocculation treatment, nonionic and anionic high molecular weight polymer flocculants are used for bringing micro-flocs charge-neutralized by coagulants together to make the macro-flocs by the bridging reaction. The use of polymer flocculants is essential for efficient SS removal treatment of water and wastewater. Table 4.6 shows the kinds and features of typical nonionic and anionic polymer flocculants.

(2) Relationship between properties of flocculants and their effects

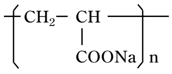
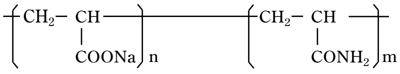
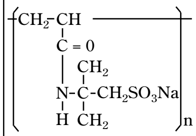
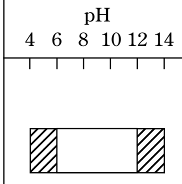
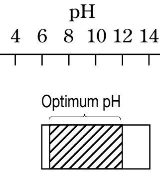
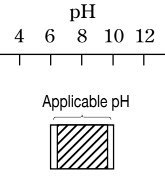
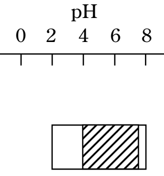
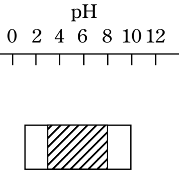
Polymer flocculants should have the sufficient adsorption ability against charge neutralized micro-flocs and the large expanded volume of their molecules in water. The large expanded volume is very important to form the loop of polymer adsorbed on micro-flocs and to make the macro-flocs by the bridging reaction as shown in Figure 4.11.

The important properties of polymer flocculants influencing on their flocculation effects are the

Table 4.5 COD removal effect of KURIDECODE L-101 against a wastewater from a dye work

COD of wastewater (mg O/*l*)	Treatment	Chemical dosage (mg/*l*)	COD of treated water (mg O/*l*)
200	Conventional	Liquid aluminum sulfate 1,000 Conventional cationic coagulant 400	90
	KURIDECODE L-101	Conventional treatement + KURIDECODE L-101 500	50

Table 4.6 **Kinds and features of nonionic and anionic polymer flocculants**

Kind and structure	Polyacrylate  $\left[CH_2-\underset{COONa}{\underset{\vert}{CH}} \right]_n$	Partially hydrolyzed polyacrylamide  $\left[CH_2-\underset{COONa}{\underset{\vert}{CH}} \right]_n \left[CH_2-\underset{CONH_2}{\underset{\vert}{CH}} \right]_m$			Partially sulfonated polyacrylamide 
Hydrolysis rate (%)	—	Above 15	15–5	Below 5	—
Ionic property	Strongly anionic	Anionic	Weakly anionic	Nonionic	Weakly anionic
Recommended dissolving concentration (%)	0.05–0.10	0.05–0.10	0.05–0.15	0.10–0.30	0.05–0.15
Effective pH range					
Typical application	Red mud separation in alumina plant, Salt water purification in soda plant, Green liquor recovery in pulp mill, Recovery of protein and fish meal (in the lower pH range)	Clarification of industrial and drinking water, Suspension treatment of wastewater including sand mud, metal oxide, metal hydroxide, etc., Treatment of high pH wastewater	Clarification of industrial and drinking water, Suspension treatment of neutral wastewater	Clarification of industrial and drinking water, Treatment of colored wastewater from pulp mill, dye work, textile factory, etc., Suspension treatment of wastewater from aluminum finishing plant, Treatment of wastewater including oils, fats and their emulsion	Treatment of colored wastewater, Suspension treatment of weakly acidic to neutral wastewater

molecular weights, ionic properties, and degrees of cross linking and branching in their molecules.

Relationship between those properties of polymer flocculants and their effects are discussed below.

(a) Molecular weight

Since the expanded volume of polymer usually increases as the molecular weight increases, polymer having the large molecular weight shows the better flocculation effect. Figure 4.21 shows the relationship between the molecular weights of polyacrylamides and their sedimentation effects against kaolin suspended in water. The polymer of higher molecular weight apparently shows the better effect.

(b) Ionic property

The most popular polymer flocculants are polyacrylamides and their partially hydrolyzed compounds. Since the amide group (-CONH$_2$) is changed to carboxyl group (-COOH) by the hydrolysis, the higher hydrolysis rate gives the higher anionic charged product.

The appropriate hydrolysis rate (strength of anionic charge) is varied depending on water pH and the dosage of coagulants mainly. The influences of pH and the dosage of aluminum sulfate on the effects of nonionic and anionic flocculants are schematically shown in Figures 4.22 and 4.23.

Generally, nonionic polymers show the better effects when pH is lower than 6.5 or the dosage of

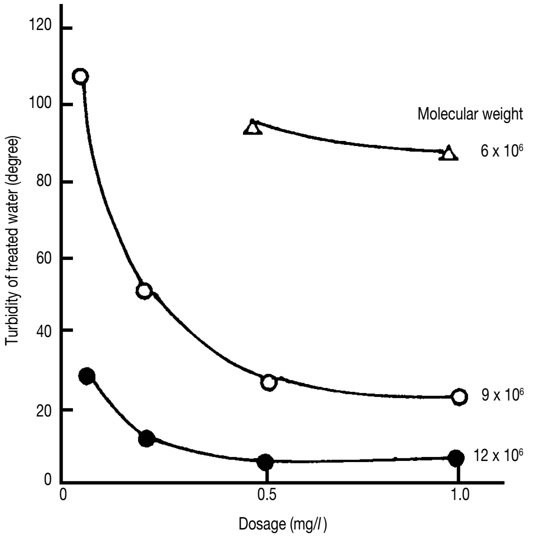


Fig. 4.21 Relationship between the molecular weight of polyacrylamide and the turbidity of treated water (sedimentation of kaolin)

coagulants is higher. On the other hand, anionic polymers are more effective in the case of higher pH of above 6.5 or lower dosage of coagulants. This tendency of anionic polymers becomes clear as their anionic charges increase.

The influence of pH on the effect of flocculants will be explained by the expanded volumes of flocculants in water. In neutral or alkaline water, the carboxyl groups of anionic polymer dissociate and their electrical repellent forces expand the polymer volume larger than nonionic one. As the result, anionic polymer flocculant shows the better effect than nonionic one.

In acidic water, no dissociation of carboxyl groups occurs and the polymer volume is shrinked because of the hydrogen bonding forces between carboxyl groups. Thus, the volume of anionic polymer becomes smaller than nonionic polymer which volume is scarcely influenced by pH. Accordingly, nonionic polymer shows the better effect in acidic water.

The dosage of inorganic coagulants gives the influence on the adsorption of polymer flocculants on the surfaces of suspended particles. Anionic polymers adsorb on the coagulated micro-flocs by using the electrostatic attractive force and the ionic bonding force of carboxyl groups with the metallic atoms originated from coagulants.

When the dosage of coagulants is low, the number of metallic atoms on the floc surface becomes small. In this case, anionic polymers can adsorb on the floc by using a part of carboxyl groups and form the loop which is effective for the subsequent flocculation of flocs. In this case, nonionic polymer can not shows the sufficient effect because of the weak adsorption ability of amide-groups with metallic atoms.

When the dosage of coagulants is very high, the whole surface of micro-floc is covered with metal hydroxide formed by the coagulant. In this case, most of carboxyl groups of anionic polymer react with the metallic atoms on the floc and the loop formation becomes difficult. Thus, the flocculation effect is deteriorated. On the other hand, nonionic polymer still enables to form the loop because of the weak bonding force of amide-groups with metallic atoms. Therefore, nonionic polymers show the better flocculation effect than anionic ones in the case of high coagulant dosing.

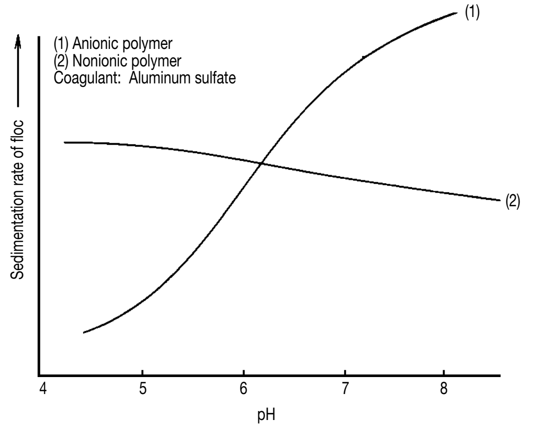


Fig. 4.22 Influence of water pH on the effects of nonionic and anionic polymer flocculants

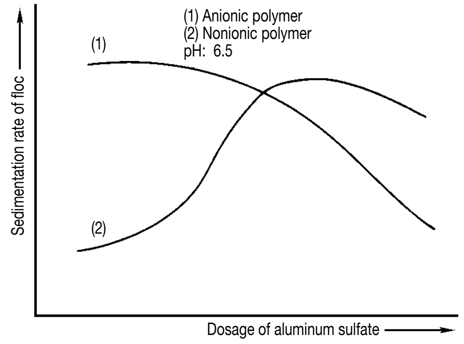


Fig. 4.23 Influence of coagulant dosage on the effects of nonionic and anionic polymer flocculants

(c) Cross linking and branching of polymer

Acrylamide sometimes forms the imide-bonding structure (-CO-NH-CO-) through the polymerization, drying and powdering processes, and it causes the cross linking and branching structure of polyacrylamide. The cross linking and branching are easily formed especially in the production of the polymers with high molecular weight over 5 millions.

The cross linking and branching structure reduces the expanded volume of polymer and the flocculation effect comparing with the polymer of straight chain molecule with the same molecular weight. Therefore, the selection of suitable polymerization, drying and powdering processes for the polymer production is very important for obtaining the straight chain polymer.

The straight chain polymer especially shows the excellent treatment effect against the aqueous suspension of high SS concentration. Figure 4.24 shows the comparative effect of a straight chain polymer and a conventional anionic polymer for the wastewater treatment of a coal preparation plant.

(3) Sulfonated polymer flocculants

In general, the flocculation effects of conventional nonionic and anionic polymers are varied depending on the changes in pH, the dosage of coagulant against the amount of SS and so on.

In actual wastewater treatment, the properties of wastewater are fluctuated but the coagulant is usually dosed with a constant rate. Accordingly, the changes in pH and the amount of metal hydroxide on the micro-flocs affect the flocculation effect of polymer flocculants. As countermeasures against the fluctuation of water quality, the excess dosing of inorganic coagulant and the use of nonionic polymer flocculant are applied (refer to Figure 4.23).

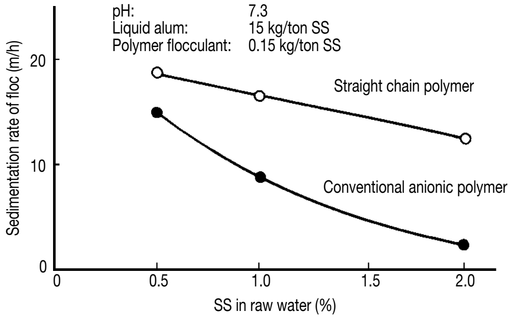


Fig. 4.24 Effects of a straight chain polymer and a conventional anionic polymer flocculants for a coal preparation wastewater

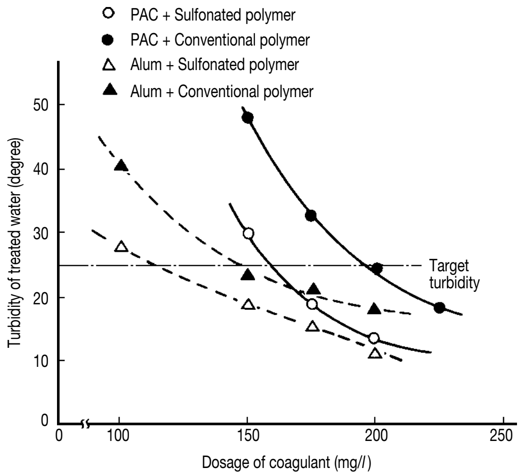


Fig. 4.25 Effects of a sulfonated polymer and a conventional polymer flocculants for a wastewater treatment in a pulp and paper mill

To solve this problem, anionic sulfonated polymer flocculants$^{6)}$ are newly developed. The sulfonate group scarcely adsorbs on metal hydroxide on the micro-floc surface and dissociates in a wide pH range. Therefore, the sulfonated polymer has the large expanded volume in water and forms the loop on the micro-floc even when water quality and the dosage of coagulants are fluctuated.

Figure 4.25 shows the comparative effects of a sulfonated polymer and a conventional weak anionic polymer flocculant on a wastewater treatment in a pulp and paper mill. The sulfonated polymer shows the stable effect against the fluctuation of inorganic coagulant dosage.

(4) Application method of polymer flocculants

Generally, polyacrylamide based flocculants are supplied as the powder products or emulsions. The contents of active ingredient of powder type and emulsion type are usually 90% or more and 20 to 40% respectively.

When a powder type flocculant is used, the powder is usually dispersed into water by using an automatic powder feeder, etc., and it is transferred into the chemical storage tank to make the perfect solution. Figure 4.26 shows a typical dissolving system for powder type flocculants.

The following cares are required to dissolve and use powder flocculants effectively.

(a) Dispersion of flocculants

When the powder is directly added into water, the lumps (fish-eyes) of polymer are formed which are difficult to dissolve for a long time. This is not

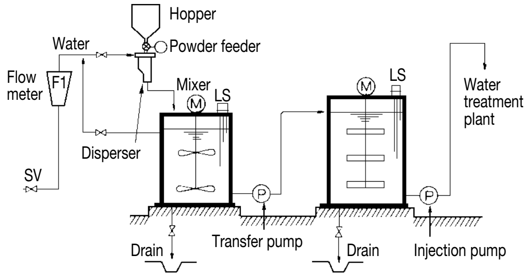


Fig. 4.26 A typical dissolving system of powder type flocculants

only a loss of chemicals but also causes the clogging of injection pump.

Therefore, the dispersers are usually used to evenly disperse the powder on water film. Automatic powder feeders are usually equipped with built-in dispersers. In the case of the manual dissolution, the use of a handy dispersing unit shown in Figure 4.27 is convenient for the easy dissolution of powder flocculants.

In the case of no dispersing unit, an easily dispersible flocculant, EDP FLOC®, is available, in which a special substance is formulated to improve the dispersion property. The dispersion condition of EDP FLOC is shown in Photo 4.1 (p.4-34) comparing with a conventional flocculant.

(b) Duration and stirring for dissolving flocculants

Dissolution of powder flocculants is generally required 30 to 90 minutes depending on the kinds of them, their grain sizes, etc.

The strong stirring of flocculants to dissolve them reduces their molecular weights and decreases their effects. Therefore, the use of propeller type mixer, the mixing by using volute pump and so on should be avoided.

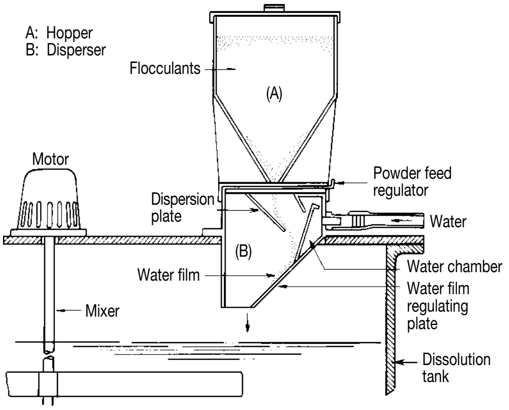


Fig. 4.27 Handy disperser of powder flocculants

(c) Water quality for dissolving flocculants

As SS and multivalent metallic ions, such as calcium and ferric ions, in water for dissolving flocculants reduce the effects of flocculants, the use of water including low SS and metallic ions is recommended as much as possible.

(d) Order of chemical dosing and mixing condition

Polymer flocculants are dosed into water after the formation of micro-flocs by using coagulants and pH control agents.

The mixing blade tip velocity of clarifier is usually controlled in the range of 0.2 to 1.0 m/s. The retention time in reaction chamber of clarifier is generally 10 to 20 minutes.

4.2.7 Coagulation and Flocculation Tests

(1) Jar test

Jar test is utilized for obtaining the required informations and data on coagulation and flocculation treatment. Those informations include following items:

① Selection of suitable coagulant and flocculant, and their dosages,
② Determination of optimum pH,
③ Prediction of treated water quality and sludge volume generated.

The test conditions, such as rotation speed of stirrer and stirring time, have to be determined according to the conditions of actual treatment system.

(2) Column flotation test

A column flotation test is performed to examine the conditions of air flotation treatment. The test conditions should be determined based on the operational conditions of actual plant.

(3) Others

Test tube for sedimentation is used for measuring the sedimentation rate of flocs and the sludge volume precipitated.

Test filter is used for determining the properties of floc for the filtration.

4.3 Sludge Treatment

The sedimentation treatment of SS in water inevitably yields the sludge. Raw sludge discharged from the equipments of sedimentation treatment includes a large volume of water, so that, the concentration and dewatering of sludge are gener-

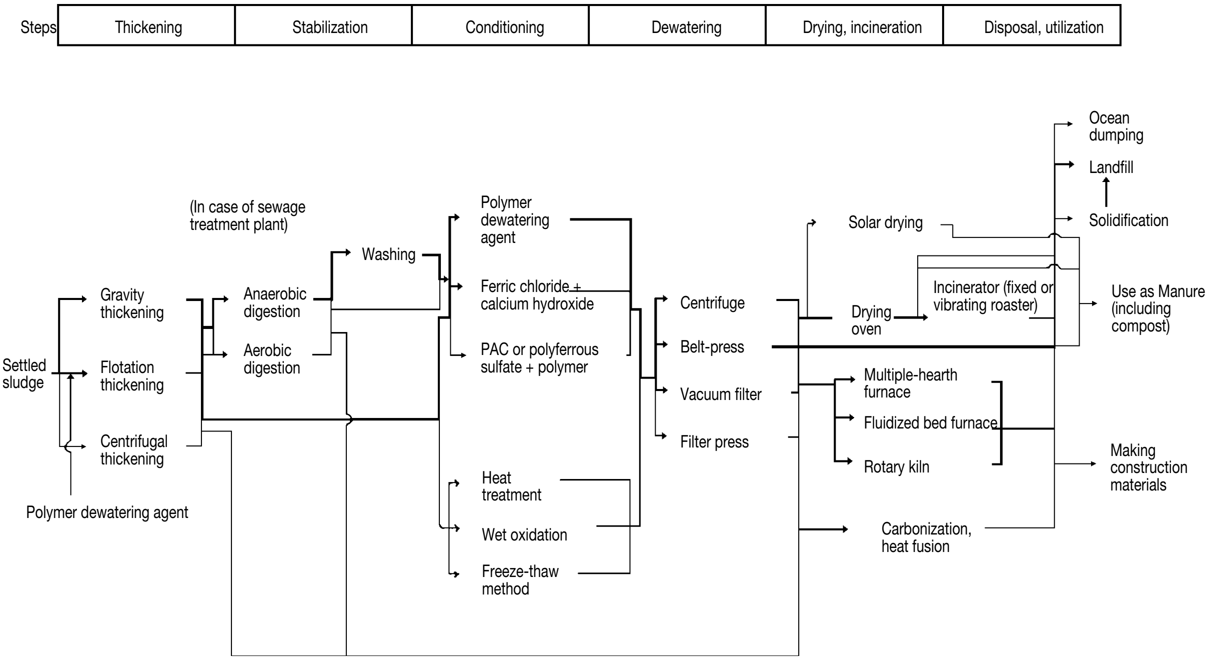


Fig. 4.28 Processes of sludge treatment and disposal

ally required prior to the final disposal.

Especially, when a sludge including organic matters is incinerated, the reduction in the water content of sludge is very important to save the fuel cost.

In this chapter, the dewatering of organic sludge is mainly discussed considering the incineration as the final treatment.

4.3.1 Treatment of Inorganic Sludge

Most of inorganic sludges discharged from water works, mines, metal refineries, iron and steel works, etc., are already neutralized their particle charges and stabilized. Thus, the charge neutralization is unnecessary in the sludge dewatering process and the formation of strong flocs by bridging with polymer flocculants is generally easy. Nonionic and anionic polymers are used for the sludge dewatering as same as the flocculation treatment. The molecular weight of polymer for dewatering is usually smaller than that of polymer flocculants and it is around ten millions*.

The selection of an appropriate dewatering agent and a type of dehydrator (dewatering equipment) is basically identical to the dewatering of organic sludge. It is described in the Section 4.3.2.

4.3.2 Treatment of Organic Sludge

(1) Processes of sludge treatment

Since sewage, night soil and wastewater discharged from petrochemical plants, food factories, etc., include a large amount of organic matters, they are biologically treated.

Many kinds of treatment methods shown in Figure 4.28 are practiced for the treatment and disposal of primary, excess, digestion and tertiary treated sludges discharged from the biological treatment systems. Among them, the dewatering process of sludge is important in relation to the subsequent sludge treatment and disposal methods.

Since those sludges include the high concentration of organic matters and are highly hydrophilic, the dewatering of them is very difficult comparing with inorganic sludges.

Each step of sludge treatment and disposal is briefly described below.

(a) Concentration of raw sludge (thickening)

Generally, the solid content of raw sludge is only 1% or less, so that, it is concentrated gravitationally to 2 to 3% by using thickener. The concentration

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* For flocculation treatment, polymers with the molecular weight of twelve to fifteen millions are usually used in Japan.

of sludge is closely related to the dewatering performance of the sludge and the moisture content of dewatered cake. In the case of same sludge, the dewatering performance is improved as the solid content is increased through the concentration process of raw sludge as shown in Figure 4.29.

When the concentration of sludge is insufficient in a thickener, the use of cationic polymer flocculants improves the concentration.

(b) Digestion of sludge (stabilization)

In sewage treatment plants, the excess sludge from the activated sludge system is generally digested anaerobically. The content of organic matters in the sludge is reduced through the anaerobic digestion process because the organic matters are changed to methane and carbon dioxide gasses mainly.

The digestion sludge is easily dewatered comparing with the excess sludge.

(c) Conditioning of sludge

Most popular conditioning method of sludge is the use of polymer dewatering agents or ferric chloride and calcium hydroxide.

The conditioning with polymers is applied for belt-press or centrifugal dehydrators which require large floc size for the better dewatering. Ferric chloride and calcium hydroxide are used for filter press and vacuum filter type dehydrators.

Recently, another sludge conditioning method with polymer and inorganic chemicals, such as PAC and polyferrous-sulfate, has developed.

(d) Dewatering of sludge

The dewatering of sludge is the key process of sludge treatment and the disposal because sludges are generally solidified by reducing the water content to make the subsequent disposal easy.

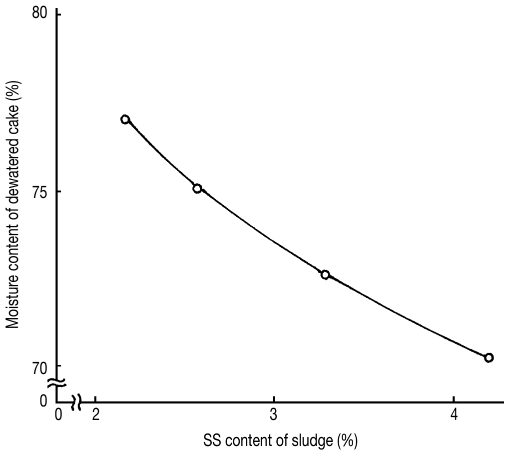


Fig. 4.29 Relationship between the SS content of sludge and the moisture content of dewatered cake

Polymer dewatering agents are superior to the ferric chloride and calcium hydroxide because the dosage of polymers is very low and around 1% against dry solid, and they scarcely increase the solid content of sludge.

(e) Drying and incineration of dewatered cake

The drying and incineration of dewatered cake further reduce the volume of cake and minimize the recontamination at the final disposal.

In large scale sewage treatment plants, the cake is continuously dried and incinerated by using fluidized bed furnaces, multistage furnaces, etc. In the small and medium scale plants, the cake is dried beforehand and then the dried cake is incinerated.

Since, odor, dust and harmful gasses, such as sulfur dioxide and nitrogen oxides, are generated in this process, countermeasures against these pollutants should be taken.

(f) Disposal and utilization of dried cake and incinerated ash

The dried cake and incinerated ash are generally landfilled.

The most common utilization method of dried cake is the use as manure for farmland and meadow. In this case, the use after the composting is more safety than the direct use of dried cake.

The production of aggregates, bricks, etc., from the ash has being studied and partially realized.

(2) Dehydrators

Suitable sludge dehydrators are selected taking several conditions, the properties and quantity of sludge to be dewatered, the target moisture content of dewatered cake, investment, the operation and maintenance costs and so on, into consideration.

At present, following five types of dehydrators are generally used:

① Centrifugal dehydrator,
② Belt press dehydrator,
③ Screw press dehydrator,
④ Filter press dehydrator,
⑤ Vacuum filter dehydrator.

The characteristics of these dehydrators are summarized in Table 4.7.

In industrial wastewater treatment plants, centrifugal dehydrators are widely used for the sludge dewatering because of the easy operation control.

In the sewage treatment systems, vacuum filter dehydrators are widely used in the present. However, they have been gradually being replaced

Table 4.7 Types of dehydrators and their characteristics

Type of dehydrator		Centrifugal	Belt press	Screw press	Filter press	Vacuum filter
Kind and dosage of dewatering agent (% against dry solid)	Organic sludge	Polymer 0.8–1.5	Polymer 0.4–1.0	Polymer 0.6–1.2	$FeCl_3$ approx. 1.0 and $Ca(OH)_2$ 30–40	$FeCl_3$ approx. 1.0 and $Ca(OH)_2$ 30–40
	Inorganic sludge	Polymer 0.2–0.5	Polymer 0.1–0.4	Polymer 0.1–0.5	$Ca(OH)_2$ or no chemical dosing	$Ca(OH)_2$ or no chemical dosing
Moisture content of cake (Organic sludge) (%)		75–85	70–82	65–80	55–70	75–85
SS recovery rate (Organic sludge) (%)		95–99	90–98	85–95	95–99	90–98
Advantages		Easy operation control, Smaller installation area	Relatively low moisture content of treated cake, Easy monitoring of dewatering condition, Lower electricity and chemical consumption	Relatively low moisture content of cake	Low moisture content of cake	—
Disadvantages		Relatively high moisture content of treated cake, Noisy in operation, Relatively higher electricity consumption	Relatively difficult chemical injection control	Lower SS recovery rate	Higher installation cost, Difficult operation control, High inorganic SS content of cake	Relatively high moisture content of treated cake, High inorganic SS content of cake
Suitable kind of sludge to be treated		Sludges from industrial wastewater, sewage, night soil, etc.	Sludges from industrial wastewater, sewage, night soil, etc.	Sludges from wastewater of pulp and paper mills, night soil, etc.	Sewage sludge, inorganic sludge, etc.	Sewage sludge, etc., Recovery of valuable matters from filtrate

by belt press dehydrators in Japan because they require the use of ferric chloride and calcium hydroxide to reduce the moisture content of cake and the volume and inorganic solid content of cakes are increased as the result.

(a) Centrifugal dehydrator

Screw decanter type centrifugal dehydrator (SD) is generally used for sludge dewatering. The structure is shown in Figure 4.30.

Sludge is fed into the rotating drum with high speed and the solids are separated from water by the centrifugal force. The separated solids are discharged from the drum into the solid chute by the rotating screw conveyer. The separated water overflows into the liquid chute.

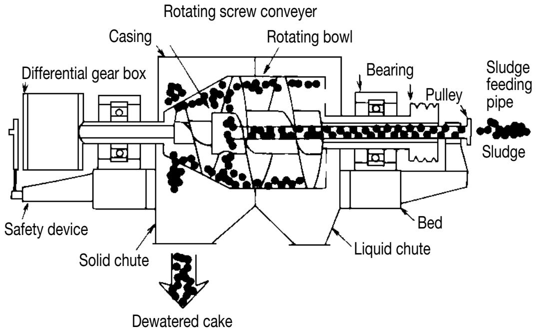


Fig. 4.30 Structure of a screw decanter type centrifugal dehydrator

The dewatering efficiency and SS recovery rate of centrifugal dehydrator are relatively stable against the fluctuation of sludge properties, such as solid content, when a dewatering agent is added at higher than the critical concentration. Therefore, the operation control of dehydrator is relativel easy.

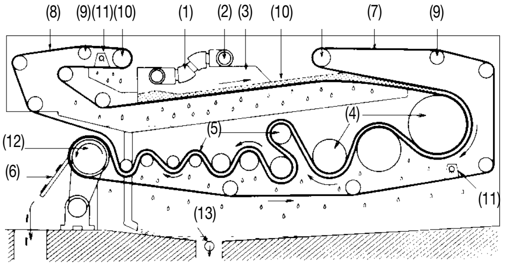
However, it is advisable to adjust the injection rate of dewatering agent according to the change in the properties of sludge by taking the target moisture content of dewatered cake and the chemical cost into consideration.

Table 4.8 shows the relationship between the typical operational conditions and dewatering effect of the dehydrator.

(b) Belt press dehydrator

The structure of a typical belt press dehydrator, HYDEPRESS PA® is shown in Figure 4.31.

Sludge is fed on the driving filter cloth and primarily dewatered at the gravity filtering zone. Then, it is compressed and dewatered between the two filter cloths.



(1) Sludge feeding pipe
(2) Sludge feeding zone
(3) Gravity filtering zone
(4) Pressing rolls
(primary compressed dewatering zone)
(5) Pressing rolls
(secondary compressed dewatering zone)
(6) Cake discharge
(7) No.1 filter cloth
(8) No.2 filter cloth
(9) Filter cloth guide rolls
(10) Filter cloth tension rolls
(11) Filter cloth washing units
(12) Filter cloth driving roll
(13) Filtrate discharge

Fig. 4.31 Structure of a belt press dehydrator

Belt press dehydrators generally make the moisture content of dewatered cake smaller with lower dosage of dewatering agent than centrifugal dehydrators. However, the belt press dehydrators require more sufficient care for the injection control of dewatering agents comparing with centrifugal ones because of the narrower range of appropriate chemical dosages.

Table 4.8 Relationship between the operational conditions and dewatering effect of centrifugal dehydrators

Operational condition to be changed	Influence on sludge treatment effect
Pool depth	Lowering*: Reduction of cake moisture because of longer drainable deck area and increased dewatering time, Reduction of SS recovery rate and treatment capacity because of shorter retention time in pool. Increasing*: Increase in cake moisture, SS recovery rate and treatment capacity.
Difference of rotating speed between screw conveyer and rotating bowl	Increasing: Increase of cake moisture and treatment capacity because of increased cake discharge rate and turbulence of compressed cake layer. Decreasing: Reduction of cake moisture and treatment capacity.
Chemical dosing point	Inside of dehydrator: Suitable for dewatering agent having faster reaction rate with SS. Inside of mixing tank: Suitable for dewatering agent having slower reaction rate with SS.

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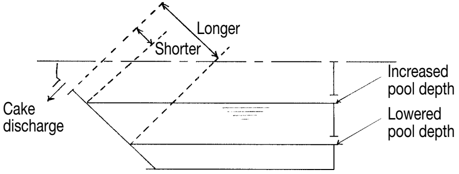

Table 4.9 shows the relationship between the typical operational conditions and the dewatering effect of belt press dehydrator.

When the rotating speed of stirrer for the mixing tank of dewatering agent is increased, the floc diameter of sludge becomes smaller but the strength

Table 4.9 Relationship between the operational conditions and dewatering effect of belt press dehydrators

Operational condition to be changed	Influence on sludge treatment effect
Driving speed of filter cloth	Increasing: Increase in treatment capacity and moisture content of cake Decreasing: Reduction of the capacity and the moisture content
Tension of filter cloth	Increasing: Reduction of cake moisture content but some probability of deterioration in cake removal from filter cloth
Rotating speed of stirrer for mixing tank of dewatering agent	Increasing: Reduction of cake moisture content and improvement of cake removal Decreasing: Increase of cake moisture content and deterioration of cake removal

of floc against compression is increased. As the results, the efficiency of gravity filtration is reduced but the efficiency of compressed dewatering is improved. Thus, the moisture content of cake is finally lowered by increasing the rotating speed.

(c) Screw press dehydrator

Figure 4.32[7)] shows the structure of a screw press.

Sludge is sent by the rotating screw with low speed of below 1 rpm and dewatered by compressing the volume in the space between the outer drum and the screw, which gradually becomes narrower from the sludge inlet to the outlet. Moreover, it is possible to accelerate the dewatering by heating with steam.

(d) Vacuum filter dehydrator

The structure of a vacuum filter dehydrator is shown in Figure 4.33.

Vacuum of 300 to 600 mm Hg is applied for the inside of rotating drum which a part is immersed in sludge. The sludge is filtered and the cake layer forms on the filter cloth surface simultaneously. The cake is further dewatered by the pressure difference between the drum inside and atmospheric pressure after leaving the sludge layer.

(e) Filter press dehydrator

The layout and sludge dewatering mechanism of this hydrator are shown in Figures 4.34 and 4.35 respectively.

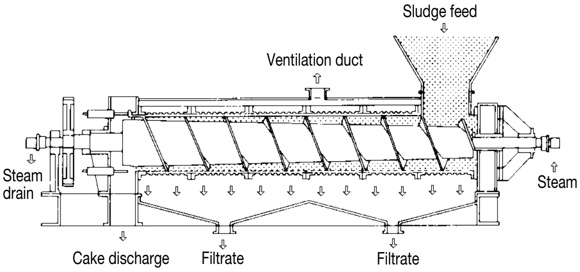

Fig. 4.32 Structure of a screw press dehydrator

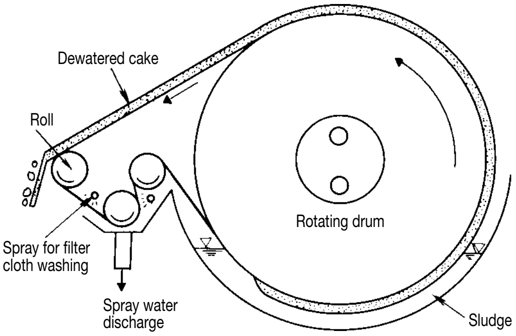

Fig. 4.33 Structure of a vacuum filter dehydrator

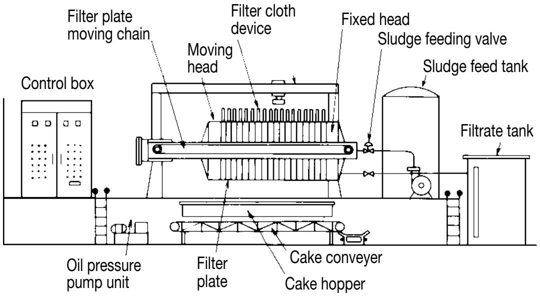

Fig. 4.34 Layout of a filter press dehydrator

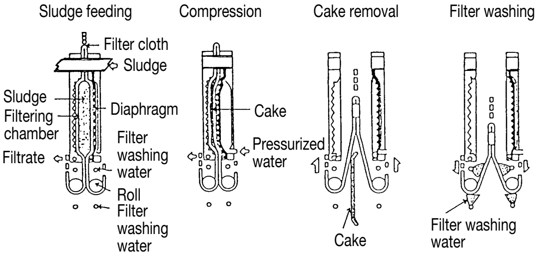

Fig. 4.35 Sludge dewatering mechanism of a filter press dehydrator

Sludge is fed into the filtering chamber lined with filter cloth and dewatered by pressing the diaphragm with pressurized water (7–15 kg/cm^2). Then, the dewatered cake is removed by opening the filtering chamber and the filter is washed by water. The number of filtering chambers is generally few to thirty.

(3) Properties of sludge influencing the dewatering effect

(a) Total solid (evaporation residue) and suspended solid contents

The total solid (TS) content of sludge is larger than suspended solid (SS) content because the TS includes the SS and the dissolved solids in water including in the sludge. However, the difference between TS and SS contents is a little in the case of organic sludges.

As the TS or SS content of sludge is closely related to the dewatering effect of the sludge, it is generally used to estimate the required dosage of dewatering agent and the dewatering effect of sludge.

Generally, the increase of TS (SS) in sludge to be treated reduces the moisture content of dewatered cake and increases the capacity of hydrator on the dry solids base. Moreover, sludge which is easily

Table 4.10 Correlation coefficients among sludge properties and the cake moisture content

Sludge properties	Correlation coefficients
TS	-0.89
$\frac{\text{VTS}}{\text{TS}}$	Below 0.5
$\frac{\text{VTS - fiber content}}{\text{TS}}$	0.78
$\frac{\text{Fiber content}}{\text{TS}}$	-0.79
Longarithm of viscosity* * (cp)	0.88

concentrated in the thickening process, generally gives the easy dewatering.

In the case of sludges including the same TS (SS) contents, the composition of sludge, especially the volatile suspended solids* (VSS) content, the fiber content, the viscosity,etc., influences the dewatering effect.

Table 4.10 shows the correlation coefficients among the moisture content of dewatered cake and those factors related to sludge property.

(b) Content of organic matters

Organic matter content (VSS or VTS) of sewage sludge has a close relationship to the content of proteins and poly- saccharides. The increase of VSS (VTS) reduces the SS content of sludge and increases the cake moisture content and the required dosage of dewatering agent.

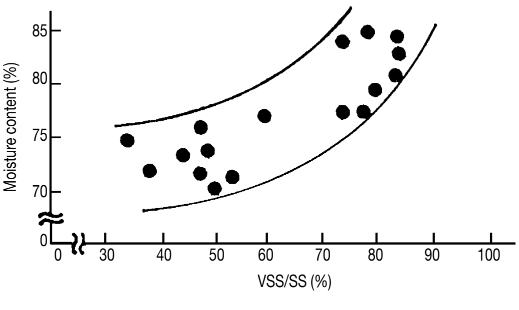

Fig. 4.36 Relationship between the VSS/SS ratio of sludge and the moisture content of cake dewatered by a centrifugal dehydrator

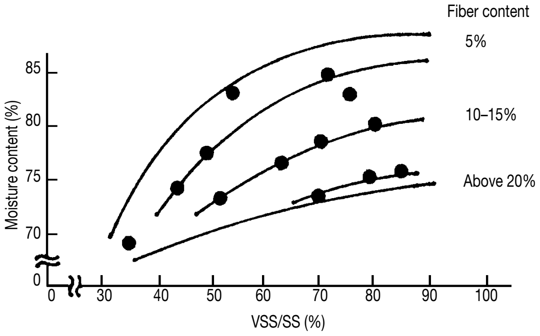

Fig. 4.37 Relationship between the VSS/SS ratio of sludge and the moisture content of cake dewatered by a belt press dehydrator

Figures 4.36 and 4.37 show the typical relationship between the VSS/SS ratio of sludge and the moisture content of dewatered cake under a dewatering treatment by using a centrifugal and a belt press dehydrator respectively.

As the increase of fiber content in sludge reduces the moisture content of cake as shown in Table 4.10 and Figure 4.37, the use of (VSS - fiber content)/ SS or (VTS - fiber content)/VTS is recommended for discussing the relationship between sludge properties and the dewatering effect in the case of sludges from sewage and night soil treatment plants, pulp and paper mills, etc., which include considerable amount of fiber.

Figures 4.38 and 4.39 show the relationship between the VSS/SS ratio of sludge and the appropriate cationized ratio of polymer dewatering agents for the sludge dewatering by the centrifugal

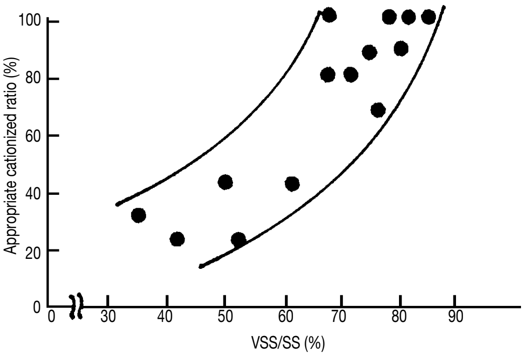

Fig. 4.38 Relationship between the VSS/SS ratio of sludge and the appropriate cationized ratio of polymer dewatering agent for the dewatering with a centrifugal dehydrator

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* The VSS content means the organic suspended solid content of sludge. The VSS content is almost same to the volatile total solid (VTS) content in the case of organic sludge.

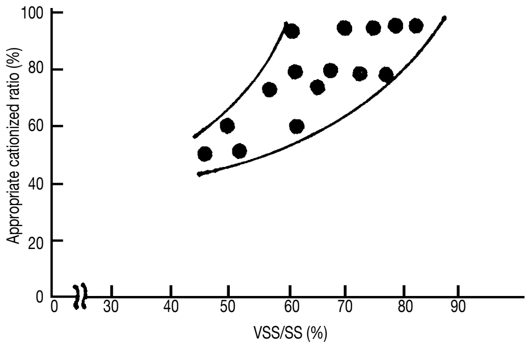

Fig. 4.39 Relationship between the VSS/SS ratio of sludge and the appropriate cationized ratio of polymer dewatering agent for the dewatering by a belt press dehydrator

and belt press dehydrators respectively. Dewatering agents with the higher cationized ratio are suitable for the dewatering of sludge having the higher VSS/SS ratio.

(c) Fiber content

Since fibers connect flocs together and increase the mechanical strength of flocs, the increase of fiber content in sludge improves the water removal in the compression dewatering and the cake removal from filter cloth.

Equation (4.3) shows the relationship between the fiber content and the moisture content of cake dewatered by a belt press dehydrator. The increase of 1% of fiber content reduces the cake moisture around 0.5%.

$$W = 84.1 - 0.465\frac{F}{SS} - 0.341SS + 0.018SVI \quad \text{.............................} \ (4.3)$$

where

W = moisture content of dewatered cake (%)
F = fiber content of sludge (%)
SS = suspended solid content of sludge (%)
SVI[*1] = sludge volume index

SVI is calculated by using equation (4.4).

$$SVI = \frac{SV}{MLSS} \times 10^4 \quad \text{.............................} \ (4.4)$$

where

SV[*2] = sludge volume (%)
MLSS[*3] = mixed liquor supended solids (mg/*l*)

(d) Colloid equivalent and sticky substance content

Organic sludge includes sticky substances, such as proteins and polysaccharides, which are anionic high molecular weight substances and are stably hydrated. Sludge having high negative colloid equivalent includes the high concentration of sticky organic matters and high moisture content. Dewatering of such sludge is difficult and the moistured content of the dewatered cake is generally high.

For the dewatering of sludge including the sticky substances of high concentration, the sufficient charge neutralization of sticky substances is essential. The combined use of cationic and anionic polymers, the application of amphoteric polymers and so on have been developed for the dewatering of sludge including the sticky substances of high concentration.

(e) Acid soluble metals

Acid soluble metal content of sludge is an index for judging the mixing ratio of organic sludge and coagulation sludge, and is useful for estimating the appropriate ionic property of dewatering agent. The dewatering of sludge including higher concentration of aluminum and iron becomes easier.

4.3.3 Polymer Dewatering Agents

(1) Kinds and functions of polymer dewatering agents

Sludge is flocculated by the reaction between the anionic sticky substances of the sludge and the cationic functional groups of polymer dewatering agent. To reduce the moisture content of sludge in this process, it is required to reduce the hydrated water of the sticky substances by neutralizing the electrical charge with cationic polymer. Strong cationic polymers with low molecular weight are

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[*1] SVI is an index which is related to the sedimentation condition of activated sludge. When the SVI exceeds 200, the activated sludge becomes the bulking condition and the SS often carry over from the aeration tank.

[*2] SV is the activated sludge volume of water sampled from the aeration tank, which is measured after 30 minutes from the sedimentation. When the SV is 20 to 40%, the activated sludge is generally separated very well in the sedimentation tank.

[*3] MLSS is the SS concentration of mixed liquor in the aeration tank of activated sludge system. The MLSS is around 3,000 mg/*l* under the normal operational condition of activated sludge system.

suitable for the charge neutralization.

On the other hand, the formation of large floc which is mechanically strong, is necessary to lower the moisture content of cake dewatered by dehydrators. For this purpose, weak cationic polymers with high molecular weight are suitable.

Accordingly, it is difficult that the charge neutralization and large floc formation are simultaneously carried out by using one kind of dewatering agent. To solve this contradiction, many methods, such as the CSA system[8)], have developed and applied in the field. The detail of the CSA system is described in the next section.

Table 4.11 shows the structures, applications and so on of typical polymer based dewatering agents.

(2) The CSA system and energy saving in cake drying and the incineration processes

The CSA system is a typical sludge dewatering system developed by KURITA. In the CSA system, two kinds of polymer dewatering agents are used for sludge dewatering. A chitosan based strongly cationic and low molecular weight polymer, PRESSAID® 101 or 102, is used for neutralizing the

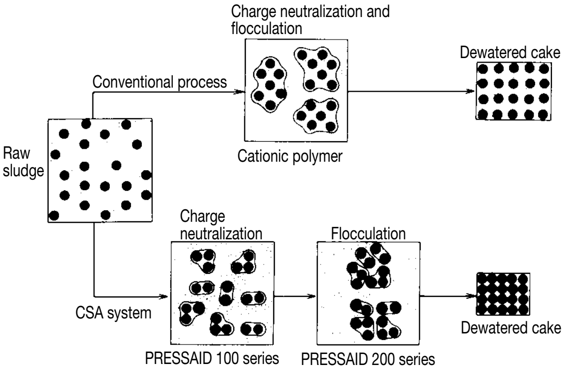
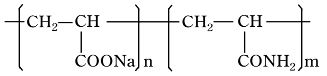
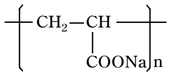
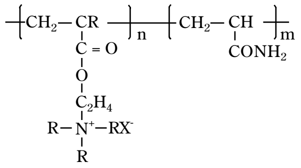
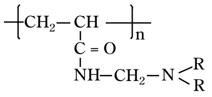
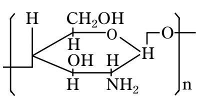


Fig. 4.40 Comparison of flocculation and dewatering processes of sludge under the CSA system and a conventional treatment

Table 4.11 Typical polymer based dewatering agents

Kind and structure	Ionic property	Application
Partially hydrolyzed polyacrylamides  $-\left[CH_2-\underset{COONa}{CH}\right]_n\left[CH_2-\underset{CONH_2}{CH}\right]_m-$	Weakly anionic	Inorganic sludges of high Al content
	Medium anionic	Inorganic sludges
	Strongly anionic	Organic sludges (for floc formation in CSA system)
Polyacrylates  $-\left[CH_2-\underset{COONa}{CH}\right]_n-$	Strongly anionic	Organic sludges (for floc formation in CSA system)
Poly-methaacrylicacid-aminoalkyl-esters  $-\left[CH_2-\underset{\substack{C=O\\ O\\ C_2H_4\\ R-N^+-RX^-\\ R}}{CR}\right]_n\left[CH_2-\underset{CONH_2}{CH}\right]_m-$	Weakly cationic	Mixture of primary and excess sludges (for SD mainly)
	Medium cationic	Organic sludges (for SD mainly)
	Strongly cationic	Organic sludges (for belt press dehydrators mainly)
Mannich modification products of polyacrylamide  $-\left[CH_2-\underset{\substack{C=O\\ NH-CH_2-N<^{R}_{R}}}{CH}\right]_n-$	Strongly cationic	Organic sludge and mixture of primary and excess sludges (for SD mainly) Organic sludges (for SD mainly)
Chitosans 	Strongly cationic	Organic sludges (for charge neutralization in CSA system)
New polymers	Amphoteric	Organic sludges which are difficult to form large flocs by conventoinal dewatering agents

charge of sludge. A high molecular weight and strongly anionic polymer, PRESSAID 201, 203 or 250, is used for the large floc formation.

Figure 4.40 shows the comparison of flocculation and dewatering processes under the CSA system and a conventional treatment.

In the conventional method, the charge neutralization and flocculation of sludge are carried out simultaneously by using one cationic polymer. In this case, the sufficient charge neutralization tends to result in the insufficient flocculation, while the insufficient charge neutralization brings the good flocculation. This contradiction may cause the insufficient reduction in the moisture content of dewatered cake.

In the CSA system, the use of two kinds of chemicals sufficiently neutralizes the charge of sludge and forms the large and mechanically strong flocs. As the result, the moisture content of cake is sufficiently reduced. The CSA system reduces cake moisture content around 3 to 8% lower than one of conventional treatment.

Figure 4.41 shows the test result of the CSA system against sludge from a night soil treatment plant. The CSA system gave the good filtering property of sludge and reduced the cake moisture content over 7% compared with a conventional treatment by using a high pressure belt press dehydrator.

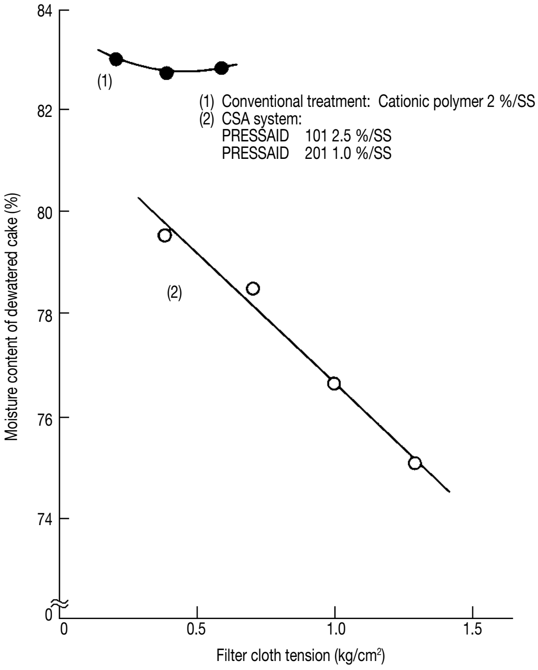


Fig. 4.41 **Comparison of sludge dewatering effects of the CSA system and a conventional treatment (sludge from a night soil treatment plant)**

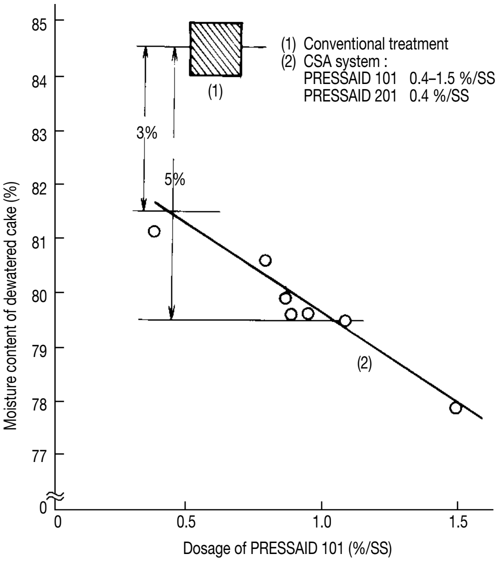


Fig. 4.42 **Comparison of sludge dewatering effects of the CSA system and a conventional treatment (mixed sewage sludge)**

Figure 4.42 shows an example of the CSA system application for the dewatering of mixed sludge of primary and excess sludges from a sewage treatment plant by using an ordinary (low pressure) belt press dehydrator.

In this case, the cake moisture content was reduced over 3% comparing with the conventional treatment. Further, the CSA system enabled to increase the throughput of sludge to two times of the conventional treatment.

As the application of CSA system reduces the moisture content of dewatered cake around 5% comparing with conventional treatments, the amount of cake is remarkably reduced as shown in Figure 4.43.

The decrease of cake amount increases the treatment capacity of equipments for the cake drying and the incineration around 30 to 50% on the dry solids base and reduces the installation cost of the system. The reduction of moisture content decreases the fuel consumption for cake drying and incineration. Figure 4.44 shows the reduction of heavy oil consumption for the incineration by decreasing the moisture content.

Table 4.12 shows the reduction of fuel consumption by applying the CSA system for the treatment of sewage and night soil sludges.

A large reduction in cake moisture by applying the CSA system is expected to develop the new disposal methods of dewatered cake. For instance, studies are being made on the incineration of mixture of municipal garvage and the cake, the direct production of compost from dewatered cake and so on.

Photo 4.2 (p.4-35) shows the appearances of de-

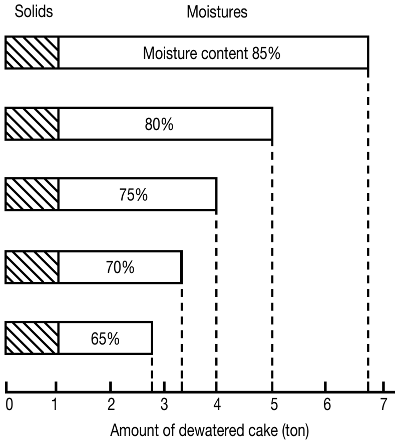


Fig. 4.43 Relationship between the moisture content and the amount of dewatered cake

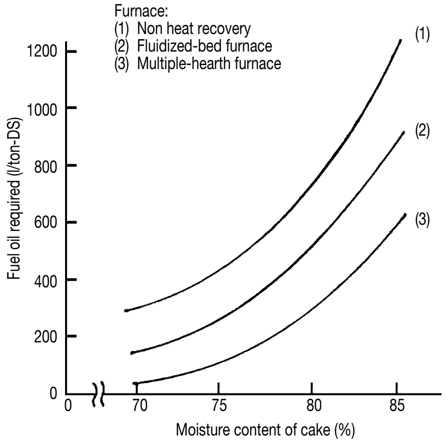


Fig. 4.44 Reduction of fuel oil consumption for cake incineration by decreasing the cake moisture content

Table 4.12 Reduction of fuel consumption for cake drying and incineration by the application of the CSA system

Plant, sludge and dewatering equipment	Cake drying and incineration system	Chemical treatment	Average moisture content of cake (%)	Throughput as dry solids (DS-t/day)	Fuel oil consumption (L/t-DS)	Moisture content reduction (%) (Fuel oil reduction) (%)	Remarks
A sewage plant, Mixed raw sludge, Belt-press	Drier + incinerator (Lucas furnace)	Conventional process	86.4	2.22	880	3.9 (36)	
		CSA	82.5	2.87	566		
B sewage plant, Mixed raw sludge, Belt-press	Fluidized-bed furnace	Conventional process	81.7	14.0	462	5.8 (50)	
		CSA	75.9	18.9	230		
C sewage plant, Mixed raw sludge, Belt-press	Rotary kiln + afterburner	Conventional process	81.0	9.2	1,098 Nm^3/t-DS*	4.0 (37)	Cake throughput was increased at approximately the same burning conditions.
		CSA	77.0	13.3	693 Nm^3/t-DS*		
D night soil treatment plant (anaerobic digestion), Oxidation + excess + coagulation sludge, Centrifugal	Rotary drier	Conventional process	87.7	0.20	1,760	3.7 (59)	Fuel oil required to evaporate 1 kg moisture decreased from 0.261 to 0.159.
		CSA	84.0	0.29	720		
E night soil treatment plant (anaerobic digestion), Excess + coagulation sludge, Centrifugal	Rotary drier + deodorizer furnace	Conventional process	85.5	0.22	2,761	4.8 (54)	Fuel oil required to evaporate 1 kg moisture decreased from 0.36 to 0.24.
		CSA	80.7	0.22	1,276		

* Fuel gas consumption

watered cake treated with a conventional treatment and the CSA system by using a belt press dehydrator.

(3) Amphoteric polymer dewatering agents

Cationic polymer dewatering agents adsorb to negatively charged sludge particles by using the cationic functional groups and flocculate the particles. However, as the expanded length of the polymer is maximally around 10^{-4} mm and smaller than the diameter of sludge particles (10^{-1} to 10^{-2} mm), the flocculation by cation polymer is generally insufficient.

In the case of amphoteric polymers, the cationic functional groups neutralize the electrical charges of particle and the anionic functional groups react with the free cationic groups of the other polymer molecular. Then, the apparent molecular length of polymer becomes longer. Further, the anionic groups react with the metal atoms including in the particles. As the result, amphoteric polymers improve the flocculation of sludge flocs comparing with conventional cationic polymer dewatering agents.

Amphoteric polymers also reduce the amount of inorganic coagulant required for the charge neutralization of sludge. The combined treatment of amphoteric polymers and inorganic coagulants enables to reduce the moisture content of dewatered cake as same as the CSA system.

Typical application results of amphoteric polymers, KURIFIX® CP-500 series, for sludge dewatering by centrifugal dehydrators are shown in Table 4.13. The use of amphoteric polymers reduces the moisture content of dewatered cake and increases the throughput of sludge as compared with conventional cationic polymer treatments.

In the case of sludge dewatering by using belt

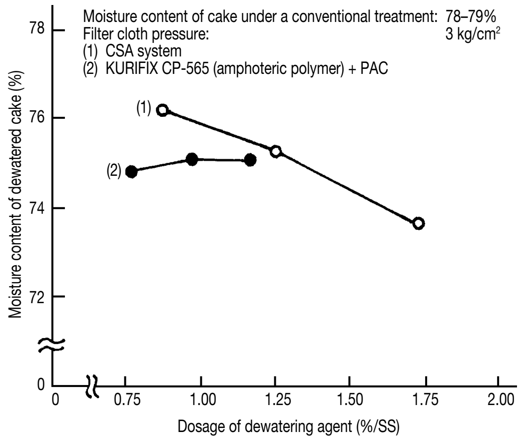


Fig. 4.45 Effect of an amphoteric polymer treatment with PAC on sludge dewatering by a high pressure belt press dehydrator

Table 4.13 Typical application results of amphoteric polymers for sludge dewatering by centrifugal dehydrators

Factory	A night soil treatment plant		B night soil treatment plant		C automobile factory		D petrochemical factory	
Kind of sludge	Excess + coagulation		Excess + digestion + coagulation		Excess + coagulation		Oily + coagulation	
Dewatering agent and the dosage (%/SS)	DAM type (weakly cationic) 4.0	KURIFIX CP-513* 2.2	DAM type (medium cationic) 4.5	PAC + KURIFIX CP-513* 3.5	Mannich type 0.9	KURIFIX CP-511* 0.7	DAM type (weakly cationic) 1.5–2.0	KURIFIX CP-563* 2.0
Moisture content of dewatered cake (%)	86	83	85	83.5	82	79	85–90	70
Throughput of sludge (kg-DS/h)	40	75	55	55	72	100	70	95
Advantages of KURIFIX CP-500 series treatment	Reduction of cake moisture of 3%, Increase of sludge throughput of 88%, Reduction of total treatment cost of 30%		Improvement of SS recovery rate from 88% to 99%, Reduction of cake moisture content		Reduction of cake moisture of 3%, Increase of sludge throughput of 40%, Reduction of chemical cost of 23%		Reduction of cake moisture of 15 to 20%, Remarkable improvement of SS recovery rate	

* Amphoteric polymer

press dehydrators, the combined use of KURIFIX CP-500 series chemicals and inorganic coagulants is very effective.

Figure 4.45 shows the effect of this treatment for sludge dewatering by a high pressure belt press dehydrator.

PAC or poly-ferrous-sulfate is usually used as the inorganic coagulant for KURIFIX CP-500 series treatment.

Photo 4.3 a) (p.4-36) shows the flocs of sludge formed by applying this combined treatment. An appropriate stirring condition forms strong pellet type flocs with the diameter of above 10 mm. This treatment has realized the direct dewatering of low concentration sludge without any other concentration process of sludge.

Moreover, the pellet type flocs are easily dewatered by a belt press dehydrator and the moisture content of the cake becomes very low. The removal of the cake from the filter cloth is also very good and the contamination of filter cloth is minimized as shown in Photo 4.3 b).

(4) Deodorization of sludge dewatering process and dewatered cake

Since sludge dewatering by polymers hardly increases the total solids of sludge, this method has been substituted for the dewatering using calcium hydroxide and ferric chloride. However, this method is difficult to lower the generation of unpleasant odor caused by hydrogen sulfide, methyl mercaptan, etc., in sludge dewatering process and from the dewatered cake.

Special sludge dewatering chemicals having deodoring function (KURINCAKE®), or deodorants (KURIRASER®), are used for solving this problem.

KURINCAKE series chemicals are polymer dewatering agents including essential oils, etc. The KURINCAKE removes and counteracts those odors. Table 4.14 shows the reduction of unpleasant odor by the KURINCAKE.

4.3.4 Testing Methods for Sludge Dewatering

Actual sludge dewatering conditions are widely different depending on the type of dehydrator to be used. Therefore, appropriate test apparatus and conditions have to be selected for each type of dehydrator.

In this section, the testing methods for centrifugal and belt press dehydrators are described. Testing methods for vacuum filter and filter press dehydrators are referred to “the Testing Methods for Sewage”[9] of Japan Sewage Works Association.

(1) Centrifugal dehydrator

In centrifugal dehydrators, sludge receives the centrifugal force of which is one to three thousand times of the gravity and is intensively stirred. Therefore, sludge and dewatering agent have to be intensively mixed to form the flocs in the dewatering test. After formation of the flocs, a gravitational filtration test, capillary suction time (CST) test[10] and so on are carried out by using the flocs to select a suitable dewatering agent or to evaluate the effect.

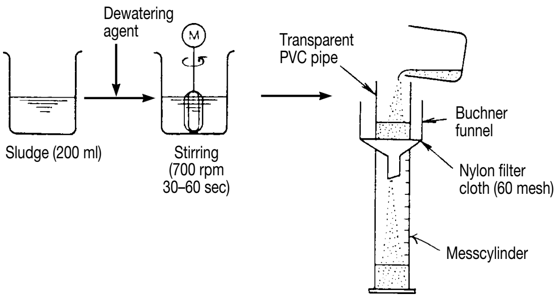


Fig. 4.46 Procedure of a gravitational filtration test for centrifugal dehydrators

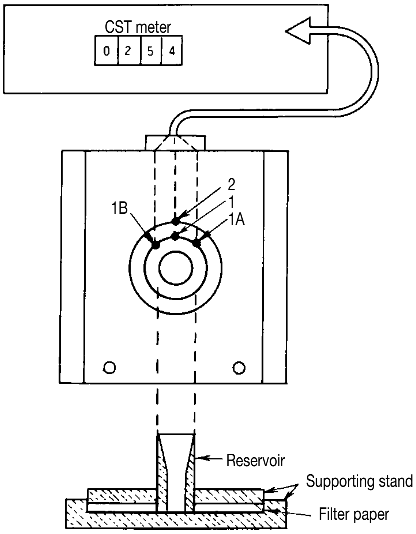
Table 4.14 Reduction of unpleasant odors by KURINCAKE

Case No.	Dehydrator	Point of odor concentration measuring	Odor concentration*	
			Conventional treatment	KURINCAKE treatment
A	Belt press	Sludge feeding point	31,000	5,500
B	Belt press	Chamber of cake transport conveyer	9,800	550
C	Centrifugal	Chamber of cake transport conveyer	23,000	9,800
D	Centrifugal	Chamber of cake transport conveyer	3,100	2,300
E	Centrifugal	Chamber of cake transport conveyer	17,000	4,200

* Odor concentration is the dilution rate of a sample with clean air, which the odor becomes to not smell by the examiners.

Figure 4.46 shows a typical test procedure of the gravitational filtration test. In this test, to obtain larger volume of filtrate in shorter period means the better dewatering property of the sampled sludge flocs.

Figure 4.47 shows the test apparatus for measuring the CST. In the CST test, a sample of sludge floc is added into the reservoir and the time of which water permeates from the point 1 to the point 2 of filter paper is measured. In this test, the shorter CST means the better dewatering property of sludge flocs. In the case of test results shown in Figure 4.48, the dewatering agent A shows the better effect than the agent B.



1, 1A, 1B, 2: Sensors for detecting water in filter paper

Fig. 4.47 CST testing apparatus

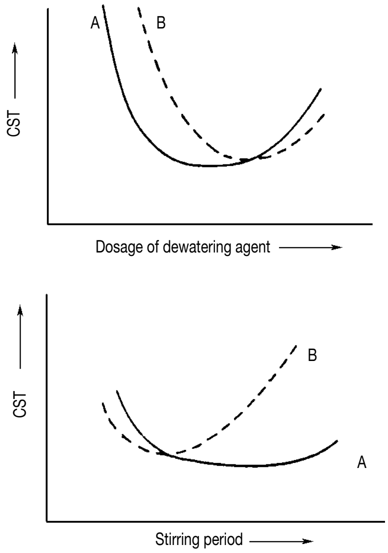


Fig. 4.48 An example of CST test result (comparison of performances provided by dewatering agents A and B)

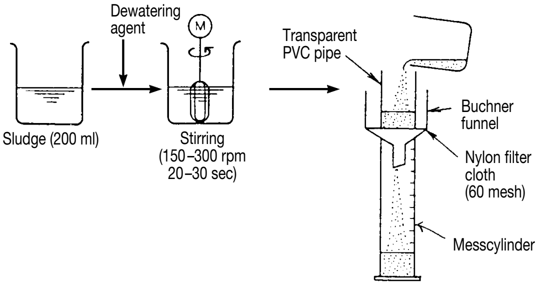
In the case of centrifugal dehydrators, low cationic and high molecular weight polymers or amphoteric polymers are generally show the sufficient dewatering effect.

(2) Belt press dehydrator

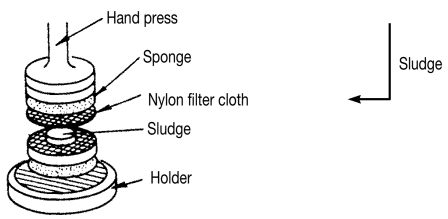
In the case of belt press dehydrators, the gravitational filtration test is carried out as same to the centrifugal hydrators but the stirring condition after dosing dewatering agent is different. After the filtration test, the sludge remaining on the nylon filter cloth is used for the squeezing test. Figure 4.49 shows the test procedure for belt press dehydrators. In the squeezing test, the squeezing pressure and the test period are determined according to the actual operational conditions of dehydrator.

Among those test results, the moisture content of dewatered cake and the easiness of cake separation from the filter cloth are important factors for evaluating the effect of dewatering agent.

In the case of belt press dehydrator, high cationic and relatively low molecular weight polymers generally form the dewatered cake which includes the low moisture content and is easily removed from the filter cloth.



(a) Gravitaional filtration test



(b) Sludge squeezing test

Fig. 4.49 A sludge dewatering test for belt press dehydrators

4.4 Safety of Polymer Flocculants

Acrylamide monomer, acrylic acid monomer, etc., which are raw materials of polymer flocculants, are chemically very active and generally toxic.,[11),12)] However, their polymers are chemically stable and their toxicities are generally very low.

In this section, the toxicities of polymer flocculants are briefly reviewed.

Regarding the safety of polymer flocculants, the report by the World Health Organization (WHO) water works groups, "Influence of Polymer Use in Water Works on Human Health".,[13)] is a valuable reference.

(1) Acute toxicity

Lethal dose 50 (LD50) is used to estimate the acute toxicity of polymer flocculants. The LD50 means the amount of the substance which may cause the death of half of the animals taking the substance.

The LD50 of acrylamide based polymer flocculants against mice or rats is reported over 1,000 mg/kg or over 4,000 mg/kg.,[14)–18)] The LD50 of ferric chloride and aluminum chloride are 900 mg/kg (rats) and 1,130 mg/kg (mice).,[19)] respectively, which are used as coagulants for drinking water treatment.

Since polymer flocculants are not absorbed.,[14),16),18),20),21)] into the human body, their toxicities will be very weak.

(2) Chromic toxicity and influence on breeding of animals

Studies have made on the maximum dosage which is not different from that in the control groups physiologically and histopathologically when the substance is given to test animals continuously for a long time. Also, the genetic effect was studied.

McCollister, et al.,[20)], reported that the maximum non-effective dosage of some nonionic and anionic polymer flocculants are 500 mg/kg day and 2,000 mg/kg day for rats and beagle dogs respectively in the test during two years. Those values of a cationic polymer flocculant are also reported 607 mg/kg day and 580 mg/kg·day.,[15),17)] respectively.

According to three generation breeding test with white rats, no influence was observed on their breeding and offsprings when the feeds including 500 to 2,000 mg/kg[22)] of a cationic polymer flocculant were given them.

(3) Absorption and accumulation in living body

A polyacrylamide based flocculant labeled with ^{14}C (radioisotope) was given to mice and carps together with their feeds and the behavior of ^{14}C was studied.,[17)–20),23)] According to the reports, the flocculant entering the body was quickly discharged through digestive organs as excrement, and no absorption and accumulation of the flocculant was observed after 7 days of feeding.

The absorption and accumulation in plants were also studied.,[14),16),22),24)] by using similar method, and no influence was observed.

(4) Acrylamide monomer content

Since acrylamide monomer is toxic, the monomer content of polymer flocculant for using drinking water treatment is regulated to be 0.05% or below by the Environmental Protection Agency (EPA) of U.S.A., and so on. There is no regulation for the other use. Most of polymer flocculants include the monomer of below 0.2% in Japan.

The EPA approves the use of polymer flocculants with the specified concentration or below for drinking water treatment, which satisfy the monomer content of below 0.05% and the other safety data.

Since polymer flocculants include the sufficiently low concentration of acrylamide monomer and their dosage is also low generally, the monomer concentration in the treated water will be extremely low. Moreover, Arimitsu, et al.,[17),25)] reported that the monomer of low concentration was biologically decomposed in a short time.

(5) Influence on aquatic lives

The LC50 is generally used as an index showing the safety of chemicals for aquatic lives.

The LC50 values of nonionic and anionic polymer flocculants are over 300 to 1,000 mg/*l* and their toxicities are low.

The LC50 of cationic polymers in fresh water is as low as 0.21 to 1.0 mg/*l*. The dead fishes were damaged in their gills and the oxygen content of their bloods were lowered.,[15),24)] Hence, it is supposed that they were suffocated by adsorption of the polymers to the gills. However, as cationic polymer flocculants strongly adsorb on suspended particles in suspension treatment process, they are hardly discharged to public waters. The concentration of cationic polymers in treated water is generally lower than 0.1 mg/*l*.

(6) Influence on plants

Influence of polymer flocculants on the germination, primary growth and cultivation of rice plant, Japanese radish, etc., are reported.[14)–17)] The results show the no practical influence on those plants, for instance, rice plant normally grew up even when 100 mg/l of a flocculant were added into the cultivating water.

It is reported[15),17)] that there is no considerable difference in the growths of plants cultivated by adding sludges dewatered by using a cationized polyacrylamide, calcium hydroxide and ferric chloride or no chemicals.

(7) Influence on activated sludge and microorganisms

No unfavorable influence of cationized polyacrylamide on activated sludge and microorganisms, such as E. coli, were reported.[15),17)]

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5. Water Treatment for Air Conditioning Systems

5.1 Introduction

The number of office buildings and shopping centers which have the floor areas of greater than 3,000 m^2 has been steadily increasing every year in Japan as shown in Figure 5.1. Those buildings generally have own air conditioning systems. Among them, buildings constructed for new city plannings or urban renewals employ the district air conditioning systems and the number of the systems reached 127 on the end of August, 1997 in Japan.

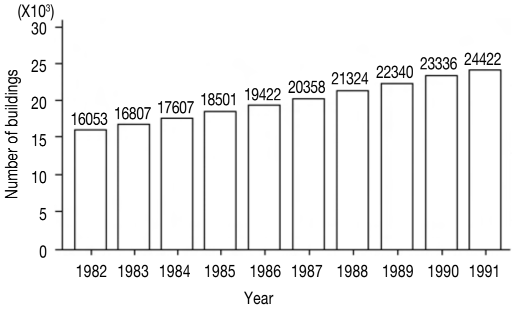


Fig. 5.1 Transition in the number of office buildings and shopping centers with the floor areas of more than 3,000 m^2 (Japan)

The requirement for energy conservation in cities has encouraged the increase of cogeneration systems in which electric power is generated by using gas and/or oil, and the waste heat is effectively utilized as the heat source for the air conditioning system. The use of heat pump systems utilizing heat-storage water or ice tanks, and the employment of new types of air conditioning systems have become popular for energy saving.

Air conditioning systems, and water and hot water supply systems are essential for comfortable living in large size buildings. Water is used for the various purposes. Since the purposes and conditions of its use are different for each systems, the water treatment method is different for each system.

There are three main objectives of water treatment in the field of air conditioning.

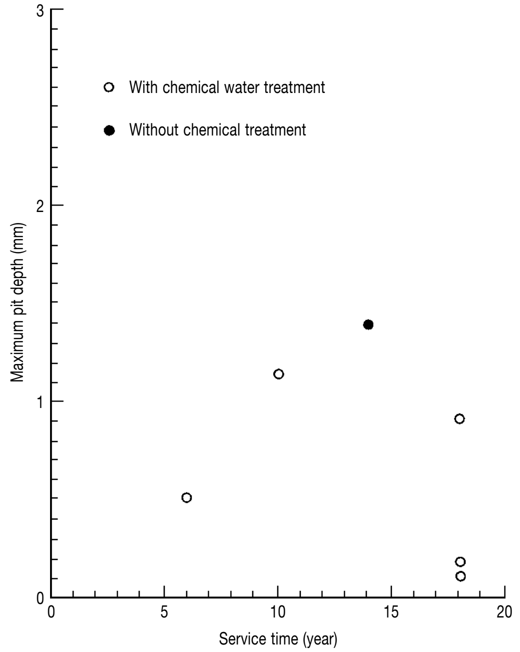
The first is to prolong the service lives of the pipings and equipments. The (a) and (b) of Figure 5.2 show the relationships between the service time and the maximum pit depth of water pipings in cooling tower systems and closed water recirculating systems. In the both pipings, the maximum pit depth remains 1.2 mm or less after 10 to 20 years service time by applying suitable chemical water treatments.

The second is the contribution to energy and water conservation. Figures 5.3 and 5.4 show the survey results on the trouble occurrences of thirty refrigerating machines for air conditioning plants under no chemical treatment. Since those machines were operated without water treatment, the 60% of them experienced the high pressure cutout and the 80% of them experienced the cleaning of heat exchangers. This survey suggests the increase in the electricity consumption of refrigerating machines under inadequate water treatment conditions.

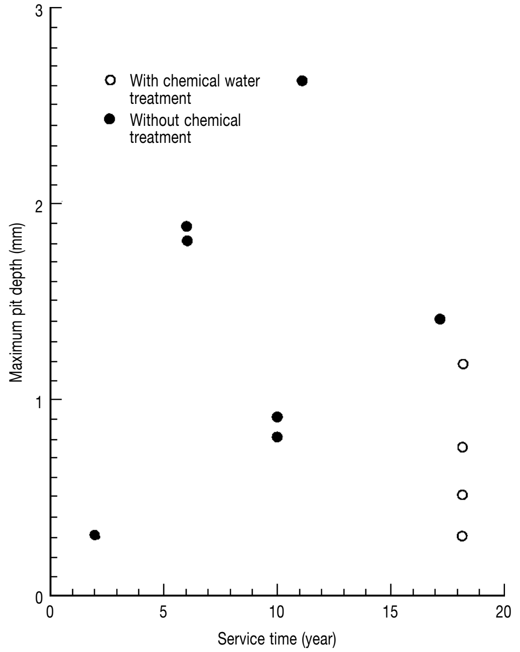
As mentioned in the chapter 3, an increase in the cycles of concentration by applying a suitable water treatment remarkably reduces the water blowdown from cooling tower systems. The reduction of blowdown contributes not only water saving but also cost saving for water supply and water discharge into sewerages.

The third is to create a comfortable living space. Recently, the contamination of drinking water has become a serious social problem, and legal measures have been enacted for the operation and maintenance of water supply systems. For example, the problem of the water contamination with trihalomethanes has to be solved by applying an adequate water treatment.

More reliable water treatment and water quality control are required for the latest air conditioning systems. The main purpose of water treatment



(a) Pipings in cooling tower systems



(b) Pipings in closed systems

Fig. 5.2 **Relationships between the service times and the maximum pit depths of water pipings in cooling tower systems and closed water recirculation systems for air conditioning systems**

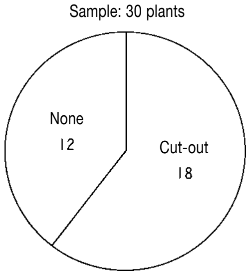


Fig. 5.3 **Situation of high pressure cut-out of the refrigerating machines for air conditioning systems (without chemical treatment)**

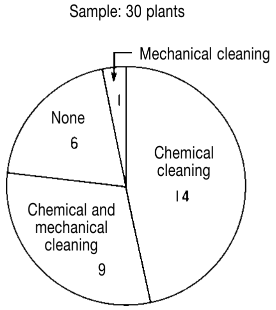


Fig. 5.4 **Types of cleaning for heat exchangers of refrigerating machines (without chemical treatment)**

for air conditioning systems is changing from the performance of treatment chemicals to the provision of comprehensive services including environmental protection, safety cares for natural lives and so on. In the present, the application of expert systems for water treatment is progressing to automatically control the system operation, to estimate the efficiency and to monitor the chemical treatment effect.

In this chapter, the present situation and future trend of chemical water treatments for the air conditioning systems are discussed.

5.2 Water Treatment for Cooling Water Systems

Tap water is generally supplied to cooling water systems used for air conditioning systems in buildings. The recycle of cooling water is carried out by using cooling towers mentioned in the chapter 3 of this handbook.

Problems occurring in air conditioning systems include the corrosion penetration of heat exchanger tubes, the leakage of cooling water from the piping, the reduction of refrigerating machine efficiency and the increase in the energy consumption, such as electricity, gas and steam. Those problems must be prevented by applying an adequate chemical water treatment for the safe and efficient system operation.

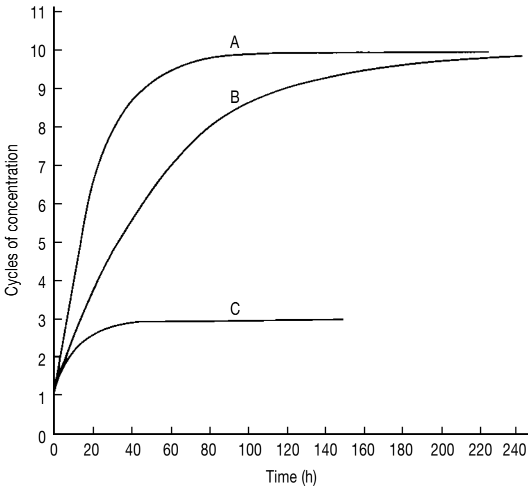
5.2.1 Characteristics of Cooling Water Systems for Air Conditioning Systems

Figure 5.5 shows the relationship between the change in the cycles of concentration and the operation time in air conditioning cooling water systems. The curve A in the Figure 5.5 shows the example of a small cooling tower used for a packaged air-conditioner, and the curve B shows the example of a middle size cooling tower used for centrifugal refrigerating machines or absorption refrigerating machines. The air conditioning cooling water system generally has a small holding water volume against the circulating water rate. The ratio of the holding water to the circulating water is extremely small and about 1:100 to 1:150 in case of small cooling towers. In case of middle or large size cooling towers, the ratio is about 1 : 10 to 1 : 30. Therefore, if no blowdown is carried out in the cooling tower, the cycles of concentration increases within a short time. In the cases of A and B, the cycles of concentration reach 10 or more because the windage loss is 0.1% or less. When the blowdown of 0.35% against the circulating water is made, the cycles of concentration reaches around 3 as shown in the curve C.

Figure 5.6 shows an example of the relationship among the total blowdown, make-up water and the cycles of concentration in a cooling tower system. A decrease of the blowdown reduces the make-up water quantity, but increases the cycles of concentration, which may increase the probability of trouble occurrence.

The employment of an appropriate blowdown and water treatment chemicals, such as corrosion inhibitors, scale inhibitors and biocides, controls the water quality in an appropriate range and prevents the trouble occurrence.

Usually, the operation loads of air conditioning cooling water systems fluctuate widely. Consequently, the cycles of concentration and cooling water quality change even when a constant blowdown is carried out. Therefore, the installation of an automatic control system which controls the blowdown and the chemical injection is required to maintain the cooling water quality in an appropriate range.



Conditions

System	A	B	C
Circulating water (m^3/h)	15.6	390	390
Holding water (m^3)	0.3	20	20
Evaporation loss (%)*	0.9	0.9	0.9
Windage loss (%)*	0.1	0.1	0.1
Blowdown (%)*	0	0	0.35

* Against circulating water

Fig. 5.5 **Changes of the cycles of concentration with time in air conditioning cooling water systems**

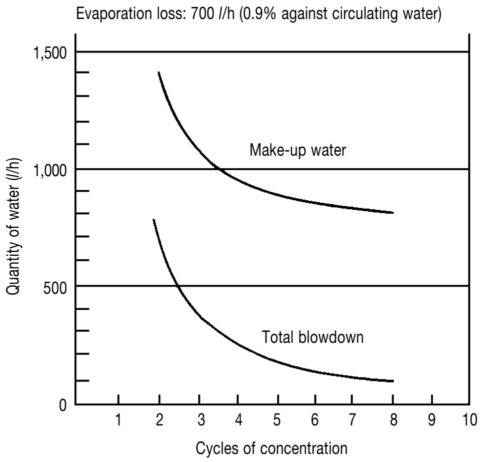


Fig. 5.6 **Relationship among the cycles of concentration, make-up water and total blowdown in a cooling tower system**

The sizes of cooling towers for air conditioning systems are widely different depending on the size of the building and the cooling load. If automatic control systems are installed in every cooling tower, the installation cost becomes too expensive for small size systems. Therefore, it is suitable to apply advanced treatments for large-size cooling towers and to use simplified water treatments for small size cooling towers.

The causes of troubles in air conditioning cooling water systems and their countermeasures are essentially same to those of industrial cooling water systems described in the chapter 3.

5.2.2 Water Treatment Methods for Large or Medium Size Cooling Water Systems

Large or medium size cooling water systems are generally used for cooling centrifugal or absorption refrigerating machines. In some cases, packaged air conditioners are installed on each floor in a large building and the cooling of these machines is carried out by using large cooling towers. Here, a large or medium size cooling water system is defined as a cooling water system which has the cooling capacity of 100 RT* or more.

As previously discussed, various problems, such as corrosion, scale and slime, occur in cooling water systems and a chemical water treatment is applied to prevent these problems. Moreover, the application of the chemical water treatment contributes the energy and water saving.

Especially after 1980, the following items have influenced on the water treatment methods in Japan:

① Shortage of water resources in large cities,
② Nutrification problems in closed water areas located near large cities,
③ Requirement to reduce the life cycle cost (LCC) of buildings,
④ Prevention of Legionnaires disease.

To reply for those requests, non-phosphorus multi-functional cooling water treatment chemicals (Non-P multi-chemicals) have been developed. The Non-P multi-chemicals prevent all kinds of problems, such as corrosion, scaling and slime (biofouling), under the high cycle number operation of cooling water systems and scarcely influence the environment.

Table 5.1 Standard control range of cooling water quality for a Non-P multi-chemical treatment

Chemical dosage (mg/l)		100–300
Cooling water	pH	7–9
	Calcium hardness (mg $CaCO_3/l$)	700 and below
	Silica (mg SiO_2/l)	250 and below
Water temperature (°C)		40 and below

Table 5.1 shows the standard control range of cooling water quality under the treatment with Non-P multi-chemicals. The treatment effects of Non-P multi-chemicals are described below.

(1) Corrosion control

Non-P multi-chemicals include low molecular weight polymers as corrosion inhibitors for carbon steel. The polymer forms an extremely thin and noncrystalline protective film composed of calcium carbonate mainly on the metal surface. This film acts as a barrier against the diffusion of oxygen and water to the metal surface. Then it reduces the corrosion rate. The increase in the pH and silica concentration of cooling water promotes the passivation of carbon steel in the coexistence of the polymers and inhibits the corrosion.

Triazoles formulated in the Non-P multi-chemicals prevent the corrosion of copper and copper alloys.

Table 5.2$^{1)}$ shows the corrosion inhibition effects of a Non-P multi-chemical. The corrosion inhibition rates of the Non-P multi-chemical are above 90% for carbon steel and above 80% for copper. Photographs 5.1 and 5.2 (p. 5-33) show the conditions of the cooling water piping and the condenser of a centrifugal refrigerating machine which were treated with the Non-P multi-chemical.

(2) Scale control

Polymers formulated in the Non-P multi-chemicals change the shape of the micro-crystals of calcium carbonate and reduce the crystal growth rate. This function of scale inhibitors is called “crystal distortion”.

A Non-P multi-chemical provides the sufficient calcium carbonate scale inhibition for the cooling water of high calcium hardness of 700 mg $CaCO_3/l$ as shown in Figure 5.7.

Figure 5.8 shows the inhibition effect of the Non-P multi-chemical on silica scale. The application of Non-P multi-chemical inhibits the scaling up to the silica concentration of 250 mg SiO_2/l. Figure

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* RT: Refrigeration ton = the refrigeration capacity necessary to change 1 ton of demineralized water to ice at 0°C in 24 hours,
Japanese RT = 3,320 kcal/h

Table 5.2 **Corrosion inhibition effect of a Non-P multi-chemical**

Chemical treatment	Cooling water system	Corrosion rate (mg/dm^2·day)	
		Carbon steel	Copper
Yes	A	2.6	0.01
	B	1.3	0.07
	C	—	0.3
	D	1.3	0.2
	E	9.4	0.13
	F	3.5	0.19
	G	1.3	0.11
	H	1.2	0.2
	I	2.7	0.32
	Average	2.7	0.17
No	J	—	0.35
	K	76.1	0.28
	L	35.5	—
	M	50.9	1.75
	Average	54.2	0.79

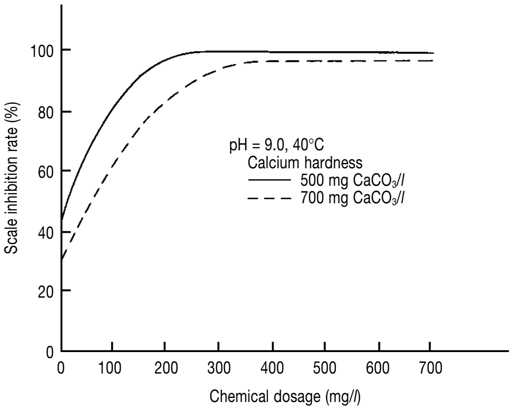


Fig. 5.7 **Inhibition effect of a Non-p multi-chemical on calcium carbonate scale**

5.9 shows the relationship between the scaling rate of silica and the skin temperature of heat exchanger tube at the silica concentration of 340 mg SiO_2/l under the Non-P multi-chemical treatment. When the skin temperature is 40°C or less, the scaling of silica is perfectly prevented by using the Non-P multi-chemical.

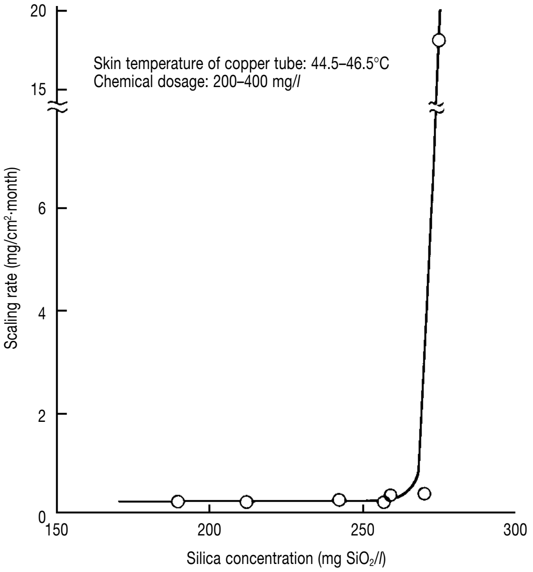


Fig. 5.8 **Inhibition effect of a Non-P multi-chemical on silica scale**

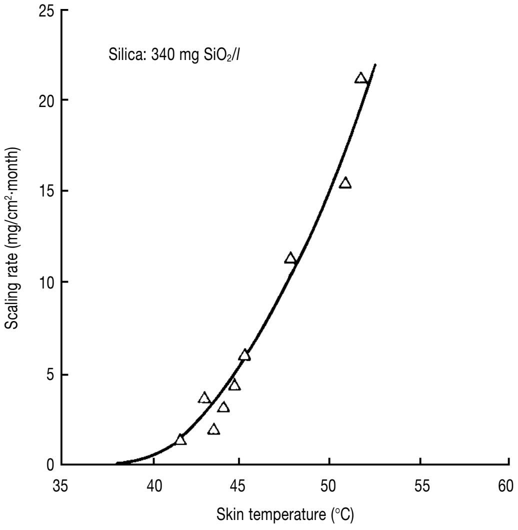


Fig. 5.9 **Relationship between the skin temperature of heat exchanger tube and the scaling rate of silica**

(3) Slime (biofouling) control

The slime control agents including in the Non-P multi-chemicals decrease the stickiness of microbiological flocs and prevent their adhesion on metal surfaces as slime. Since the slime control agents are non-oxidizing type, they scarcely promote the corrosion of carbon steel and copper.

Figure 5.10 shows the prevention effect of the Non-P multi-chemical on slime adhesion to a heat exchanger. The fouling factor is kept at 5 X 10^{-5} $m^2 \cdot h \cdot {}^\circ C/kcal$ or less by applying the Non-P multi-chemical.

When biofouling adheres to a metal surface, the surface of the metal becomes non-uniform and an under-deposit corrosion may occur. Figure 5.11 shows the influence of slime adhesion on the pitting corrosion of copper heat exchanger tube of a refrigerating machine. The reduction of tube wall thickness is observed beneath the biofouling. The maximum pit depth under the slime is about 1.5 times deeper than that at clean surface²⁾.

Photographs 5.3 and 5.4 (p. 5-33) show the conditions of slime adhesion on the condensers of refrigerating machines treated without and with a slime control agent respectively.

(4) Control of Legionella pneumophila growth

Legionella pneumophila (L. pneumophila) causing Legionnaires' disease proliferates with an algal growth in heavily fouled cooling water systems³⁾.

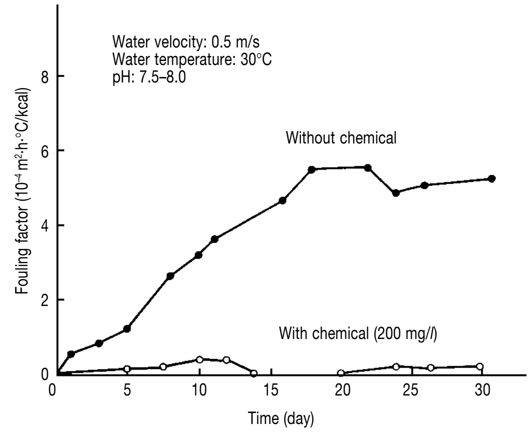


Fig. 5.10 Prevention effect of a Non-P multi-chemical on slime adhesion to a heat exchanger

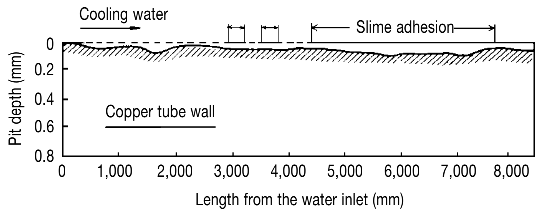


Fig. 5.11 Influence of slime adhesion on the pitting corrosion of the copper tube of a refrigerating machine heat exchanger

The slime control agent formulated in Non-P multi-chemicals inhibits the growth of algae and L. pneumophila. Table 5.3 shows the inhibition effect of the Non-P multi-chemical on L. pneumophila growth in a cooling water system. The detection ratio of L. pneumophila growth is decreased to about 10% by applying the Non-P multi-chemical. Recently, more effective biocides for L. pneumophila growth have been developed. Therefore, combined treatments of the Non-P multi-chemicals with those biocides are also applied.

(5) Control method of cooling water quality

Cooling water quality must be controlled within a control range to obtain the sufficient chemical treatment effect, and to realize the safe and efficient operation of air conditioning cooling water systems.

In the case of air conditioning cooling water systems, the manual control of the blowdown is generally very difficult because the operation load and operating period widely fluctuate. Therefore, an automatic water quality control system is necessary to maintain the cooling water quality in a specified range.

(a) Automatic cooling water quality control system

Figure 5.12 shows the flow-diagram of an automatic cooling water quality control system. This system controls the electrical conductivity of cooling water by controlling the overflow-blowdown from the tower basin, when the electrical conductivity reaches to the upper limit of the control range.

In this system, a required amount of water treatment chemical is injected into the system proportionally to the make-up water amount. Recently, an automatic control system with solar batteries has developed and it requires no additional power supply source.

(b) Side stream filter

High cycle number operation of cooling water system is realized by removing the suspended

Table 5.3 Inhibition effect of a Non-P multi chemical on L. pneumophila growth

Chemicals	Growth of L. pneumophila		Detection ratio of L. pneumophila growth
	Not detected	Detected	
Untreated	9 systems	14 systems	61%
Treated	28 systems	3 systems	10%

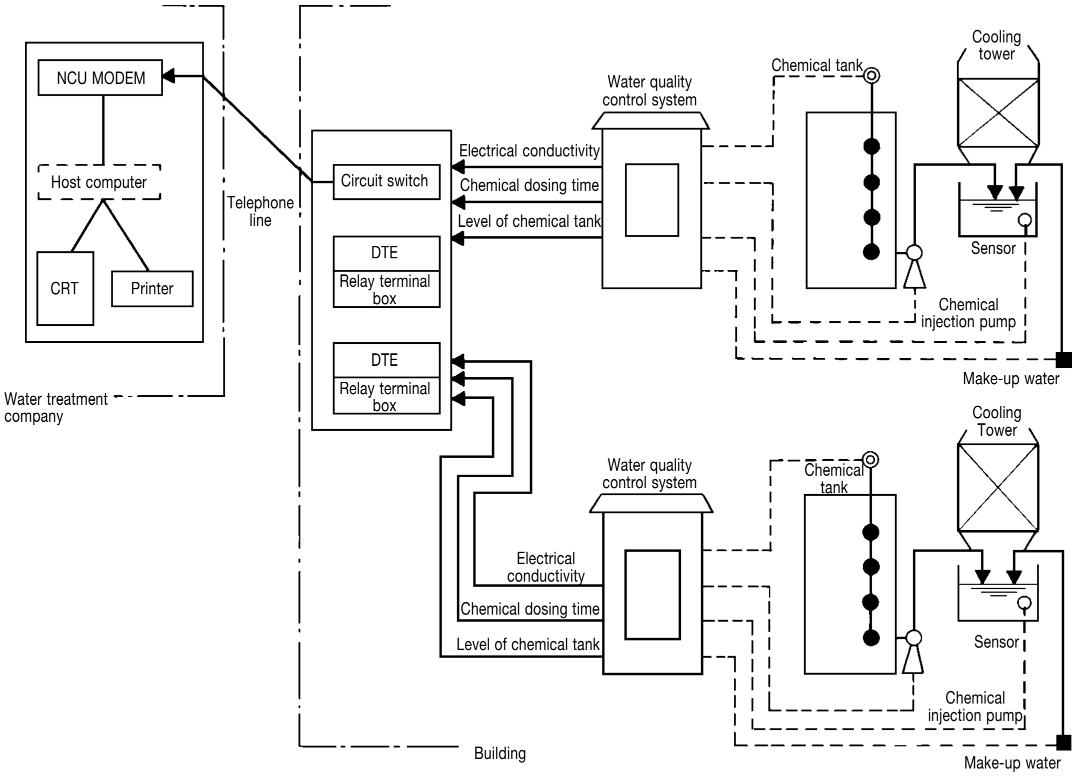


Fig. 5.12 Flow diagram of an automatic operation control system utilizing data communication system for multi-cooling-tower systems

solids from the system using a side stream filter with a suitable chemical treatment. Recently, the installation of filters with the automatic operation control systems becomes popular. Figure 5.13 shows an example of a side stream filter installation.

(c) Utilization of data communication system

The popularization of automatic cooling water quality control system realizes the perfect non-man control in buildings. For this purpose, the combination of the automatic control system with data communication system has been developed in Japan. In this system, a host computer in a water treatment company is connected with automatic cooling water quality control systems installed in many buildings through telephone lines. If an irregularity happens in a cooling water system, the water treatment company simultaneously detects the irregularity through the data communication system, and informs the countermeasure or sends the engineer to the customer. Figure 5.12 shows a flow diagram of this control system.

5.2.3 Water Treatment Methods for Small Size Cooling Water Systems

Formerly, chemical water treatment was seldom applied for small cooling towers with the capacity of 100 RT or less, because the cost of chemical injection system was relatively high, and no operator was employed. Therefore, when the operational efficiency dropped, the equipment was cleaned by using chemical cleaning agent to recover the efficiency. However, the chemical cleaning requires the stoppage of the air conditioning and the considerable cost. To solve these problems, tablet-type water treatment agents requiring no maintenance control have been developed and applied. Photograph 5.5 (p. 5-34) shows a tablet-type water treatment agent. Two types agents are marketed; first one is the multi-type-chemical which includes a corrosion inhibitor, scale inhibitor and biocide, the second is a biocide for L. pneumophila. Tablet-type cooling water treatment agents are used in the following method.

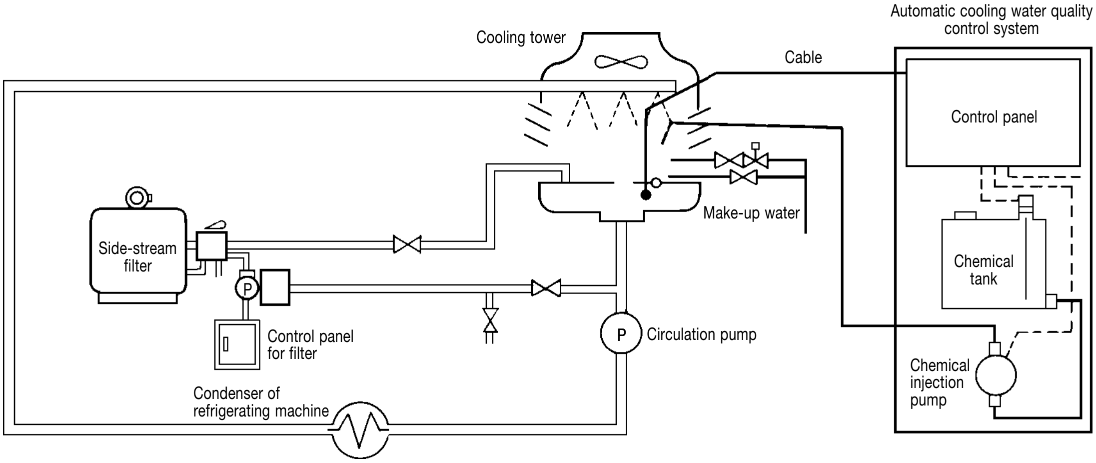


Fig. 5.13 An example of side-stream filter installation for a cooling tower system

(1) Application method

Generally, the tablet-type agent is put into a cooling tower basin to float it on the water surface. In a cooling tower having the water distribution decks on the top, the agent is set on the decks. When using two or more packs of these chemicals, all packs must be connected together using coupling pins as shown in Photograph 5.5.

(2) Dosage

One pack of tablet-type cooling water treatment agent is used for each 20 to 30 RT of cooling capacity of the cooling tower.

(3) Effective period

Since these chemicals dissolve in water very slowly, the effective period after dosing chemicals is generally 2 to 3 months.

(4) Effect of tablet-type agents

The effect of the tablet-type agents is not so perfect but it is enough for the safe and efficient operation of small size air conditioning cooling water systems.

Photographs 5.6 and 5.7 (p. 5-34) show the algalcidal effect of a tablet-type agent in a cooling tower.

5.2.4 Energy-Saving Operation of Refrigerating Machines

The adhesion of scale and slime on the condenser or absorber of a refrigerating machine decreases the efficiency because of their much lower thermal conductivities than those of metals. For a centrifugal refrigerating machine, the lowering of heat transfer efficiency increases the refrigerant gas condensation temperature and proportionally increases the discharge pressure at the high-pressure side. When the discharge pressure has increased, the work load (electricity consumption) of the compressor increases. In other words, the consumption of electricity increases through the process shown in Table 5.4.

(1) Changes in refrigeration cycle due to the adhesion of scale

The above phenomenon is shown in a Mollier diagram of Figure 5.14. When the discharge pressure at the high-pressure side rises as the result of scale or slime adhesion, the excess compression work load (electricity consumption) is required as compared to the normal condition.

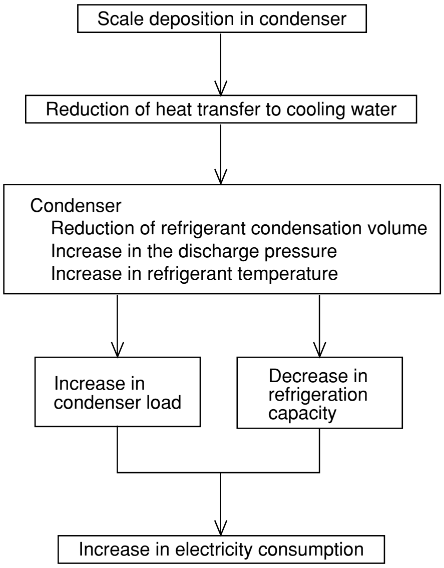
For absorption refrigerating machines, an excess fuel is consumed by scale adhesion as shown in Figure 5.15.

(2) Monitoring method of refrigeration efficiency

Operating data of a refrigerating machine, such as the inlet temperature of cooling water and the evaporation pressure of refrigerant, are always changing with time. Therefore, the following method is used for confirming the efficiency of the refrigerating machine.

When a fouling has adhered to the heat exchanger (condenser), the heat transfer is disturbed and the difference between the temperatures of the refrigerant and the cooling water increases as shown in Figure 5.16. There-

Table 5.4 Increase in the electricity consumption of a refrigerating machine by the scaling of condenser



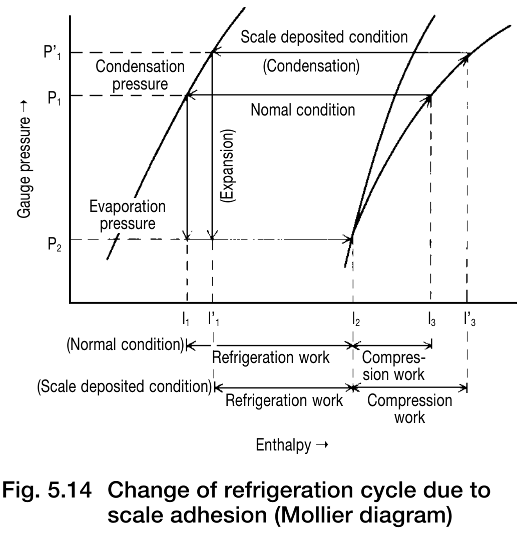
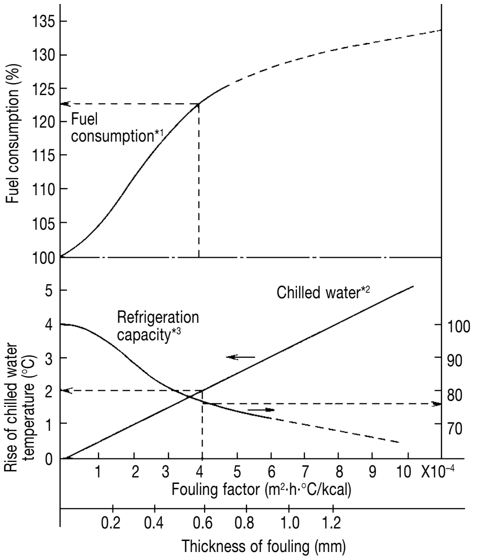


Fig. 5.14 Change of refrigeration cycle due to scale adhesion (Mollier diagram)

fore, the fouling condition is monitored from the difference between the refrigerant condensation temperature and the outlet cooling water temperature. This temperature difference is called Leaving Temperature Difference (LTD) and is shown by equation (5.1).

LTD = Refrigerant condensation temperature - outlet cooling water temperature ··· (5.1)



*1 Fuel consumption of designed condition is made 100%.
*2 When the refrigeration capacity is constant.
*3 When the chilled water temperature is constant.

Fig. 5.15 Relationship between the scale adhesion and the fuel consumption of an absorption refrigerating machine

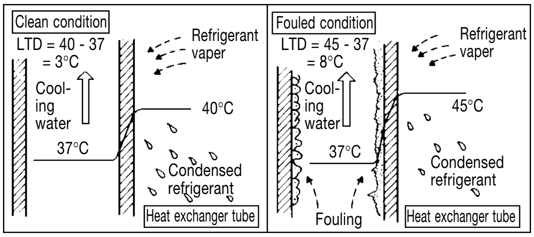


Fig. 5.16 Temperature change of a refrigerant by the fouling adhesion in a condenser

Table 5.5 shows the relationship between the LTD and the fouling condition of heat exchanger.

Recently, a computer program based on Mollier diagram is used for checking the operation condition of centrifugal refrigerating machines. When the daily operation data of a refrigerating machine are put into a computer, the LTD, electricity consumption and so on are calculated. The quantitative diagnosis of the fouling condition, such as energy loss and the energy-saving effects of chemical treatment, is carried out.

(3) Case studies of energy-saving operation of refrigerating machines

Figure 5.17 shows the changes in the LTD of a centrifugal refrigerating machine with a capacity

Table 5.5 Relationship between the LTD and fouling condition of heat exchangers

LTD*	Fouling condition
3–5°C	Clean
5–10°C	Fouling adhesion may be occurred
10°C and above	Possibility of high pressure cut out due to the heavy fouling adhesion

* Designed LTD: about 3°C

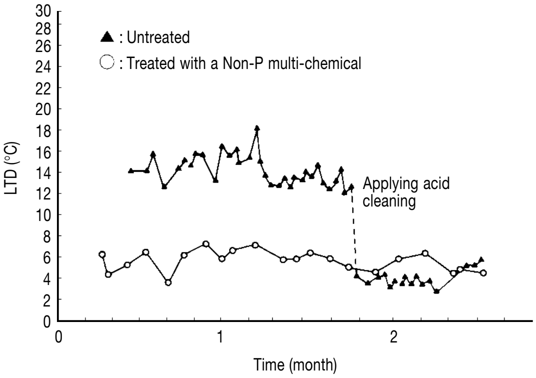


Fig. 5.17 Changes in the LTD of a centrifugal refrigerating machine and the effect of a chemical treatment

of 400 RT, under no chemical treatment and a Non-P multi-chemical treatment.

Under no chemical treatment, the average LTD was high at around 14°C, and a "high pressure cut-out" of the refrigerating machine occurred. Then, the machine was cleaned by acid and a Non-P multi-chemical was applied for the cooling water system. After that, the average LTD was kept at around 6°C and the refrigerating machine was operated without any high pressure cut-out, even in summer time under the high operation load.

Table 5.6 shows the energy-saving effect of a Non-P multi-chemical treatment for a centrifugal refrigerating machine. The electricity saving of 76,000 kWH per month was realized by applying the chemical treatment.

Figure 5.18 shows the change in the LTD of a centrifugal refrigerating machine experiencing the high pressure cut-out caused by slime adhesion. The electricity consumption of this machine increased around 20% against the designed value before the high pressure cut-out.

The shock dosing of a slime removal agent showed the sufficient effect as same as that of the brush-cleaning. At present, the slime removal agent is dosed at a specified interval. This treatment keeps the increase of LTD in an allowable range and realizes a considerable energy saving.

5.3 Water Treatment of Closed Recirculating Water Systems for Air Conditioning

5.3.1 Closed Water Recirculation Systems with Heat Accumulation Tanks

Recently, the employment of closed water recirculation systems with heat accumulation tanks has become popular for air-conditioning systems in Japan in order to effectively utilize the electricity after midnight and to reduce the peak electricity consumption during the summer.

The heat accumulation using electricity at night gives the users many advantages, such as an incentive taxation and a special discount for the electricity cost. However, troubles caused by water sometimes occur in those systems.

A typical problem is the corrosion of the copper tube of the fan coil unit (FCU) and the air handling unit (AHU)[4)–6)]. Photograph 5.8 (p. 5-35) shows an example of the corrosion of the copper tube of an AHU in a closed system treated without chemicals.

(1) Characteristics of heat accumulation water quality and problems

(a) Dissolution of "lye"* from concrete water-tank

Most heat accumulation tanks are built of concrete. "Lye" dissolves into water from newly-constructed concrete tanks to be applied the insufficient waterproof treatment. This "lye" increases the pH and hardness of the heat accumulation water.

The pH sometimes exceeds 10. The pH increase of over 9 accelerates the corrosion of copper-base materials. Also, the increased pH promotes the hardness scale deposition on the heat exchangers of the FCU, AHU and refrigerating machines, and reduces their thermal efficiencies. In addition, the deposition of porous scale often causes the under deposit corrosion.

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* Alkaline component dissoluted from new concrete tank

Table 5.6 Energy saving effect of a chemical water treatment for a 400 RT centrifugal refrigerating machine

Chemical treatment	LTD (°C)	Electricity consumption (kW/h)	Saving in electricity (kW/month)	Saving in electricity cost* (1000 Yen/month)
Untreated	14	457.7	76,176	1,371
Treated	6	351.9		

* 1 kW = 18 Yen

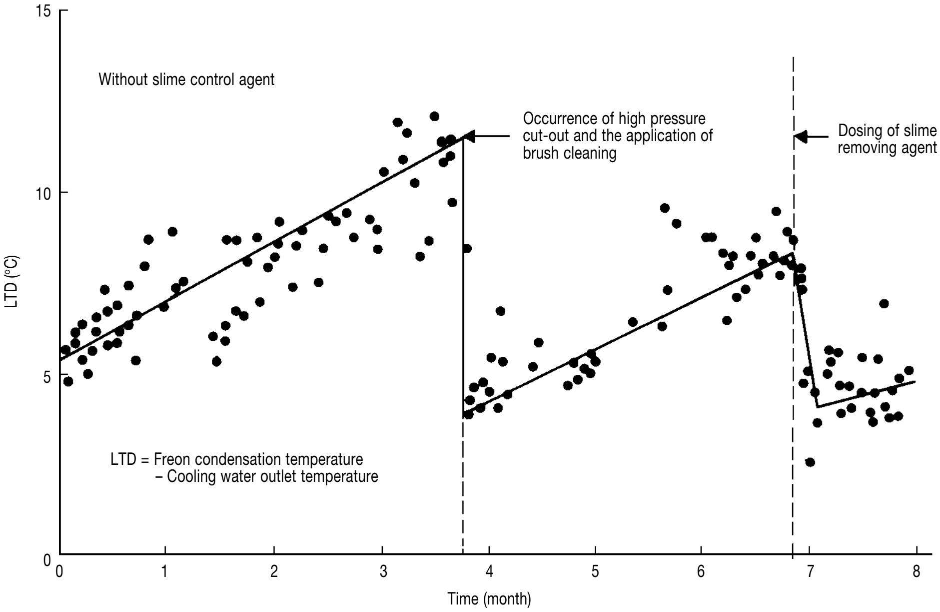


Fig. 5.18 Change in the LTD of a centrifugal refrigerating machine caused by slime adhesion

(b) Contamination of heat accumulation water with underground water

Because most heat accumulation tanks are built in underground, the formation of cracks in concrete walls causes the contamination of heat accumulation water with the seawater or polluted underground water.

The water contamination with seawater increases the chloride ion concentration and accelerates the corrosion of piping, FCU and AHU.

The contamination with underground water polluted with organic matters accelerates the growth of microorganisms in the heat accumulation water, then causes slime problems and microbiologically influenced corrosion.

In the design and construction stages of the concrete tanks, a sufficient consideration should give to prevent the cracking of the concrete wall. However, if some cracks have developed after the construction, the cracks must be repaired by the pressurized injection of quick-setting cement and/or the pasting of rubber sheet over the cracks.

(2) Presence of copper oxide film on FCU and AHU tube surfaces

Through the FCU and AHU manufacturing processes, such as the welding, tube expansion and degreasing, non-uniform copper oxide films form on the copper tube surfaces as shown in Photograph 5.9 (p. 5-35). When the oxide film contacts with water including dissolved oxygen, the defective points of the oxide film act as local anodes and the surrounding oxide film acts as the cathode of corrosion reaction. Then the local corrosion proceeds at the anodes and results in the water leakage of the tubes after several months to few years from the operation start-up.

(3) Countermeasures

(a) Inhibition of general corrosion and scale

In closed systems with heat accumulation tanks, the retention time of water is extremely long.

Therefore, the agents applied for this system should show not only the good corrosion and scale inhibitions but also the sufficient stabilities. Polyphosphate-zinc-polymer based corrosion and scale inhibitors or phosphonate-zinc-polymer-based chemicals are generally applied for these systems to satisfy the above requirements. Nitrite based chemicals are normally used in general closed cooling water systems but they are difficult to provide the stable corrosion inhibition for this system, because most nitrite ion are oxidized to nitrate ion by nitrification bacteria.

Table 5.7 shows an example of the water quality control limit when a polyphosphate-zinc-polymer treatment is applied. This water treatment gives the good corrosion inhibition on carbon steel and copper in the cold water tank at 7° C to 12° C, and in the hot water tank at 40° C to 45° C. Table 5.8 shows the typical corrosion test results in this system.

Table 5.7 Water quality control limits for closed water recirculating system with heat accumulation tank under a polyphosphate-zinc-polymer treatment

pH	(25° C)	6.5–8.5
Electrical conductivity	(μ S/cm)	Below 2,000
Calcium hardness	(mg $CaCO_3/l$)	Below 120
Chloride ion + Sulfate ion	($Cl^- + SO_4^{2-}$ mg/l)	Below 500

Table 5.8 Corrosion inhibition effect of a polyphosphate-zinc-polymer treatment in a closed water recirculating system with heat accumulation tank

Water temperature (° C)	Chemical treatment	Material	Corrosion rate (mg/dm^2·day)
7–12 (Cooling season)	No	Carbon steel	37.5
		Copper	0.5
	Yes	Carbon steel	0.9
		Copper	0.1
40–45 (Heating season)	No	Carbon steel	98.1
		Copper	2.8
	Yes	Carbon steel	2.0
		Copper	0.2

(b) Pitting corrosion inhibition for copper and copper alloys

The pitting corrosion troubles of the copper tubes of FCU and AHU have been often reported in Japan. The corrosion of copper generally occurs when the corrosion potential of copper exceeds the pitting potential of 150 mV, saturated calomel electrode or 192 mV, Ag/AgCl electrode. The presence of copper oxide film and the biofouling on the copper tube surface increases the corrosion potential higher than the pitting potential. Therefore, to prevent the pitting corrosion, the corrosion potential has to be kept lower than the pitting potential by preventing the fouling of the metal surface.

Recently, a pitting corrosion inhibitor has been developed. This inhibitor removes various foulings from the copper surface and prevents the increase in the corrosion potential. Then it prevents the pitting corrosion. Figure 5.19 shows the change in the corrosion potential of copper tube when this inhibitor was applied for a heat accumulation tank with the capacity of 1,000 m^3. The corrosion potential is reduced below the pitting potential. As the result, the pitting corrosion is inhibited.

(c) Others

Replacing water is the best countermeasure for the dissolution of lye from concrete tanks. Usually, after two or three times of complete water

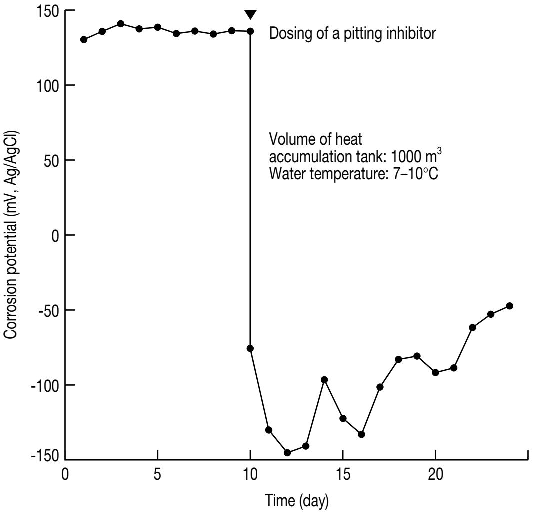


Fig. 5.19 Change in the corrosion potential of a copper tube by dosing a pitting corrosion inhibitor

replacements, the dissolution of lye becomes few.

The various contaminants including corrosion products from pipings, the trash of concrete, microorganism flocs, etc., frequently accumulate and form sludge at the bottom of the heat accumulation tank. Photograph 5.10 (p. 5-36) shows a sludge accumulated at the bottom of a heat accumulation tank. These contaminants sediment and adhere to the inside of copper tubes with the slow water flow velocity of 0.3 m/second or less. In these sections, oxygen concentration cells are formed, leading to the corrosion of the copper tubes. This type of copper corrosion is shown in Photograph 5.11 (p. 5-36). Therefore, the periodical water replacement and cleaning of heat accumulation tanks are necessary to prevent those problems.

5.3.2 Closed Water Recirculation Systems with Heat Pumps

Formerly, centrifugal refrigerating machines, absorption refrigerating machines or packaged air conditioning units have been used for cooling, while steam or hot water from boilers have been used for heating. Recently, heat pump units have been frequently used for cooling and heating to save energy. Large-size air conditioning systems mainly use water-cooled heat pump units. Small-size air conditioning systems generally use air-cooled heat pump units. Both types of heat pump units have the closed water recirculation systems using for heating and cooling.

(1) Problems and their countermeasures

In the closed water recirculation system, the water quality is scarcely deteriorated by external causes. Therefore, scale problem rarely occurs and the main problem is the corrosion of pipings, AHU and so on. Nitrite based inhibitors are frequently applied for preventing the corrosion of this system. Generally, copper corrosion inhibitors are used together with the nitrites. Figures 5.20 and 5.21 show the corrosion inhibition effects of a nitrite-based inhibitor on carbon steel and copper respectively. The corrosion rate is sufficiently reduced by applying the 5,000 mg/*l* of the corrosion inhibitor.

Photograph 5.12 (p. 5-36) shows the condition of the inner surface of a carbon steel pipe which has been treated by a nitrite based corrosion inhibitor for 15 years. The corrosion of the pipe is minimized and the surface condition is very good.

In the high temperature systems of above 60° C or in the corroded systems, the pH of the circulating water tends to rise to 10 or higher because of ammonia and/or caustic soda formation by the decomposition of sodium nitrite. In that case, a corrosion inhibitor including a pH buffering agent has to be applied to minimize the pH increase causing copper corrosion.

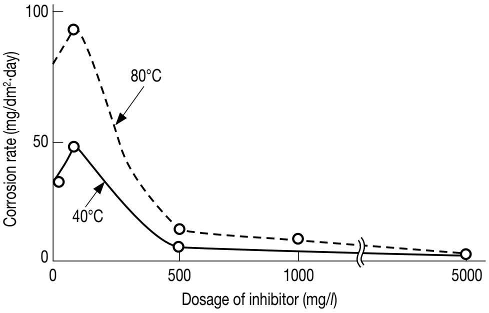


Fig. 5.20 Corrosion inhibition effect of a nitrite based inhibitor on carbon steel

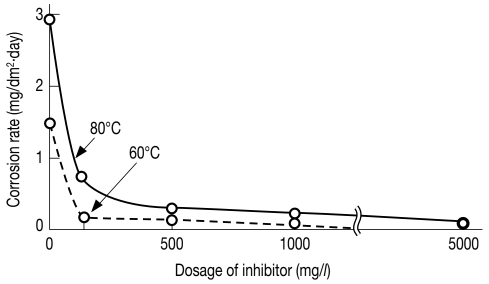


Fig. 5.21 Corrosion inhibition effect of a nitrite based inhibitor on copper

(2) Treatment of hot water boilers

In the closed systems with heat pump units, hot water boilers are often installed to increase the heating capacities of systems in winter season. In these boilers, scaling troubles scarcely occur because of no evaporation of boiler water but the corrosion troubles are often caused by dissolved oxygen.

For hot water boilers used for heating only, nitrite based corrosion inhibitors with pH buffering agents are used. Figure 5.22 shows the effect of a nitrite based one.

In the case of hot water boilers using for air conditioning and hot water supply, corrosion inhibitors must be sufficiently safe for human health. For this purpose, natural products and food additive grade chemicals are generally used as the corrosion inhibitors. Figure 5.23 shows the effect

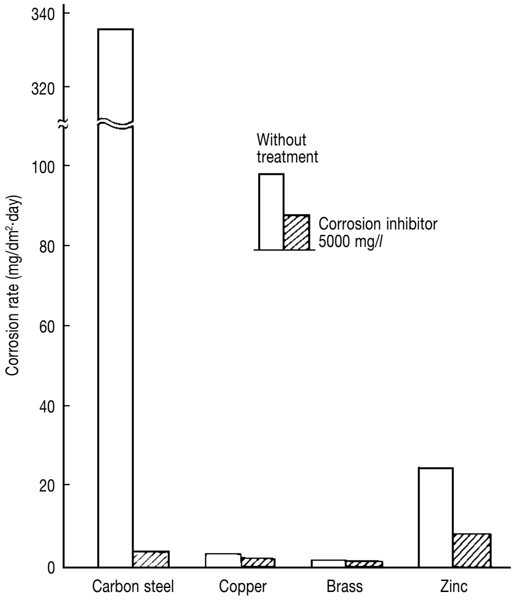


Fig. 5.22 Corrosion inhibition effects of a nitrite based inhibitor on the various metals of a hot water boiler

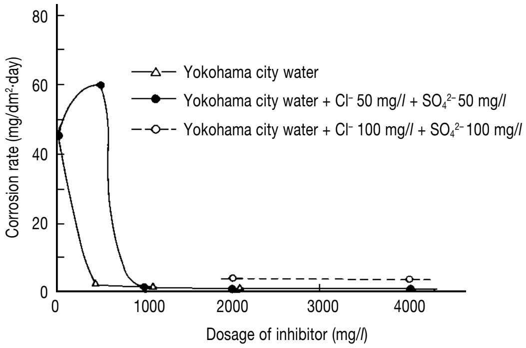


Fig. 5.23 Corrosion inhibition effect of a food additive grade inhibitor on carbon steel in hot water

of a food aditive grade inhibitor on carbon steel. This inhibitor shows the excellent corrosion inhibition at the dosage of above 2,000 mg/*l*.

5.4 Water Treatment for High Temperature Water Systems in District Air Conditioning Plants

5.4.1 Outline of the Systems

High temperature water of 70° C to 160° C is used as the primary heat source in district air conditioning plants. Figure 5.24 shows the flow diagram of a district cooling and heating plant including the high temperature water system. Equipments used in this system are high temperature water boiler, pipings, secondary heat exchangers, etc. The pipe lines become longer and the holding water volume becomes larger in this system. The materials to be used are mainly carbon steel, copper and copper alloys.

5.4.2 Problems and Their Countermeasures

Because the temperature is in the range of 70 to 160° C, scales, such as calcium carbonate, are formed if the tap water is supplied without treatment. The make-up water should be softened or demineralized to prevent the scale deposition. The corrosion of carbon steel due to dissolved oxygen, and the corrosion of copper and copper alloys due to high pH occur in this system. Since the construction of this system requires a long term, corrosion problems sometimes happen during the hydraulic test and the test run without corrosion inhibitor, before the start-up of plant operation. Taking such conditions into consideration, the countermeasures are described below.

(1) Corrosion inhibition of piping during plant construction

The pipings of district air conditioning plant often corrode during the construction period, because the construction period is a long and hydraulic tests are performed without corrosion inhibitor during the construction. The following treatment is recommended for the corrosion inhibition during the hydraulic tests.

Usually, a nitrite-based corrosion inhibitor and a biocide effective for nitrification bacteria are added into the water for the hydraulic test.

These agents are proportionally dosed into the supply water by using metric pumps.

(2) Flushing before plant start-up

The system is hardly cleaned if the flushing is done by using water alone. To get a sufficient flushing result, corrosion inhibitors and sludge dispersants are added into the flushing water, and the water is circulated for 3 to 4 hours. Then the water is replaced with fresh water until the total iron concentration of the circulating water decreases below 1 mg/*l*.

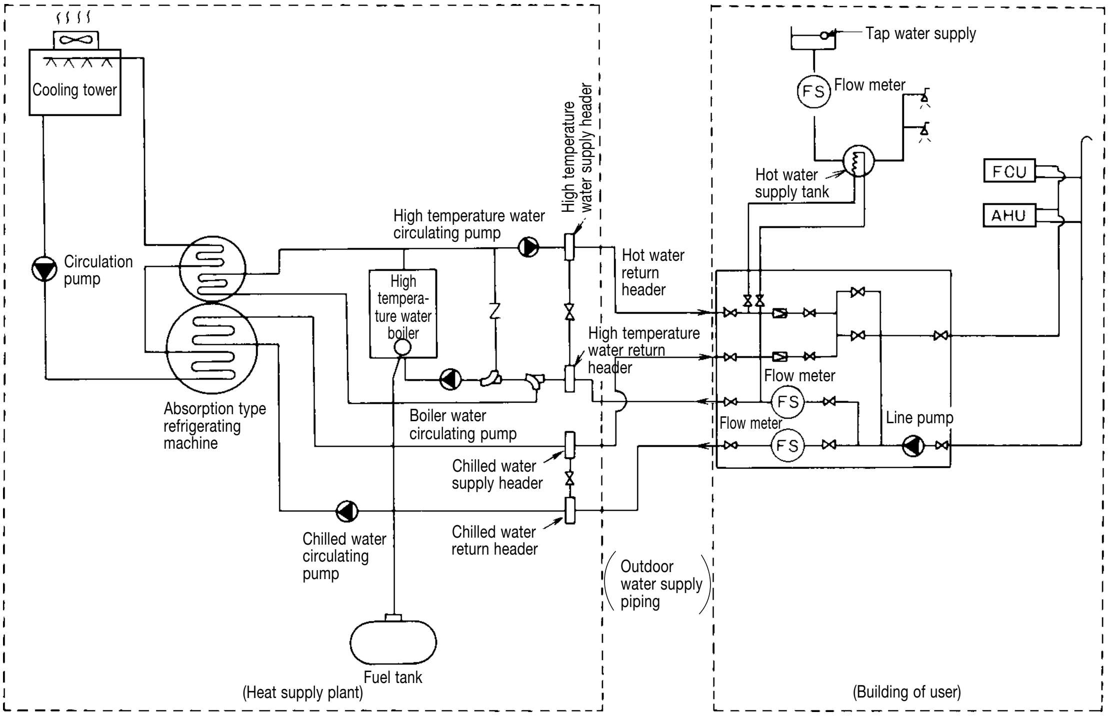


Fig. 5.24 Flow diagram of a district air conditioning plant including the high temperature water system

(3) Corrosion inhibition during operation

Amine and azole based corrosion inhibitors are used for high-temperature water systems. The amines form the adsorption film on carbon steel, and the azoles form the film composed of complex salts with copper ions on copper to prevent their corrosion. Figure 5.25 shows the effect of a corrosion inhibitor on carbon steel and copper. Table 5.9 shows the effect in an actual plant. These results indicate the sufficient effect of amine-azole based inhibitor in high temperature water systems.

(a) Dosing of corrosion inhibitor

The high temperature water circulating line is a closed system but a small amount of water, such as pump sealing water, leaks from the system. This leakage is usually smaller than 0.02% against the water circulation rate. Since the amount of actual leakage is different in each system, the amount should be confirmed and corrosion inhibitors have to be proportionally injected against the leakage to keep the specified concentrations in the water.

The injection point of corrosion inhibitor is generally the high temperature water circulation line and the chemicals should be injected by using metric pumps.

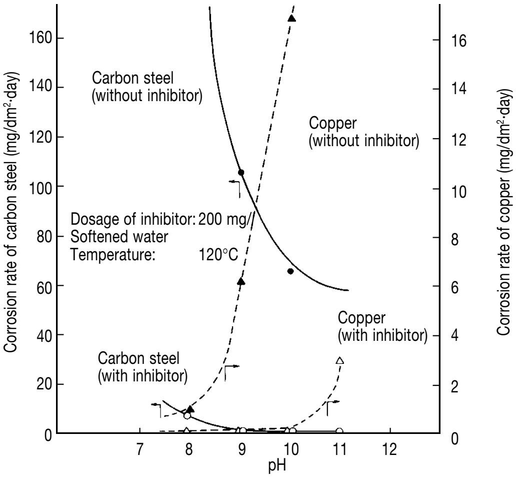


Fig. 5.25 Effects of a corrosion inhibitor on carbon steel and copper in high temperature water

Table 5.9 Effects of a corrosion inhibitor for high temperature water systems

Plant name			A	B
Test period		(month)	5	4.5
Water temperature		(°C)	120–150	70–140
Dosage of corrosion inhibitor		(mg/*l*)	200	500
Corrosion rate		(mg/dm^2·day)	Carbon steel: 3–7 Copper: 0.2–0.6	Carbon steel: 1–5 Copper: 0.1–0.4
Water quality	pH		8.3–9.3	7.8–9.1
	Electrical conductivity	(μ S/cm)	150–200	300–450
	Total iron	(mg/*l*)	Below 1.0	Below 1.0
	Total copper	(mg/*l*)	Below 0.05	Below 0.05

(b) Water quality analysis

The quality of circulating water should be periodically analyzed more than once a month to confirm whether the quality is in the control range or not. If it is not, countermeasures, such as the increase of the chemical dosage, must be taken.

5.5 Water Treatment for Advanced Air Conditioning Systems

5.5.1 Cogeneration Systems

(1) Outline of cogeneration systems

Recently, cogeneration systems supplying electricity and heat simultaneously come into the limelight. "Cogeneration" means the simultaneous creation of electricity and thermal energy from the primary energy sources of natural gas, oil and so on. The energy efficiency of conventional electricity generation systems is around 35%, because these systems exhaust the remaining heat after electricity generation. On the other hand, the cogeneration system recovers and utilizes the remaining heat, consequently the energy efficiency increases up to around 70 to 80%.

As shown in Table 5.10, diesel engines, gas engines or gas turbine engines are used as electric power generators in the cogeneration systems. The waste heat after electricity generation is recovered and utilized for air conditioning and hot water supply systems. Figures 5.26 to 5.28[7] show the typical flow diagrams of cogeneration systems.

(2) Water treatment methods

Cogeneration systems using gas turbine generators are suitable for relatively large scale users. Heat recovery is mainly carried out by the waste heat boiler. A cooling water system and a closed water recirculating system for air heating and cooling are generally installed in the cogeneration system. Water treatment methods used for these systems are described in the chapter 2 and, the sections 5.2 and 5.3.

Cogeneration systems using diesel engine generators or gas engine generators are suitable for the relatively small scale users. Heat recovery is done from the engine cooling water. A hot water supply system and a closed water recirculating system for air heating and cooling are generally employed for this type of cogeneration system. The water treatment methods for these systems are referred to the section 5.3.

5.5.2 Heat Accumulation Systems with Ice

(1) Outline of the heat accumulation system

Heat accumulation system with ice, in which ice is used as the heat accumulation medium, has been in practical use since 1986 in Japan. A conventional water heat-accumulation system accumulates heat by utilizing the sensible heat with the change in water temperature. A heat accumulation system with ice utilizes the latent heat of melting ice. The heat accumulation capacity of a heat accumulation system with ice is 10 to 12 times of that of a conventional water heat accumulation system. Therefore, the installation area of this system is small and the 1/3 to 1/9 of the conventional system.

In heat accumulation systems with ice, various types of ice-making and ice-melting methods are applied. However, heat pumps are generally used for the heat exchanging.

(2) Water treatment methods

Water treatment methods for this type of system are basically the same as for a heat accumulation system using water.

Table 5.10 Types and characteristics of electric power generators for cogeneration systems

Electric power generator	Diesel engine	Gas turbine	Gas engine
Outline of system	Electricity is generated by diesel engines. Waste heat is recovered as hot water.	Electricity is generated by gas turbines. Waste heat is recovered as steam.	Electricity is generated by gas engines. Waste heat is recovered as hot water.
Power generation efficiency (%)	35–40	20–35	30–35
Heat recovery efficiency (%)	35–45	45–50	35–50
Total efficiency (%)	70–85	65–85	65–85
Fuel	A-class heavy oil, kelosene or LPG	A-class heavy oil, kerosene, LPG or city gas	LPG or city gas
Power generation capacity (kW)	Below 5,000	Above 500	500–1,000
Problems	Large amount of NO_X generation and high level noise	Relatively large installation space	Relatively high equipment cost

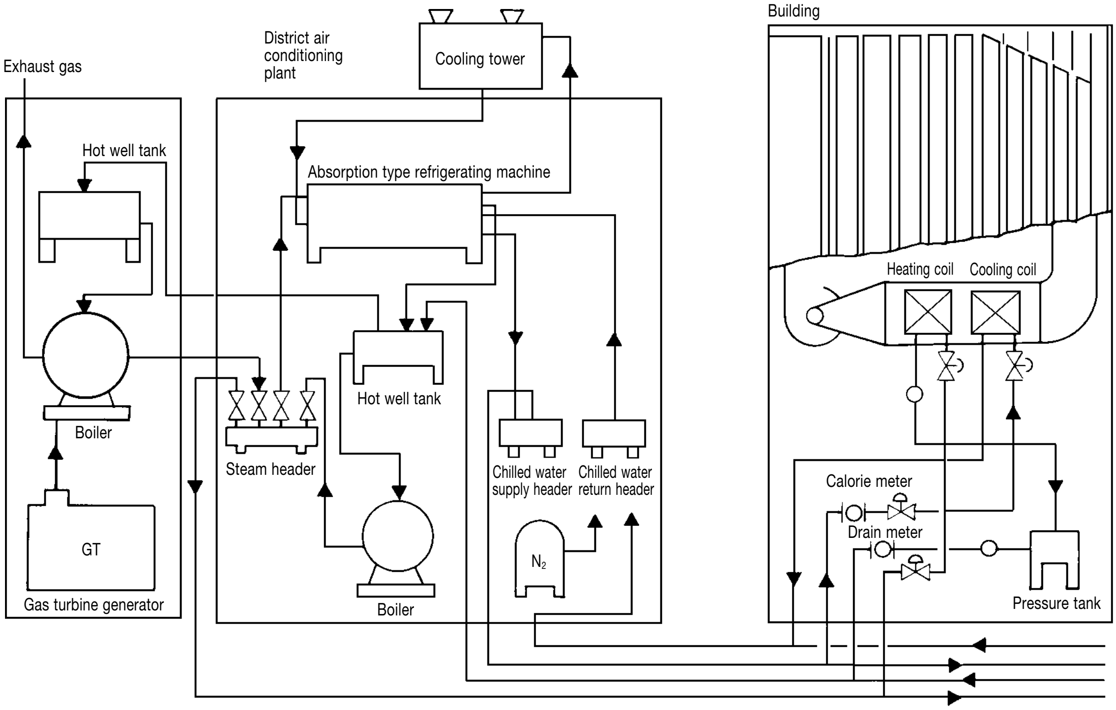


Fig. 5.26 Flow diagram of a cogeneration system using a gas turbine generator

Table 5.11 shows the effect of a phosphonate-zinc-polymer based corrosion inhibitor in a heat accumulation system with ice. The corrosion rates of carbon steel and copper are sufficiently lowered to below 3.3 mg/dm^2·day and below 0.2 mg/dm^2·day respectively through the cooling and heating seasons.

5.5.3 Systems Using Antifreezes

Antifreezes are used for antifreeze circulating

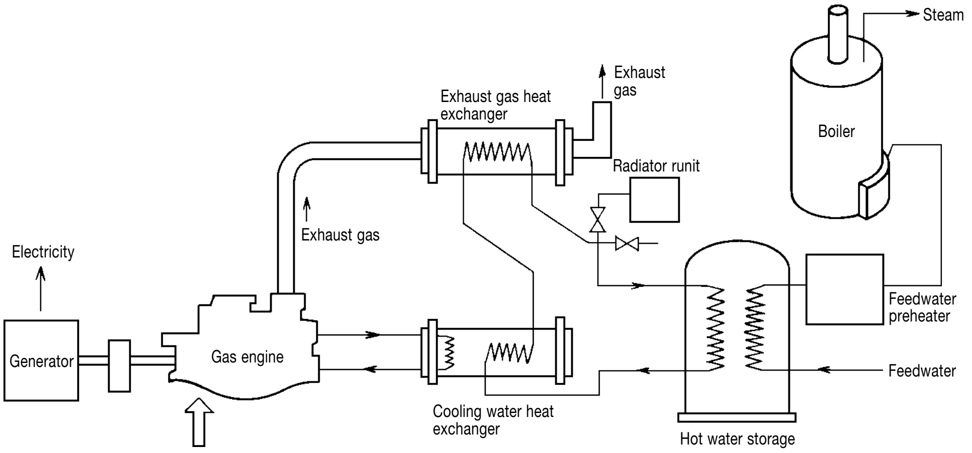


Fig. 5.27 Flow diagram of a cogeneration system using a gas engine generator

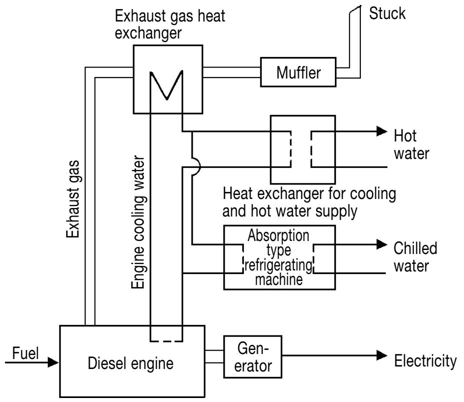


Fig. 5.28 Flow diagram of a cogeneration system using a diesel engine generator

Table 5.11 Corrosion inhibition effect of a phosphonate-zinc-polymer based inhibitor in a heat accumulation system with ice

Material	Test period (day)	Corrosion rate ($mg/dm^2 \cdot day$)
Carbon steel	34	0.7
	62	3.3
	66	1.9
	128	2.0
	162	1.9
Copper	34	0.2
	62	Below 0.1
	66	Below 0.1
	128	Below 0.1
	162	Below 0.1

heat accumulation systems utilizing ice, heating tower type heat pump systems, floor heating systems, solar systems and so on. The antifreezes require to show the good corrosion inhibition, not only under low temperature but also at high temperature. Moreover, they must be highly safety. To satisfy those requirements, propylene glycol including corrosion inhibitors composed of natural products and food additive grade chemicals is used as the antifreeze. Table 5.12 shows the corrosion inhibition effect of this type of antifreeze. Photograph 5.13 (p. 5-37) shows the appearances of the test coupons after the corrosion tests. In an antifreeze containing 25% of propylene glycol, the cast iron, carbon steel, solder and cast aluminum are severely corroded. However, the antifreeze including corrosion inhibitors shows the excellent corrosion inhibition at the high temperature of 88° C.

5.6 Troubles and Countermeasures in Water and Hot Water Supply Systems

5.6.1 Troubles

Galvanized steel pipes and copper pipes are generally used for the water and hot water supply pipings of structures such as buildings. Problems in these water supply systems are caused by corro-

Table 5.12 Effect of a formulated corrosion inhibitor for a propylene glycol antifreeze

Antifreeze	Weight loss (mg/cm^2)					
	Copper	Solder	Brass	Carbon steel	Cast iron	Cast aluminum
25% propylene glycol	0.04	3.00	0.08	5.90	13.80	1.67
25% propylene glycol including corrosion inhibitor	0.00	0.30	0.03	0.04	0.00	0.25

Notes: 1) Test method: JIS K-2234
2) Test period: 7 days
3) Temperature: 88° C
4) Copper-solder-brass and carbon steel-cast iron-cast aluminum are electrically coupled respectively.

sion. Water leakages from pipings often happen especially in the copper pipings of hot water circulation systems.

"Red water" and "blue water" caused by corrosion products of carbon steel and copper respectively are also serious troubles in hotels and so on.

"Red water" is the coloring of water with reddish brown by the corrosion products of iron, such as ferric hydroxide. Water is colored with reddish brown when the total iron content exceeds 1 mg/*l*. The "red water" causes many troubles, such as a deterioration in the taste of the drinking water, and the coloring of washings and water in baths.

The "blue water" is caused by the copper ion alone and/or by the reaction products of copper ion with higher fatty acids of soap. The blue-greenish stains on bathtubs and washbowls are formed by the concentrated copper ions as the result of the evaporation of the water drops.

Pitting corrosion and erosion corrosion of copper pipings are caused by not only mechanical factors, such as air bubble formation and excessive flow speed, but also by chemical factors, such as residual chlorine in water, and silica deposition[8].

5.6.2 Countermeasures

In this system, corrosion inhibitors are applied to solve those problems. However, the kinds of inhibitors, their dosages and so on are severely regulated for the safety and the health of people as described below.

(1) Kinds of corrosion inhibitors and their quality standards

The types of corrosion inhibitors using for water and hot water supply systems are divided into phosphate based and silicate based ones. In Japan, the quality standards for these corrosion inhibitors are stipulated by the Ministry of Health and Welfare in 1987, as shown in Table 5.13.

(2) Injection methods of corrosion inhibitors

In Japan, the injection methods and the dosages of corrosion inhibitors for water supply systems are regulated by the Ministry of Health and Welfare as shown below.

(a) Injection methods

In the case of liquid type inhibitor, the inhibitor must be injected into the water supply line by a pump proportionally to the amount of supply water.

In the case of solid type inhibitor, the inhibitor is added into a dissolver installed in a bypass piping and the inhibitor solution dissolving with the water flow is injected into the water supply line by a ejector.

Figure 5.29 shows the typical injection methods of the liquid type and solid type inhibitors.

(b) Dosages

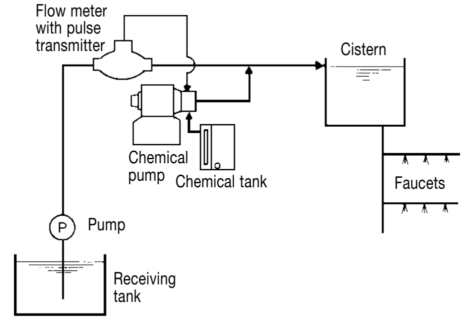
The dosages of corrosion inhibitors for water supply systems must be limited to a minimum concentration for preventing the "red water" problems. The standard dosages are below 5 mg P_2O_5/l for phosphate based inhibitors, below 5 mg SiO_2/l for silicate based inhibitors and below 5 mg $P_2O_5 + SiO_2/l$ for phosphate-silicate based inhibitors. Even in the initial stage of chemical injection, the maximum dosage must be controlled lower than 15 mg $P_2O_5 + SiO_2/l$.

5.6.3 Safety of Corrosion Inhibitors

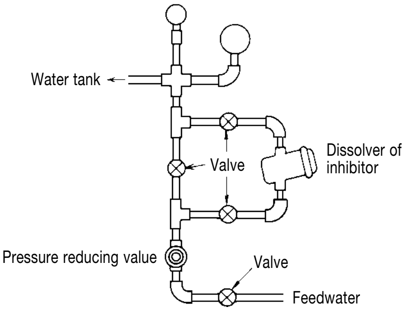
Various tests including chronic toxicity testing, carcinongenicity tests and so on are carried out to determine the safety of the phosphate and silicate based corrosion inhibitors for water supply systems. When these inhibitors are appropriately

Table 5.13 Kinds of corrosion inhibitors for water and hot water supply systems

Item	Kind	Class 1		Class 2		Class 3	
		No. 1	No. 2	No. 1	No. 2	No. 1	No. 2
Main ingredient	Phosphate as P_2O_5	51% and more within indicated value ±1%	11% and more within indicated value ±0.5%	—	—	Total two components 51% and more within indicated value ±1%	Total two components 11% and more within indicated value ±0.5%
	Silicate as SiO_2	—	—	62% and more within indicated value ±1%	13% and more within indicated value ±0.5%		
Appearance		Colorless, white or slightly colored solid	Colorless liquid	Colorless or slightly colored solid	Colorless liquid	Same as Class 1, No. 1	Colorless liquid
Impurities	Arsenic	2 mg/kg and below	Same as Class 1, No. 1 as solid	Same as Class 1, No. 1	Same as Class 1, No. 1 as solid	Same as Class 1, No. 1	Same as Class 1 No. 1 as solid
	Cadmium	2 mg/kg and below					
	Lead	15 mg/kg and below					
	Mercury	0.2 mg/kg and below					
	Insoluble matter	0.05% and below					



a) Injection method of liquid type corrosion inhibitor



b) Injection method of solid type corrosion inhibitor

Fig. 5.29 Injection methods of corrosion inhibitors for water supply systems

used according to their application standards, the safeties of these chemicals are confirmed by the test results. The following data are abstracted from the reports concerning the safety of these inhibitors.

Acute toxicity tests, subacute toxicity tests, chronic toxicity tests (including carcinongenicity tests), teratogenesis tests and mutagenesis tests were conducted to study the safety of sodium polyphosphate and sodium metasilicate. The test results are given here. For mice, the LD50 (lethal dosage of 50% of animals tested) of sodium polyphosphate was 7,572 mg/kg as P_2O_5 for males and 9,973 mg/kg as P_2O_5 for females. For rats, the LD50 was 3,053 mg/kg as P_2O_5 for males and 3,263 mg/kg as P_2O_5 for females. The maximum non-effective dose in chronic test for rats, was 750 mg/kg·day as P_2O_5 for males and 1,250 mg/kg·day as P_2O_5 for females. In the toxicity tests for sodium metasilicate, the LD50 for mice was 820 mg/kg as SiO_2 for males and 770 mg/kg as SiO_2 for females. In tests for rats, the LD50 was 1,153 mg/kg as SiO_2 for males and 1,349 mg/kg as SiO_2 for females. In chronic tests for rats, the maximum non-effective dose was 79.2 mg/kg·day as SiO_2 for males and 105.0 mg/kg·day as SiO_2 for females.

No teratogenesis, mutagenesis, or carcinogenicity was observed for either sodium polyphosphate or sodium metasilicate.

The present standards regulate the dosage of corrosion inhibitors in the water at the tap, below 15 mg $P_2O_5 + SiO_2/l$ for the initial dosing and below 5 mg $P_2O_5 + SiO_2/l$ for the maintenance dosing against all of phosphate based, silicate based and phosphate-silicate based inhibitors. When a person whose weight is 60 kg, regularly drinks 2 liters a day of water including a corrosion inhibitor of 15 mg/l at the maximum value, the amount of inhibitor ingested will be 0.5 mg/kg·day. This value is 1/1,500 and 1/158 against the maximum non-effective dose of polyphosphate of 750 mg/kg·day for rats, and that of metasilicate of 79.2 mg/kg·day for rats respectively. Also, if the person drinks the water including 5 mg/l of inhibitor at the maintenance dosing, the quantity of the inhibitor taken will be 0.17 mg/kg·day. This value is 1/4,500 and 1/475 against the maximum non-effective quantities of polyphosphate and metasilicate, respectively.

According to the above considerations, phosphate based, silicate based and phosphate-silicate based corrosion inhibitors will be safe to use, as long as they are appropriately applied according to the standards.

5.6.4 Functions and Effects of Corrosion Inhibitors

(1) Chelating and dispersing effects of polyphosphates on iron ions

Polyphosphates have the capability of chelating metal ions and dispersing their precipitates with the low concentrations. In the neutral water, iron reacts with dissolved oxygen and water to produce ferrous hydroxide [$Fe(OH)_2$]. Ferrous hydroxide changes to ferric hydroxide [$Fe(OH)_3$] in the presence of dissolved oxygen and water. Ferric hydroxide changes to hydrated ferric oxide ($Fe_2O_3 \cdot nH_2O$).

Polyphosphates prevent the generation of "red water" by chelating the ferrous ion (Fe^{2+}) as shown in Figure 5.30. Consequently the transformation of ferrous ion to ferric ion is retarded. Simultaneously, polyphosphates keep the fine particles of ferric hydroxide and ferric oxide in the dispersed state shown in Figure 5.31.

Figure 5.32 shows the relationship between the ratio of polyphosphate concentration against total iron in water and the prevention effect on ferric hydroxide precipitation. When the ratio is kept at 3 or more, the ferric hydroxide precipitation is perfectly prevented.

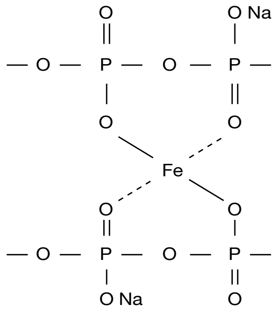


Fig. 5.30 Chelating of ferrous ion by polyphosphate

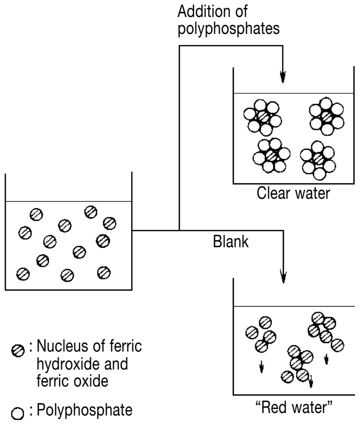


Fig. 5.31 Prevention of "red water" by the dispersing effect of polyphosphate on iron hydroxide

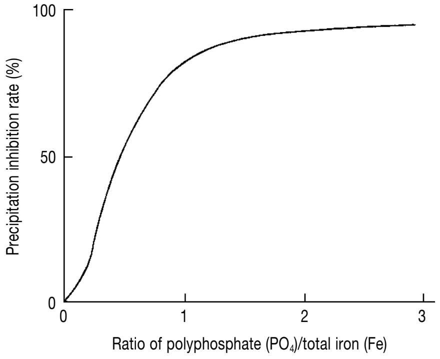


Fig. 5.32 Inhibition effect of a polyphosphate on ferric hydroxide precipitation

(2) Corrosion inhibition effect of polyphosphates

Polyphosphates inhibit metallic corrosion by reacting with calcium ions in water to form the protective film composed of calcium phosphate mainly on the metal surface.

Polyphosphates show the better corrosion inhibition on carbon steel at even a low concentration under the higher water flow velocity as shown in Figure 3.30(P. 3-21). Though, the dosage of polyphosphate is regulated at 5 mg P_2O_5/l from the viewpoints of health care, the polyphosphate shows the sufficient corrosion inhibition and lowers the total iron of hot water as shown in Figure 5.33.

(3) Prevention of "red water" by polyphosphates

Figure 5.34 shows the inhibition effect of a polyphosphate on "red water". Generally, "red water" is prevented by the addition of 3 mg P_2O_5/l or more of polyphosphates.

As shown in Figure 5.33, the use of polyphosphate based inhibitor reduces the total iron in water by lowering the corrosion rate of carbon steel. When the total iron concentration is reduced to 1 mg/*l* or less, "red water" problem is prevented.

(4) Corrosion inhibition effect of polyphosphates on copper

Polyphosphates form the amorphous protective film including copper ions, and prevent the formation of copper metasilicate ($CuSiO_3 \cdot H_2O$) and copper oxide (CuO) on the copper surface. As the result, the oxidation of copper by oxygen or chlorine in water is retarted and the pitting corrosion of copper is inhibited by keeping the corrosion potential of copper below the pitting potential of 150 mV as shown in Figure 5.35[9]. Since silicates increase the corrosion potential of copper, the application of silicate based corrosion inhibitor should be avoided for copper pipings.

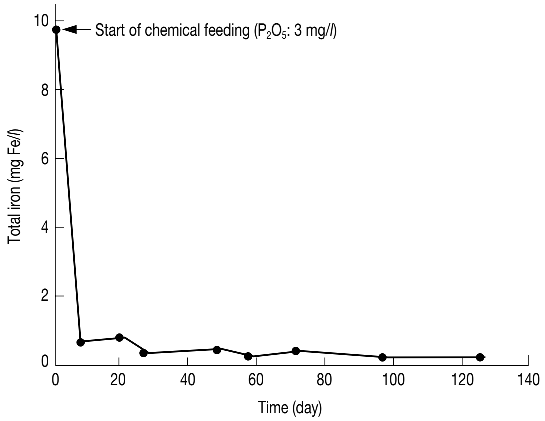


Fig. 5.33 Decrease of total iron in a supply water by adding a polyphosphate based inhibitor

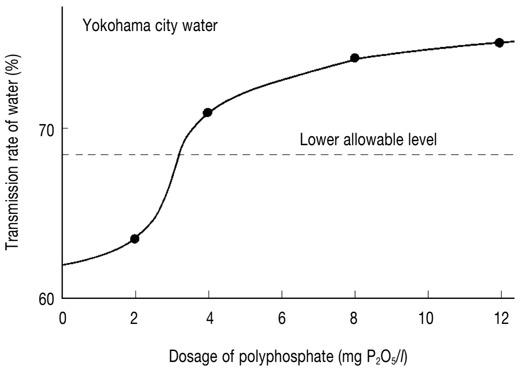


Fig. 5.34 Inhibition effect of a polyphosphate on "red water"

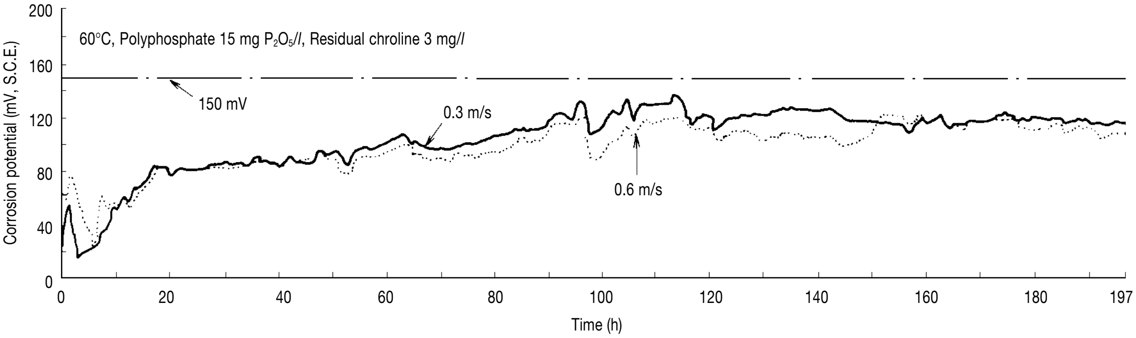


Fig. 5.35 Corrosion potential of copper tube under a polyphosphate based corrosion inhibitor treatment

5.7 Water Treatment for Humidifiers

Recently, advancements in computer and various precision equipments are remarkable. As the maintenance of these equipments requires a constant temperature and humidity, air conditioning has become very important.

The installation of humidifier and dehumidifiers is indispensable for maintaining a constant humidity. The ultrasonic type humidifier tends to be employed instead of the heating type humidifier which consumes much electricity. Table 5.14 shows the types and features of humidifiers.

5.7.1 Cause of “White Powder”

Ultrasonic humidifiers atomize the water by ultrasonic. The atomized fine water particles are discharged from humidifier to the rooms by a fan and so on. Since fine water particles evaporate in this process, the dissolved salts (Na^+, Ca^{2+}, Mg^{2+}, Cl^-, SO_4^{2-}, SiO_2, etc.) in the water float in air as the fine particles and finally deposit as “white powder” on the surfaces of cathode-ray tubes, relay terminals, various terminals, etc. This “White powder” causes various problems on computer operation and so on.

5.7.2 Prevention Method of “White Powder”

In order to prevent the “White powder”, the salts in water have to be perfectly removed. That is, demineralized water must be used for humidifiers.

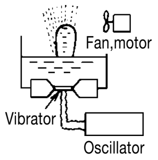
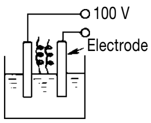
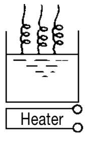
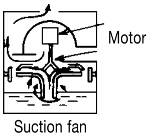
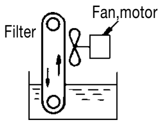
(1) Cartridge-type demineralizers

A cartridge-type demineralizer is suitable for producing demineralized water easily. This apparatus consists of H-form strongly acidic cation exchange resin and OH-form strongly basic anion exchange resin packed separately or as the mixture in cartridges. The cartridge is replaced when the purity of treated water has decreased to a specified level after treating some amount of the raw water. Figure 5.36 shows a typical installation method of a cartridge-type demineralizer.

(2) Small-size reverse osmosis unit

In case that a large volume of water is required for the humidifier, small-size reverse osmosis unit is generally used for the pretreatment of raw water, because the demineralization cost is lower than that of the cartridge type. The dissolved salt concentration is reduced up to about 1/10 of raw water by treating with the reverse osmosis unit,

Table 5.14 Types and features of humidifiers

Type	Ultrasonic type	Electrode type	Electric heater type	Centrifugal spray type	Evaporating filter cloth type
Principal figure					
Electricity consumption (W)	40–60	100–400 This value changes largely due to water quality and water level.	300–450	20–30	20–25
Humidification capacity (cc/h)	250–500	100–400 This value changes largely due to water quality and water level.	300–500	150–500	400–600 This value changes due to humidity of air.
Humidification starting time from the operation start-up	Fast	After several minutes	Approximately after 20–30 minutes	Fast	Fast
State of humidifying particles	Minute water particle	Steam	Steam	Bigger water particles than ultrasonic type	Vapor

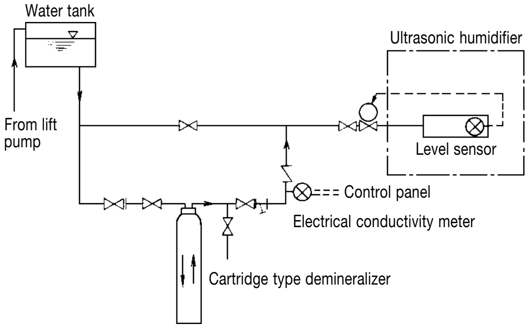


Fig. 5.36 Typical installation method of a cartridge type demineralizer

and then the demineralizer is used as a polisher. Figure 5.37 shows the flowsheet of a reverse osmosis unit.

5.8 Chemical Cleaning

5.8.1 Chemical Cleaning of Cooling Water Systems

Problems caused by water occur in the cooling water systems for air conditioning. These problems are divided into three kinds of corrosion, scale and slime. They reduce the thermal efficiency of heat exchangers and the water flow rate. These problems also cause the "high pressure cutout" of refrigerating machines, as well as water leakage from pipings.

Methods for removing scale, slime and corrosion products from heat exchangers and pipings are classified into mechanical cleaning, such as high-pressure water jet cleaning, brushing and "pig" cleaning, and chemical cleaning. Chemical cleaning is described in this section.

(1) Kinds of chemical cleaning agents

Usually, the following chemicals are used for chemical cleaning:

[Inorganic chemicals]

Hydrochloric acid, phosphoric acid, nitric acid, sulfuric acid, sulfamic acid, fluoric acid, hydrogen peroxide, sodium hypochlorite, sodium hydroxide, etc.

[Organic chemicals]

Citric acid, gluconic acid, oxalic acid, tartaric acid, EDTA and its derivatives, polyelectrolytes (polymers).

Since these chemicals have different removal effects against each substance to be removed and sometimes show the synergistic effects with other agents, the mixtures of these chemicals are often applied in fields. Corrosion inhibitors are generally applied together with cleaning agents to reduce the corrosion rate during cleaning.

(2) Selection of cleaning agents

Prior to chemical cleaning, the composition and volume of the deposit, the holding water volume of system, the materials of the system to be cleaned and so on should be sufficiently examined.

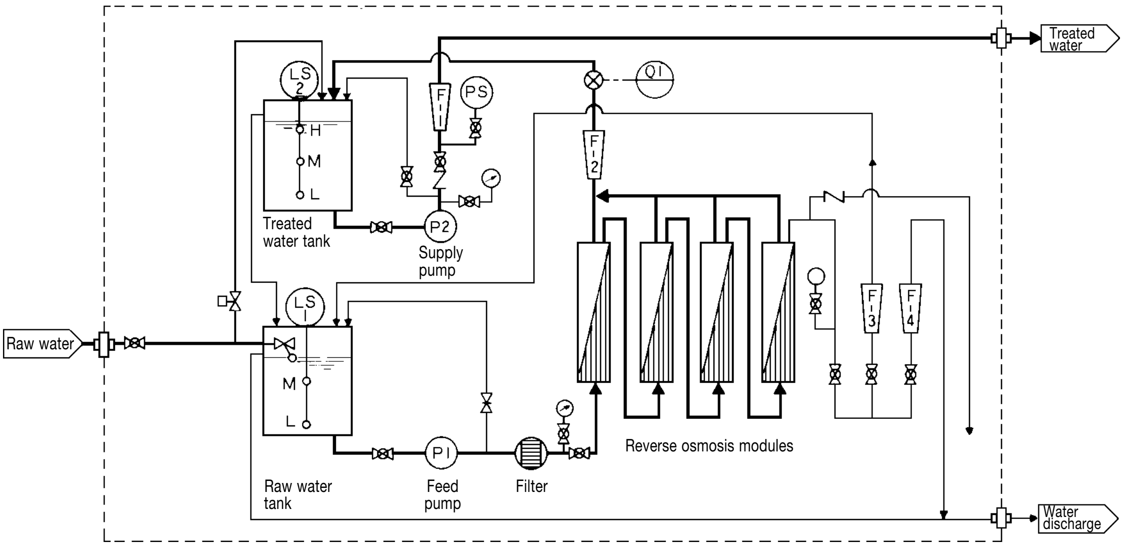


Fig. 5.37 Flow diagram of a small size reverse osmosis unit

(a) Selection of cleaning agents from the composition of deposits

The deposits in the cooling water system for air conditioning are classified into organic and inorganic substances. The most of inorganic matters are calcium salts, silica, sand and corrosion products, such as iron oxide, zinc oxide and copper oxide. The most of organic matters are bacteria and algae. The determination of composition of these deposits helps to select the proper cleaning agents as follows;

① Iron oxide scale: hydrochloric acid, phosphoric acid, citric acid, oxalic acid, EDTA, etc.,
② Calcium and zinc scale: hydrochloric acid, sulfamic acid, EDTA, polymers, etc.,
③ Silica scale: fluoric acid, sodium hydroxide, etc.,
④ Slime: hydrogen peroxide, sodium hypochlorite, etc.

Figure 5.38 shows a simple method for identifying the composition of deposits.

(b) Suitability of cleaning agents for the materials in the system

Table 5.15 shows the compatibility of cleaning agents with materials in the system.

Table 5.15 Compatibility of cleaning agents with structural materials

Kinds of agents / Materials	Acidic		Neutral	Alkaline
	A^{*1}	B^{*2}		
Carbon steel	○	○	○	○
Copper and copper alloys	○	○	○	○
Austenite stainless steels	×	○	○	○
Zinc	×	×	○	×
Concrete	×	×	○	×
Polyvinyl chloride	○	○	○	○

○ Suitable × Unsuitable
*1 Hydrochloric acid based
*2 Sulfamic acid based

(3) Standard specification of cleaning

In the actual cleaning work, the determination of chemical concentrations, cleaning period, temperature, flow velocity and so on, are important as well as the selection of cleaning agents. Table 5.16 gives the examples of the KURITA's standard specifications for the cleaning of air conditioning cooling water systems.

(4) Cleaning methods

The cleaning methods are classified into two categories, ① system cleaning (cleaning of the entire cooling water system) and ② equipment cleaning (cleaning of the heat exchanger of a refrigerating machine by using a temporary pump and tank). The proper cleaning method for the objective apparatus should be selected considering the amount of deposits and the applicable process of cleaning.

Figure 5.39 shows the procedure of cleaning for air conditioning cooling water systems.

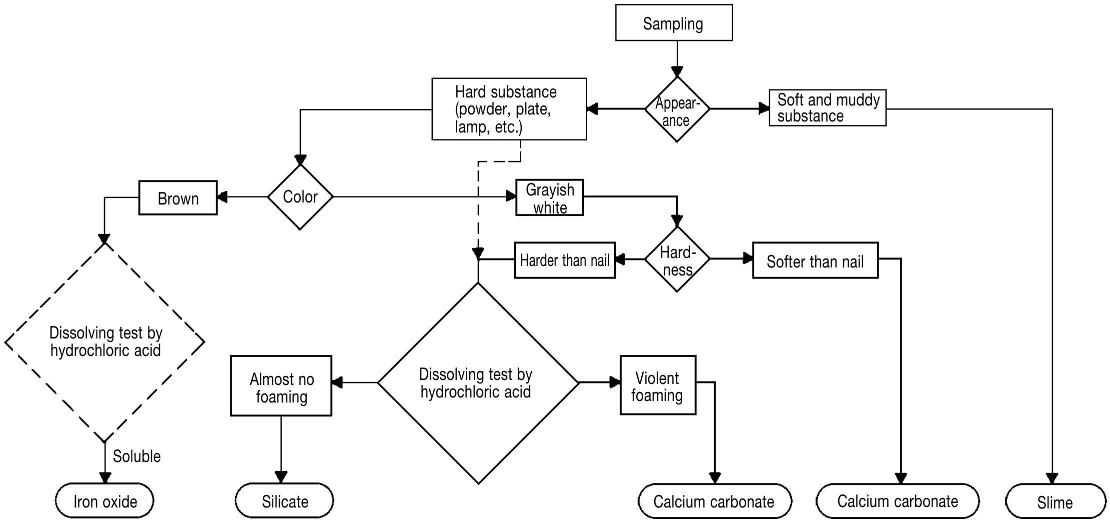
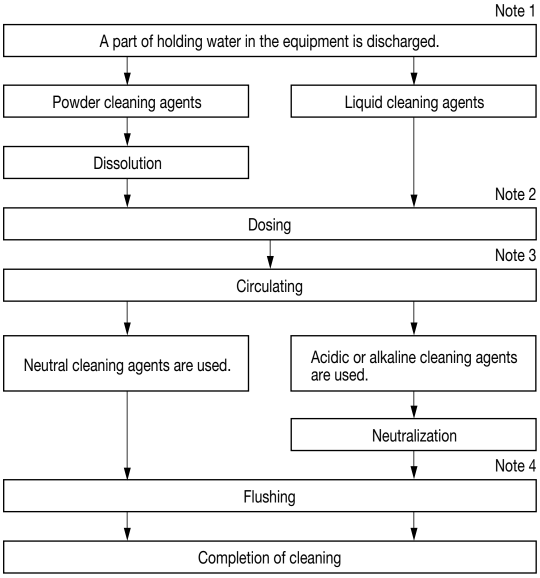


Fig. 5.38 Simple identification method of deposits in heat exchanger tubes

Table 5.16 KURITA's standard specifications for the chemical cleaning of air conditioning cooling water systems

Cleaning agents	Hydrochloric acid based	Salfumic acid based	Neutral	Alkaline	
Dosage (%)	10–50	10–20	10–20	10–20	
Cleaning period (h)	0.5–2.0	0.5–2.0	0.5–1.0	12–24	6–10
Temperature (°C)	Below 50	Below 60	Room temp.	Room temp.	60–80
Flow velocity (m/s)	0.3–3.0				



Note 1. Water is discharged with the volume of which corresponds to the dosing volume of the cleaning agent.

Note 2. The specified volume of cleaning agent is fed before water circulation.
1) Liquid agent is fed without dillution.
2) Powder agent is fed after dissolving with water.

Note 3. The water is circulated for a specified period. Required volume of neutralizing agent is fed if acidic or alkaline cleaning agent is used.

Note 4. After the completion of cleaning or neutralization, the equipment is flushed by water until the circulating water becomes clear.

Fig. 5.39 Cleaning procedure of cooling water systems for air conditioning systems

(5) Cautions in chemical cleaning

Following cautions should be taken in each process of cleaning;

(a) During cleaning

① Cooling tower fan must be stopped.

② Pay full attention to ventilation and fire, because gases (CO_2, O_2, H_2, etc.) generate during the cleaning.

③ Maintain the prescribed duration, temperature, chemical concentration, etc., to prevent the corrosion of the structual materials of the system.

④ Prepare an antiforming agent because foams may frequently generate during the cleaning and neutralization processes.

⑤ In case of equipment cleaning, inject the cleaning agent from the bottom of heat exchanger and vent the air completely from the heat exchanger.

(b) Wastewater neutralization

When acidic or alkaline cleaning agents are used, the neutralization of waste cleaning solution is necessary. The neutralization is completed when the pH of the cleaning solution becomes neutral.

(c) Wastewater discharge

① Do not allow the entering of discharge water into a drinking water system or well.

② If sulfamic acid based cleaning agent is used, never discharge it into an agricultural waterway even after the wastewater is neutralized. It retard the growth of farm products, especially rice plant.

③ If hydrogen peroxide is used, the decomposition treatment must be required to cope with the COD regulations, because 0.47 mg/l of COD is yielded per 1 mg/l of residual H_2O_2.

(6) Case studies of chemical cleaning

(a) Slime removal

Slime is easily removed from heat exchangers, piping and so on by using high concentration of peroxide based chemicals and so on even during system operation. The effects of slime removal agents are referred to the section 3.4.7,(6).

(b) Removal of corrosion products

Generally, corrosion products of carbon steel, copper, etc., are cleaned by using acids, such as hydrochloric acid, during the operation stoppage of systems.

Recently, an on-stream removal method using phosphate based chemicals for the corrosion product of steel has been developed and has shown

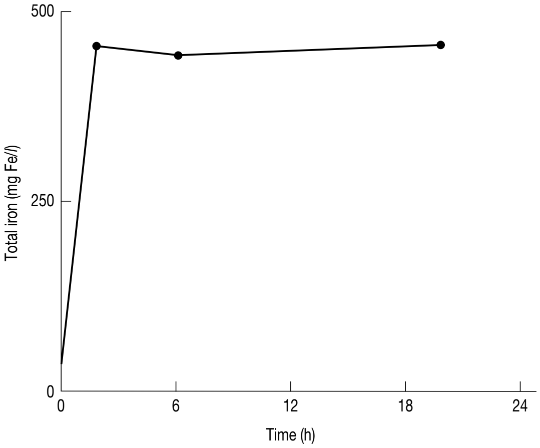


Fig. 5.40 Removal effect of a phosphate based cleaning agent on the corrosion product of steel

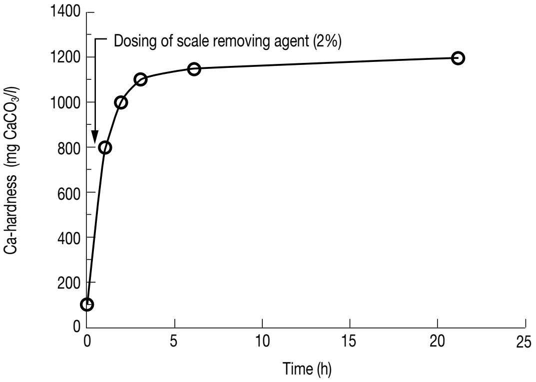


Fig. 5.41 Increase of calcium hardness in cooling water by removing calcium carbonate scale

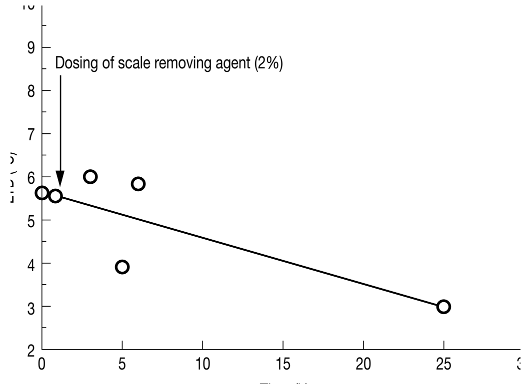


Fig. 5.42 Reduction of the LTD of a refrigerating machine condenser by removing the calcium carbonate scale

the excellent effect. Figure 5.40 shows the effect of this treatment. Most of corrosion product was removed during 2 hours from the chemical dosing and the total iron of circulating water reached 460 mg Fe/*l*. This chemical has the corrosion inhibition effect on carbon steel and the dispersing effect on removed iron oxide and iron hydroxide.

(c) Removal of calcium carbonate scale

Calcium carbonate scale is usually removed by using acid base cleaning agents during system stoppage.

A polymer based cleaning agent for calcium carbonate has been developed recently. This cleaning agent shows the excellent removing effect on calcium carbonate in a neutral pH range and realizes the on-stream scale removal.

Figure 5.41 shows the increase of calcium hardness in the circulation water by a polymer based cleaning agent. Figure 5.42 shows the reduction of the leaving temperature difference (LTD) of a condenser for a refrigerating machine by the scale removal.

The LTD is the temperature difference between the condensation temperature of the refrigerant and the cooling water temperature at the outlet of the condenser. The LTD is increased by scaling of condenser and is decreased by the scale removal.

5.8.2 Chemical Cleaning of Closed Water Recirculation Systems

In the closed systems, problems, such as the decrease of water flow rate, occur due to the corrosion products of carbon steel and so on. Generally, acid cleaning is applied for removing corrosion products. However, this method causes many problems, such as the clogging of branch pipes and strainers by sludges, and the acceleration of the corrosion by the residual acidic cleaning agent. Recently, an On Stream Scale Remover (OSSR) of neutral type has been developed and it is applied for the system cleaning without the operation stoppage.

(1) Features of the OSSR

The OSSR for closed water systems provides the excellent dissolution effect against corrosion products. Since the OSSR dissolutes the corrosion products by the strong chelating power on iron ions, the reprecipitation of removed corrosion products scarcely occurs in the pipings, strainers and so on. As the OSSR is a neutral-type agent, the neutralization of the discharged water is not required. The OSSR scarcely corrodes metals during the cleaning.

(2) Cleaning method

The OSSR with the dosage of 10 to 15% is injected from the pressure gauge mounting at the delivery side of the circulation pump. Then the water is circulated. The cleaning period is usually 4 to 10 days.

(3) Case study

The OSSR was applied for a closed system where the circulation rate was remarkably reduced by the adhesion of corrosion products during 12 years operation. Figure 5.43 shows the treatment results. The total iron in the circulating water increased gradually, due to the dissolved corrosion products. Accompanying this, the water circulating rate increased and the pressure of the circulating pump decreased. During this cleaning, the air conditioning system was continuously operated in the same way as usual.

5.8.3 Chemical Cleaning of Water Supply Systems

(1) Laws and regulations for water supply systems in Japan

As the pollution of drinking water in buildings and apartment houses has become a social problems, legal measures for water supply installations and their maintenance have being taken in Japan since 1970.

The measuring of residual chlorine, water quality examination, cleaning of water tank, etc., for buildings with the floor areas of 3,000 m^2 or more, have been required after 1975. The rules of designation by the Minister of Health and Welfare have introduced for the consignors who perform such maintenance and examination. Table 5.17 shows the water quality standards for building water supply, enacted by the Ministry of Health and Welfare of Japan.

(2) Present conditions of water supply system

A typical tap water supply system of buildings is shown in Figure 5.44. The water received in the tank is pumped to the elevated tank, and then supplied to end faucets by the gravity.

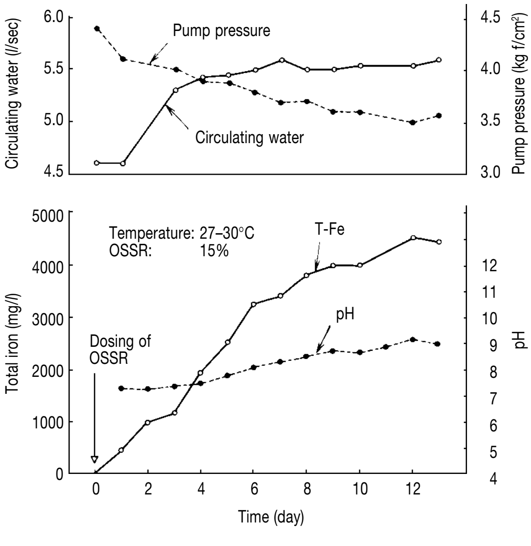


Fig. 5.43 Cleaning effect of an OSSR in a closed water system for air conditioning

Table 5.17 Ministerial ordinance on water quality

NO_3-N and NO_2-N	Not more than 10 mg/*l*
Cl^-	Not more than 200 mg/*l*
COD_{Mn}	Not more than 10 mg/*l*
Generic bacteria	Not more than 100 colonies in 1 m*l* of sample water
Enteric bacteria	Not to be detected
CN^-	Not to be detected
Hg	Not to be detected
Organic phosphorus compounds	Not to be detected
Cu	Not more than 1.0 mg/*l*
Fe	Not more than 0.3 mg/*l*
Mn	Not more than 0.3 mg/*l*
Zn	Not more than 1.0 mg/*l*
Pb	Not more than 0.1 mg/*l*
Cr (VI)	Not more than 0.05 mg/*l*
Cd	Not more than 0.01 mg/*l*
As	Not more than 0.05 mg/*l*
F	Not more than 0.8 mg/*l*
Hardness ($CaCO_3$ mg/*l*)	Not more than 300 mg/*l*
Evaporation residue	Not more than 500 mg/*l*
Phenols	Not more than 0.005 mg/*l* as phenol
Anionic surfactant	Not more than 0.5 mg/*l*
pH	5.8–8.6
Odor	Not objectionable
Taste	Not objectionable
Color	Not more than 5 degrees
Turbidity	Not more than 2 degrees

Remarks: For CN^-, Hg and organic phosphorus compounds, "not to be detected" means that the analysis result is lower than the quantitative limit of the analysis method.

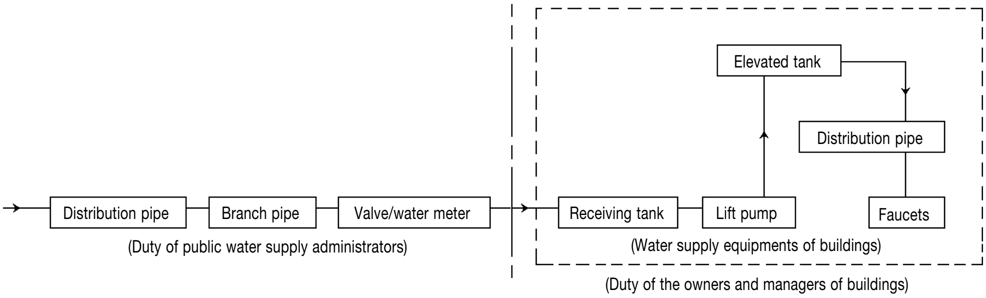


Fig. 5.44 Scope of a water supply installation and the water flow

The tap water is retained in the receiving tank and elevated tank for some period in an open air, then the residual chlorine concentration decreases. After that, it is supplied through supply pipes to the end faucets. Therefore, clean tap water in received tank may sometimes become "water not fit for drinking" at the end faucets, due to the effects of the malfunction of installations, insufficient maintenance, corroded pipings, etc.

Table 5.18 shows the investigations of actual conditions of water qualities in Tokyo and Osaka[9].

As shown in Table 5.18, most of the items judged as "not suitable for drinking" are color and total iron. Accordingly the problems relating to "red water" account to 80 to 90%.

According to the investigations in Tokyo from 1983 to 1985, the growth of algae was found in 47 water tanks, or about 34% of 138 water tanks made of FRP.

(3) Chemical cleaning of water tanks

(a) Cleaning agents for water tanks

Organic acid or phosphoric acid based cleaning agents composed of substances authorized as food additives, are most suitable for the chemical cleaning of drinking water tanks. The main function of these chemicals is to dissolve the iron oxides adhering to the wall surfaces of water tanks.

Table 5.18 Investigation results of the tap water qualities of buildings in Tokyo and Osaka

Unsuitable items	Number	Remarks
Color	58	Relating red water
Iron	28	
Odor, taste	11	
Trubidity	6	
Zinc	3	
Lead	1	
Number of enteric bacteria	3	
Phenol	1	
Ammonical nitrogen	1	

Number of installations inspected	413 places
Number of unsuitable installations for water quality standard	65 places
Ratio of unsuitability	15.7%

(b) Cleaning methods

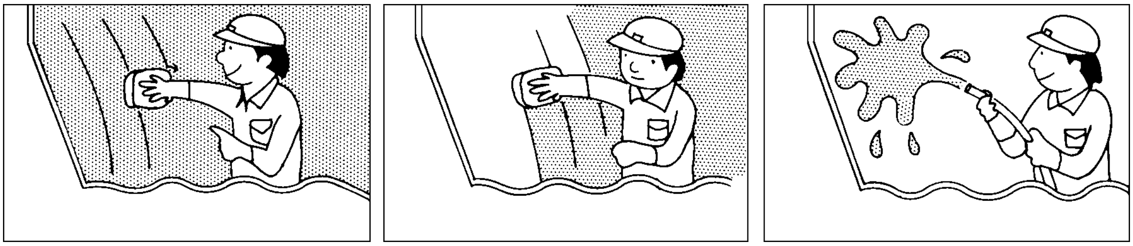
Generally, the contaminated areas of water tanks are coated with the cleaning agent by using sponges or brushes. Then the dirt and contamination are scrubbed off. Because there are many regulations enacted by the Japanese Ministry of Health and Welfare, as well as the other laws, regarding the cleaning of water tanks, the water tank cleaning must be done in accordance with these laws and regulations. After cleaning by an acidic cleaning agent, the water tank must be washed with clean water. Then the tank water must be checked using special test paper to confirm that the water includes no residual chemical. Then sterilization is done by using a chlorine based agent. Figure 5.45 shows the method for water tank cleaning.

(4) Chemical cleaning of water supply systems

In Japan, the cleaning of water tanks, water receiving tanks, elevated water tanks, etc., is compulsory, but the cleaning of pipes is not compulsory. However, the water quality is inspected at the end faucets, the maintenance of piping cleanliness is inseparable from the cleaning of water tanks.

(a) Cleaning agents for water supply systems

Hydrogen peroxide based cleaning agents are most suitable for the chemical cleaning of water supply systems. Hydrogen peroxide decomposes to water and oxygen in contact with iron oxides and iron bacteria which cause "red water". Then the iron oxides and iron bacteria are removed from the piping and dispersed by the bubbles of oxygen generated. Simultaneously, it sterilizes the system and prevents the growth of microorgan

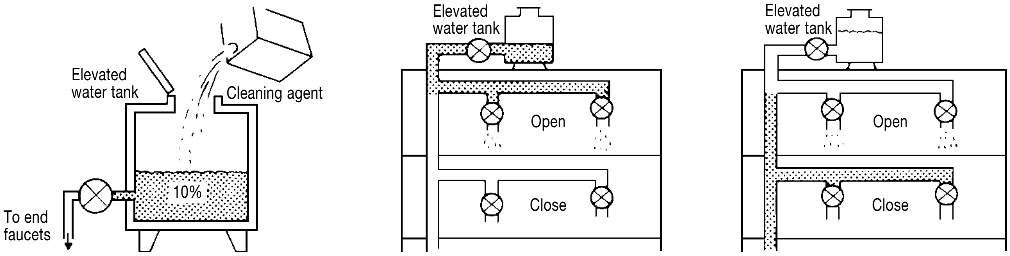


(1) Using sponge, coat the inner wall of tank with the cleaning agent.

(2) Leave it for a while, then wipe off fouling by the sponge soaked in fresh cleaning agent, before the surface dries.

(3) After wiping off the agent, wash the wall surface thoroughly by water.

Fig. 5.45 Example of a water tank cleaning method



1. Water of elevated tank is reduced to 1/2 to 1/3 of the full volume of the tank.
2. Cleaning agent of 10% to the water volume is fed and agitated.

1. Faucets of the highest floor are opened, and are closed when the cleaning agent solution (yellow colored) comes out.
2. After the solution is supplied throughout the highest floor, the same operation is made to the lower floors in turn.
3. When the solution is supplied throughout all the floors, leave it for 2 to 3 hours.

1. Elevated water tank is washed and filled with clear water.
2. Faucets of the highest floor are opened to discharge the cleaning solution in the piping and perform water washing.
3. After the piping on the highest floor is washed, the same operation is made to the lower floors in turn.
4. Residual cleaning agent concentration is tested by a testing paper and the washing is completed when no agent is detected.

Fig. 5.46 A method of water supply system cleaning

isms which cause a disagreeable odor and taste of water. Hydrogen peroxide scarcely damages piping materials.

(b) Cleaning method

Figure 5.46 shows the cleaning method for water supply systems. The cleaning must be performed in accordance with the notification of the Japanese Ministry of Health and Welfare and the other organizations. Since the water receiving tank is usually cleaned at the same time, preliminary arrangements, such as determination of cleaning period, the period of suspension of water supply, transportation schedule of equipment and materials, etc., are important.

After the cleaning, residual hydrogen peroxide concentration is checked by using a specific test paper to confirm that no hydrogen peroxide remains in the system.

5.8.4 Chemical Cleaning of Aluminum Fins

Aluminum fins are widely used for the "air side" of the heat exchangers of FCU and for the air-cooled condensers of refrigerating machines. As oils, sand, dust, the tar of cigarettes, etc., adhere to these fins as shown in Figure 5.47, they decrease

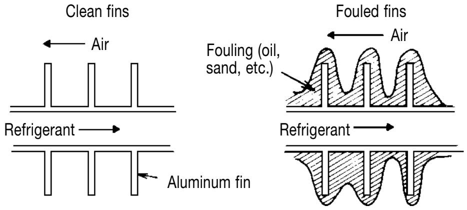


Fig. 5.47 Fouling adhesion on the aluminum fins of a heat exchanger

the cooling capacity and increase the consumption of electricity.

For the chemical cleaning of aluminum fins, cleaning agents having strong cleaning power for oils and the tar of cigarettes are used. Also spray type cleaning machines with the light weights are needed.

(1) Energy-saving by the periodical cleaning of fins

(a) Loss of energy due to the adhesion of contaminants on fins

Table 5.19 and Figure 5.48 show the increase in electricity consumption by the adhesion of contaminants on the aluminum fins for an air conditioning unit of which the “high pressure cut-out” was occurred when the atmospheric temperature rose to 33° C or above.

In that case, the cooling capacity was decreased by about 33%, and the consumption of electricity rose by about 15% when the pressure of high pressure gauge became 21 kg/cm^{2}G, compared to normal conditions.

Table 5.19 Comparison of the performances of a refrigerating machine before and after cleaning

Time	High pressure gauge (kg/cm^{2}G)	Low pressure gauge (kg/cm^{2}G)	Refrigeration capacity (kcal/h)
Before cleaning	21.2 (55° C)	4.0 (0° C)	44,041
After cleaning	17.0 (46° C)	3.7 (-2° C)	56,900

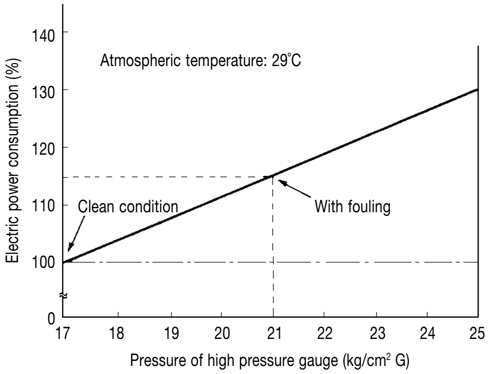


Fig. 5.48 Change in the pressure of high pressure gauge and the electricity consumption of an air conditioning unit due to fouling adhesion on the fins

(b) Energy saving by fin cleaning

Figure 5.49 shows a comparison of the operating costs (cost of electricity) for an air conditioning unit with 25 horse-powers, under following three operational conditions: ① fins were fouled, ② fins were cleaned using a cleaning agent once a year, and ③ fins were cleaned using the cleaning agent and a rinsing agent once a year.

When the aluminum fins were cleaned by using the cleaning agent and the rinsing agent, the cleaning effectively inhibited the re-adhesion of contaminants on the aluminum fins and the electricity loss was reduced by about 85% during 3 years.

(2) Selection of cleaning agent for fins

Generally, alkaline cleaning agents are used to clean up aluminum fins. Photograph 5.14 (p. 5-37) shows the effect of a fin cleaning.

After the cleaning, a hydrophilic film is formed on the surface of the aluminum. Then the spraying of the rinsing agent inhibits the readhesion of contaminants and maintaines the effect of cleaning for a long period. Photograph 5.15 (p. 5-37) shows the effect of the rinsing agent for preventing the readhesion of contaminants.

(3) Spray type cleaning machine

Photograph 5.16 shows the appearance of a small-size spray type high pressure cleaning machine.

(4) Cleaning method

Figure 5.50 shows a cleaning process of aluminum fins. In case of two workers, the cleaning period of 2 to 3 hours is required for an air conditioning unit with the capacity of 25 horse-powers.

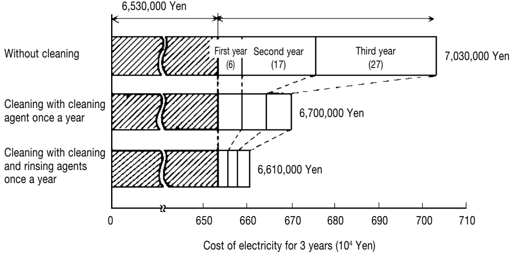


Fig. 5.49 Comparison of the 3 years electricity consumption of an air conditioning unit under different cleaning conditions

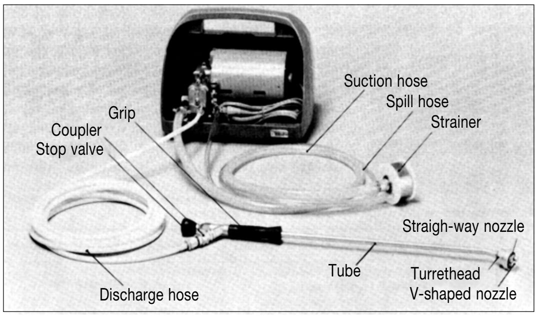


Photo 5.16 A small size spray type cleaning machine

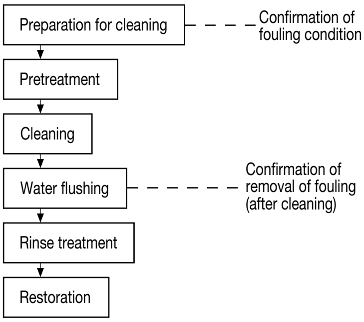


Fig. 5.50 Measures of aluminum fin cleaning

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6. Chemicals for Pulping and Papermaking Processes

6.1 Pulp Manufacturing Processes

The pulps are roughly classified into two types: woodpulp made of woods or wood chips, and deinked pulp made of waste papers. The outlines of manufacturing processes of those pulps are shown below.

6.1.1 Pulping Processes

(1) Woodpulp

Table 6.1 shows the kinds of woodpulps. The outlines of the manufacturing processes for groundwood pulp (GP) and kraft pulp (KF) are given below:

(a) Groundwood pulp (GP)

GP is manufactured by grinding wood under water showering using a grinder of the high rotating speed. Figure 6.1 shows a flow sheet of GP manufacturing process. In this method, almost all of the fibrous components of the wood are pulped, and the various other components in the wood are mixed with the GP. The GP is mainly used for manufacturing newsprint papers.

(b) Kraft pulp (KP)

The wood chips are mixed with caustic soda and sodium sulfide solutions, then this mixture is heated and cooked to make KP. Large quantities of chemicals are used in the KP manufacturing process. Figure 6.2 shows the pulping and the chemical recovery processes of a KP manufacturing plant.

The KP is a high-strength pulp and is used for making various types of papers.

(2) Deinked pulp

Recently, the recycling of waste paper has become extremely important from the viewpoint of energy saving and environmental preservation.

For making pulp from the waste papers, the printing ink must be removed from the papers. The recycled pulp made through the deinking process is called “deinked pulp”. The deinked pulp is mainly used for manufacturing newsprint and toilet papers.

In recent years, a higher demand for the whiteness of recycled pulp has encouraged the improvement of deinking chemicals and equipments for the pulping process.

This deinking process is rather complicated and requires a considerable operation cost, but it is essential for the recycling of waste paper.

Figure 6.3 shows a typical flow sheet of the deinking process for making a high quality deinked pulp.

Many kinds of chemicals are used for the deinking process. Their kinds and functions are shown in Table 6.2.

Table 6.1 Kinds of woodpulps

Kind	Treatment method	Yield (%)	Kind of wood
Groundwood pulp (GP)	Mechanical treatment	90–95	Soft wood
Refiner ground pulp (RGP)	Mechanical treatment	90–95	Soft wood
Thermomechanical pulp (TMP)	Mechanical treatment	90–95	Soft wood
Chemiground woodpulp (CGP)	Mechanical + chemical treatment	85–96	Soft wood, hard wood
Semi-chemical pulp (SCP)	Semi-chemical treatment	65–85	Hard wood
Kraft pulp (KP)	Chemical treatment	40–50	Soft wood, hard wood
Sulfite pulp (SP)	Chemical treatment	40–50	Hard wood

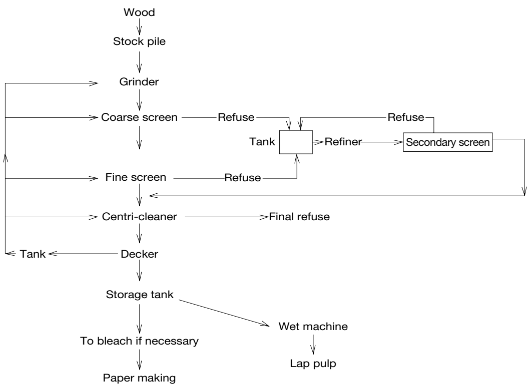


Fig. 6.1 Flow-sheet of a GP manufacturing process

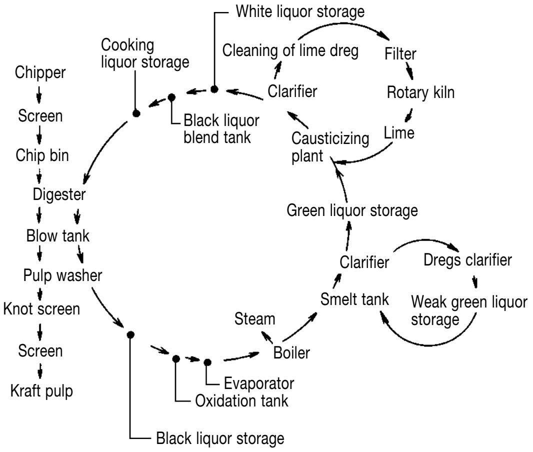


Fig. 6.2 Pulping and chemical recovery processes of a KP manufacturing plant

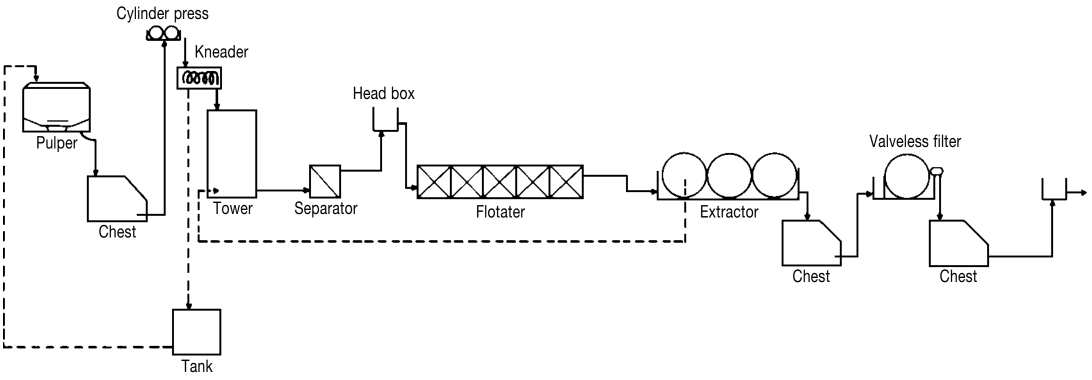


Fig. 6.3 Flow-sheet of a deinking process for making a high-quality deinked pulp

Table 6.2 Chemicals using for deinking process

Chemicals	Function
Caustic soda	Dissolving and emulsifying ink Swelling of pulp fiber to remove ink easily
Sodium silicate	Swelling of fiber Making ink in colloidal form Controlling and buffering pH
Sodium sulfite	Bleaching of pulp fiber
Chelating agents	Chelating metal ions
Surfactants	Emulsifying ink to separate from pulp Collecting of removed ink by forming bubbles to separate them

6.1.2 Bleaching Process

In bleaching process, colored impurities including in pulp are bleached by using oxidizing agents and alkalis. In this section, the chemicals using for bleaching process and the orders of using those chemicals are described for kraft pulp (KP) and sulfite pulp (SP) manufacturing processes.

(1) Chemicals

(a) Liquid chlorine

Liquid chlorine is used for the first bleaching process. It chlorinates the ligneous substances including in the pulp and promotes the dissolution of the ligneous substances in next alkaline treatment.

(b) Alkalis

An alkali is added to hydrolyze the impurities such as lignin. Caustic soda is generally used as the alkali.

Generally, 1% of caustic soda is added to the pulp slurry of 3 to 4%. Temperature is kept at about 50° C in this process.

(c) Sodium hypochlorite

Sodium hypochlorite is used for an alkaline bleaching process. It is fed together with the pulp into the bleaching tower at about 40° C.

(d) Chlorine dioxide

Chlorine dioxide is used for bleaching KP and decomposing lignin.

(2) Order of using chemicals

In the bleaching processes for SP or KP, those chemicals are used in orders described below.

The following marks are used to represent each chemical:

Liquid chlorine	CL
Alkali	A
Sodium hypochlorite	H
Chlorine dioxide	D

In bleaching process for SP, chemicals are generally used in the order shown below.

CL – A – H

Various multi-step bleaching methods are used for KP bleaching process as shown below:

CL – A – H – D
CL – A – H – A – D
CL – A – H – H – D
CL – A – D – A – D
CL – A – H – A – H – D

6.2 Papermaking Processes

6.2.1 Conditioning

The pulp from pulp manufacturing processes is mechanically and chemically conditioned before sending to papermaking processes. In the conditioning process, pulp is refined, blended and mixed with chemicals to prepare the furnish for sending to the papermaking process.

Figure 6.4 shows a typical flow sheet of the conditioning process. The additives used in this process are described below.

(1) Sizing agents

Sizing agents are chemicals used for improving the writing quality and printability of paper. Rosin is the most common one. Wax and alkyl-ketene dimer and so on are also used. Detailed informations on sizing agents are given in the section 6.3.4.

(2) Fillers

Fillers are used for improving the smoothness, printability and opacity of the paper surface. Kaolin clay, talc, calcium carbonate and so on are commonly used as fillers.

(3) Dyes

Dyes are used for adjusting the color tone of the paper.

(4) Paper-strengthening agents

Paper-strengthening agents are used for improving the tensile strength and internal tearing strength of paper.

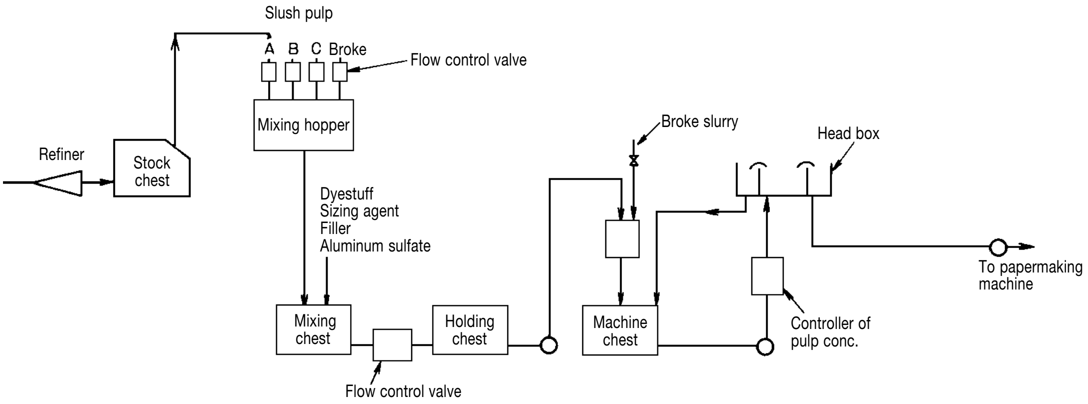


Fig. 6.4 Flow-sheet of a pulp conditioning system

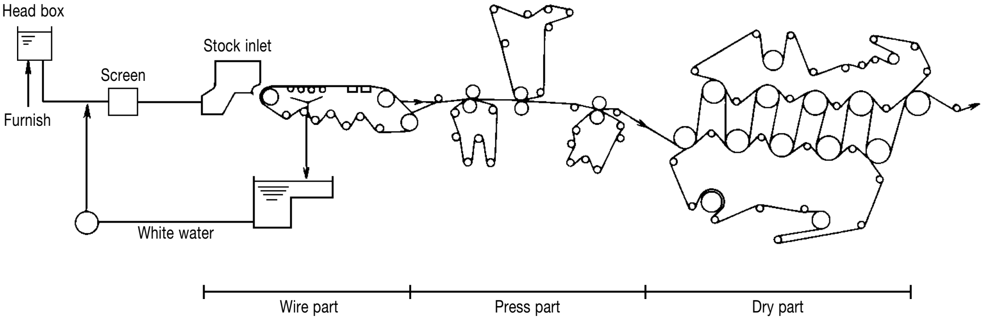
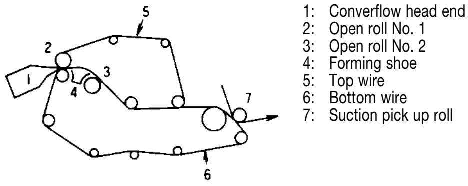
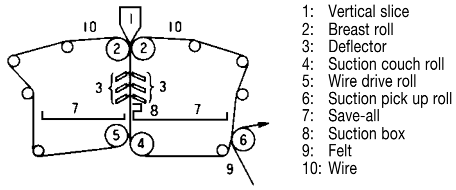


Fig. 6.5 Papermaking process using a fourdrinier paper machine



(a) Bel-Baie former



(b) Verti former

Fig. 6.6 Typical wire-arrangements of twin-wire formers

Melamine resin, urea resin, acrylic resin, starch, CMC and so on are generally used as paper-strengthening agents.

(5) Aluminum sulfate

When rosin or starch is used as the sizing agent, aluminum sulfate is used as the fixing agent.

6.2.2 Papermaking Process

Papermaking is the process of making paper from the "furnish" which comes from the conditioning process. The papermaking process is divided into the three parts of "wire part", "press part" and "dry part".

(1) Wire part

The furnish is diluted with white water to the pulp concentration of 0.3 to 1.0%. This mixture is passed through screens and filtered through the wire to form a layer of paper. The wire part is roughly classified into two types, the fourdrinier type and the cylinder type.

(a) Fourdrinier paper machine

The fourdrinier paper machine is mainly used to make ordinary papers. The paper stock fed from the stock inlet is firstly dehydrated by gravitational filtration on the wire. Then it is dehydrated by the suction strainer and sent to the press part. Figure 6.5 shows a papermaking process using a fourdrinier paper machine. A "twin-wire former" has been recently developed, which places the paper stock between the two wire sheets and suctorially dehydrates the paper layer from the both sides as shown in Figure 6.6. The twin-wire formers make high quality papers at a high speed and minimize the quality difference between the top and back sides of the paper.

(b) Cylinder-type paper machine

The cylinder-type paper machine is mainly used to make paperboards. The outline of this machine is shown in Figure 6.7. Paper stock is diluted with white water and fed into the vats.

The pulp slurry is filtered on the wire of cylinder in the vat to form paper layer on the cylinder. Layers of paper are combined by using multiple vats arranged side by side.

Filter-former is a typical cylinder-type paper machine which carries out a high-speed papermaking. Figure 6.8 shows the outline of the ultraformer.

(2) Press part

The wet paper formed at the wire part has the moisture content of about 80%. In the press part, the wet paper is pressed on the felt by the press rollers to reduce the moisture. Two to four sets of press rollers are generally used in the press part.

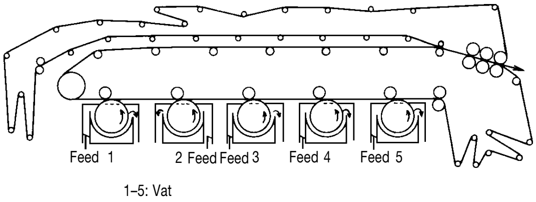


Fig. 6.7 A cylinder type paper machine

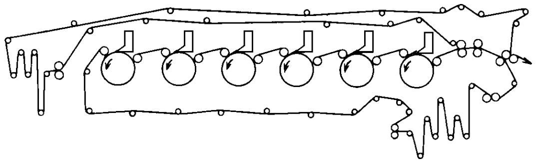


Fig. 6.8 A high-speed cylinder-type paper machine (ultra former)

(3) Dry part

At the outlet of press part, the moisture content of the wet paper becomes 55 to 70%. In the dry part, the paper is heated and dried to reduce the moisture content up to 5 to 8%.

A multi-cylinder type of drier shown in Figure 6.5 is commonly used for the dry part. Yankee drier having a large single-cylinder is also used for the dry part.

A size press for sizing the paper surface is generally installed in the dry part, and the calendar rolls increasing the paper gloss are installed after the dry part.

6.3 Chemicals Used for Pulp and Paper Manufacturing Processes

Recently, the saving of natural resources, energy and cost has been achieved in the pulp and paper manufacturing processes by making greater use of waste paper and by developing of higher-speed papermaking machines. Requirement for the paper products with high qualities and various functions has promoted the application of neutral papermaking and the production of various type of coated papers. In response to these trends, chemicals for paper manufacturing process have been also specialized and advanced very much in their functions and effectivenesses.

6.3.1 Dewatering Agents for Calcium Carbonate Slurry in the Lime Recovery System

Black liquor is yielded in the kraft pulp cooking and chemical recovery processes. After the black liquor is treated through various processes including the oxidation, concentration, combustion and redissolution, caustic soda is recovered from the black liquor by the reactions shown below.

$$CaO + H_2O \rightarrow Ca(OH)_2 \quad \text{.............................} \quad (6.1)$$
$$Na_2CO_3 + Ca(OH)_2 \rightarrow 2NaOH + CaCO_3\downarrow \quad \text{..} \quad (6.2)$$

The calcium carbonate slurry produced by the reaction (6.2) is washed using a washer. This slurry is dehydrated using a vacuum dehydrator, then dried and baked in a kiln to make calcium oxide which is reused in the caustification process.

A large quantity of oil is used as fuel for drying and baking the calcium carbonate mud in the kiln. To reduce the oil consumption in this process, the moisture content of the calcium carbonate mud fed into the kiln has to be reduced. A dewatering agent is used for the vacuum dehydrator to increase the dewatering efficiency on this mud. Nonionic surfactants are generally used as the dewatering agents. Among them, lipophilic surfactants generally show the sufficient effects. Those surfactants may adhere to the particles of calcium carbonate and the surface of the calcium carbonate will become hydrophobic. As the result, the dewatering of calcium carbonate will be promoted. The addition of dewatering agent of 50 to 300 g against 1 m^3 of calcium carbonate mud generally reduces the moisture content by 5 to 10% more than that of the no chemical treatment. Figure 6.9 shows the effects of a dewatering agent for a vacuum dehydrator. The application of dewatering agent also reduces the formation of lumpy calcium oxide in the kiln.

6.3.2 Deinking Agents

Since Japan has insufficient wood resources, waste papers are recycled as an important raw material for manufacturing pulp. The recovery rate of waste newspapers has exceeded 90% in Japan. The waste newspapers are recovered as pulp after the deinking. This deinked pulp (DIP) is used for making toilet papers and newsprint papers.

Key point in deinked pulp manufacturing is the efficient separation of the ink and foreign substances mixed with the waste paper. In order to separate the ink and the other foreign substances, a combination of the chemical treatment and the

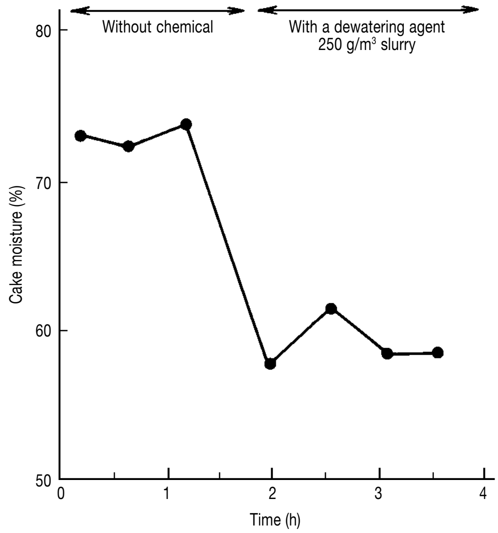


Fig. 6.9 Effect of a dewatering agent for calcium carbonate slurry in a vacuum dehydrator

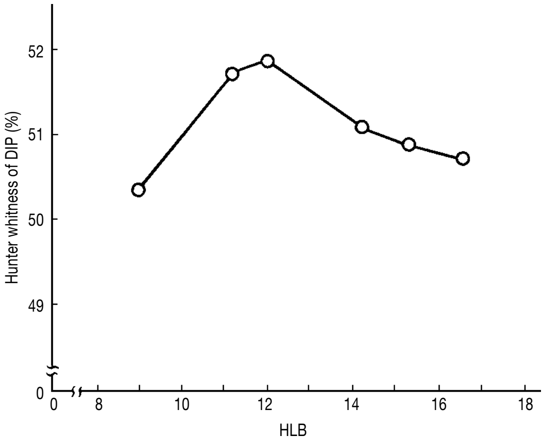


Fig. 6.10 Relationship between the HLB of surfactants and their deinking effects

mechanical treatment using screens, flotators and washers, is used. Surfactants play an important role in the chemical deinking process.

(1) Deinking agents for water wash deinking process (washing method)

In the washing method, ink removed from paper by a deinking agent is separated by washing pulp fibers with a large amount of water.

The treatment cost of this method is generally high because of a high supply water cost and a high wastewater treatment cost. Therefore, the employment of this method is not popular in Japan.

The deinking agent used in this method must have the excellent permeability, emulsification and dispersion activity against ink. Nonionic surfactants, such as higher alcohols and ethylene oxide addition products of alkylphenols, are usually used as deinking agents. When a surfactant is used, the hydrophilic-lipohilic balance (HLB) highly influences on the deinking effect. Figure 6.10 shows the relationship between the HLB of surfactants and their deinking effects.

(2) Deinking agents for the flotation method

In the flotation method, the separated ink is adsorbed on the foams generated in the flotator and the foams are removed from the system to separate the ink. A flow sheet of this deinking method is shown in Figure 6.3. In this method, it is required to use a deinking agent having the higher performance comparing with the washing method. The wetting effect, permeating effect, emulsifying power and dispersing power of deinking agents are required in the pulper, kneader and tower. The bubble forming ability of the agents and the ink-adsorption effect of the bubbles are required at the flotator. The emulsifying and dispersing actions are also required in the extractor and the valveless filter.

Recently, as kneaders are used for the fraying of waste papers to promote the deinking, a large amount of ink is removed from the waste paper and the DIP of high whiteness is obtained. Flotators with very large air volumes have used to remove a large quantity of ink from the system. Deinking agents producing foams with excellent ink-adhesion capacity are accordingly used. The major deinking agents used for the flotation method are mentioned below.

(a) Ethylene oxide addition products of higher alcohols

The ethylene oxide (EO) addition products of higher alcohols have stronger ink-adhesion powers than those of anionic surfactants. The characteristics of the addition products are controlled in a wide range by changing the types of hydrophobic groups and the mole number of EO added. Therefore, this type of chemicals has long been used as the main deinking agents.

(b) Fatty acids

Recently, as the employment of high concentration pulpers has become popular, the waste papers are generally frayed at the high temperature of 50 to 60° C. Stearic acid is used as the deinking agent

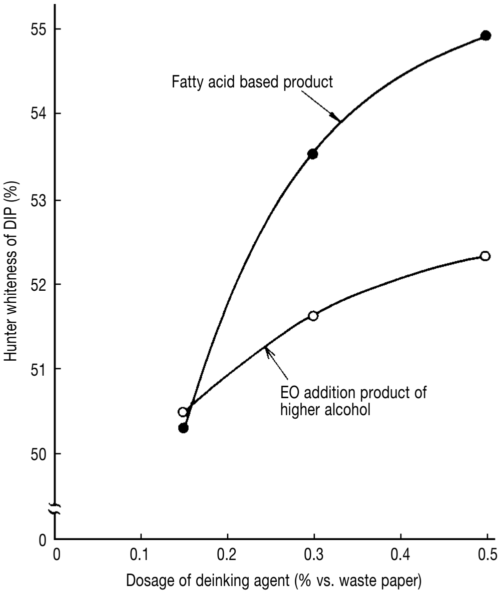


Fig. 6.11 **Comparison of the deinking effects of a fatty acid and an EO addition product of higher alcohol**

for these systems. Stearic acid is saponificated to sodium stearate in the pulper of a high temperature and high alkali concentration. The sodium stearate shows the surface-active effect and separates the ink from waste papers. Then, calcium chloride is added before the flotator to form calcium stearate. When calcium stearate deposits, a large quantity of ink adsorbs on the deposits. Thus, the ink is effectively collected and removed from the flotator.

As the ink removal effect of stearic acid is superior to that of EO addition products of higher alcohols, the whiteness of the deinked pulp is increased by several percentage comparing with the addition products as shown in Figure 6.11.

(c) Ethylene oxide and propylene oxide addition products of higher alcohols and fatty acids

The ethylene oxide and propylene oxide (EO-PO) addition products of higher alcohols and fatty acids have been recently developed as deinking agents to produce a high quality DIP with the higher whiteness and less ink residue.

Since these surfactants have PO groups which have the weaker hydrophilic property than that of EO groups, they have the greater affinity for oils and fats than that of EO addition products. As the result, their permeability to ink and the ink-adhesion capacity of the foams producing by them become stronger than those of the EO addition products.

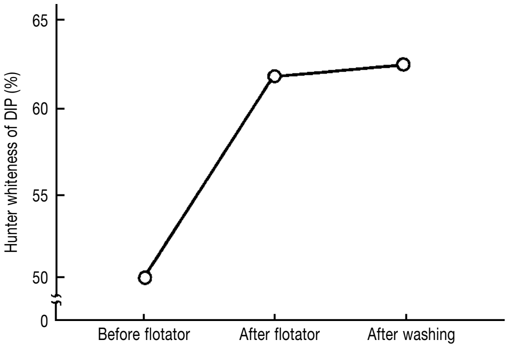


Fig. 6.12 **Change in the whiteness of DIP in each point of a DIP manufacturing plant under the treatment with an EO-PO addition product of higher alcohol**

The use of EO-PO addition product realizes a high quality DIP production in the DIP manufacturing plant employing a kneader and a flotator with a large volume of air supply. The whiteness of DIP is finally reached higher than 60% in such DIP manufacturing process as shown in Figure 6.12.

6.3.3 Retention Aids

(1) Significance of one pass retention

Previously, the overall retention (the ratio of product quantity to the total amount of paper stock fed into the papermaking system) was considered important for evaluating the efficiency of papermaking process.

Recently, One Pass Retention (OPR), that is "the retention of paper stock including fillers on the wire part to form dehydrated sheet", has been considered the most important.

When the OPR is decreased, the cleanliness of the papermaking system is decreased. This reduction in the system cleanliness reduces the cleanliness of the remained pulp recovery system, etc. As the result, the cleanliness of papermaking process is further reduced as the water-recycling in papermaking processes is progressed. The recent diversification of paper products accelerates the reduction of the system cleanliness because it increases the kinds and dosages of various chemicals using for papermaking processes. Therefore, the importance of the OPR has become greater.

The improvement of the OPR makes the following profits on the papermaking:

① Decrease in the amounts of raw materials, such as pulp and filler,
② Improvement in the drainability in the wire part and the press part, and a decrease in the volume of steam used,
③ Reduction in the amounts of white liquor used and wastewater,
④ Decrease in the fouling of system with slime and scale,
⑤ Improvement in papermaking conditions due to the decreased concentration of the inlet pulp,
⑥ Decrease in the amount of defective products.

(2) Factors related to the improvement of retention and drainability

The followings show the factors which affect the drainability in the wire and the press parts as well as the retention of filler and fine fibers:

① Properties of pulp, such as fiber length and drainability,
② Properties of the filler, such as particle size, shape and specific gravity,
③ Concentrations of pulp and filler,
④ Zeta potential of suspended particles in the system,
⑤ pH and temperature of papermaking process,
⑥ Characteristics of papermaking machine, such as the shape of machine, papermaking speed and the type of dehydrating element.

These factors are interrelated and affect each other in complex ways.

(3) Functional mechanisms of retention aids

The surfaces of fiber and filler suspending and dispersing in the pulp slurry, usually have negative electrical charges. Therefore, cationic polymers are commonly used as retention aids. This type of polymer neutralizes the negative electrical charges on the surfaces of particles and fibers. Then it coagulates them by the bridging action with its high molecular weight chain to make flocs which have the strong bonding power and good drainability. Therefore, the retention and drainability of the fibers and fillers on the wire are improved. The concentration of fine fibers and fillers in the filtered water is also decreased.

The most important properties of the cationic polymer based retention aids are their molecular weights and ionic strengths. The appropriate ionic strength of the polymer is varied depending on the types and dosages of the chemicals used in that process. However, polymers with higher molecular weights are generally more effective for improving the OPR.

Previously, polymers having the molecular weight of 1 million to 3 millions were used as the retention aids. However, polymers with higher molecular weights of 5 millions to 10 millions have been recently used to cope with papermaking by high-speed machines and to reduce the consumption of retention aids.

Figure 6.13 schematically shows a functional mechanism of the retention aids. The improvement of the drainability in paperboard manufacturing process is basically the same as that in the papermaking process. However, in the case of paperboard, not only the water filtration in the wire part, but also the squeezing out of water in the press part are important.

To improve the squeezing in the press part, an agent promoting the discharge of moisture from the coagulated paper stock is required. Figures 6.14 and 6.15 show the results of a gravity dehydration test and a squeezing test for polyacrylamide based cationic polymers having various molecular weights.

(4) Kinds and effectivenesses of retention aids

Following three types of retention aids are generally used in the fields:

① Polyacrylamide based (PAAm),
② Polyethylene-imine based (PEI),
③ Polyamide-polyamine based.

The PAAm based chemicals are also divided into anionic and cationic ones. The cationic PAAm based ones include the Mannich-modified prod-

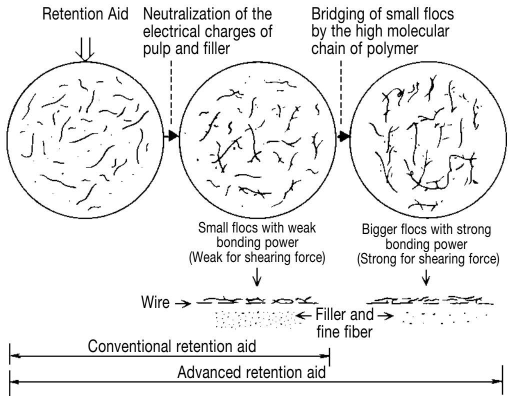


Fig. 6.13 Functional mechanisms of retention aids

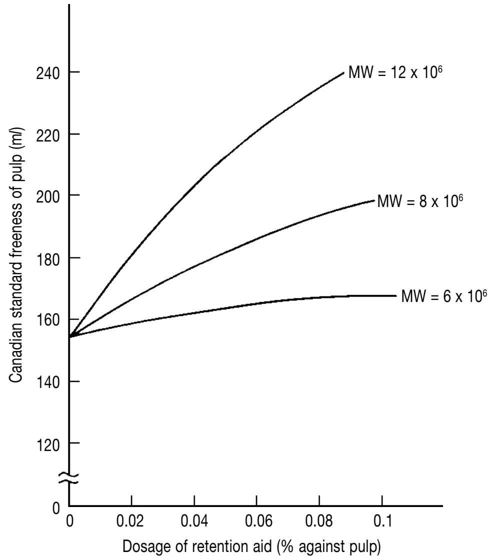


Fig. 6.14 Relationship between the molecular weights of polyacrylamide based retention aids and the drainability in the wire part

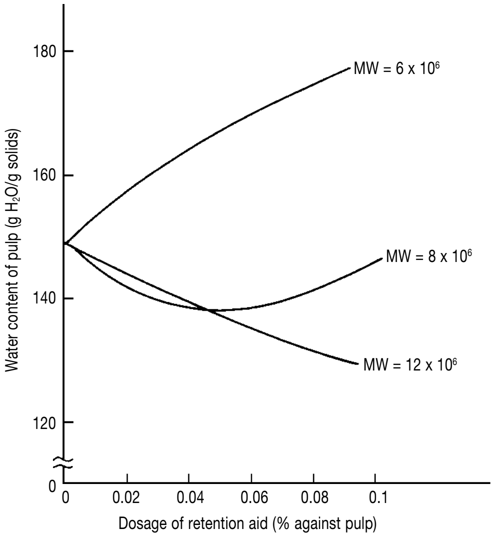


Fig. 6.15 Relationship between the molecular weights of polyacrylamide based retention aids and the squeezing in the press part

ucts of polyacrylamide, Hofman-degraded polyacrylamides and the cationic copolymers of acrylamide. Among them, partially hydrolyzed polyacrylamides (anionic) and the Mannich-modified products have the relatively high molecular weights. Table 6.3 shows the relationship between the types of polymers and their effects on the retention and drainage. The PAAm based Mannich-modified products and the cationic copolymers with high molecular weights show the sufficient effects on the retention and drainage in the both of acid and neutral papermaking processes. The effects of the other cationic polymers having the smaller molecular weights are insufficient.

Anionic polymers with high molecular weights show the good effects on the retention, but they have the insufficient effects on the drainage.

(5) Selection method of retention aids

It is important for improving the retention and drainage on site to select a retention aid of which the characteristics fit the operational conditions of the papermaking machine. Test methods for selecting the retention aids are described below.

(a) Retention test

Previously, a hand-made paper was prepared by using a sheet machine to evaluate the retention.

Table 6.3 Types and effects of retention aids on the retention and drainage of pulp

Type of retention aid		Ionic property	Effectiveness			
			In acid papermaking process		In neutral papermaking process	
			For retention	For drainage	For retention	For drainage
Polyacrylamide based	Hydrolyzed	Anionic	△	×	○	△
	Mannich-modified	Cationic	○	○	△	△
	Hofman-degraded	Cationic	△	△	×	×
	Cationic copolymer	Cationic	○	○	○	○
Polyethylene-imine based		Cationic	△	△	×	×
Polyamide-polyamine based		Cationic	△	△	×	×

○ Excellent △ Good × Not effective

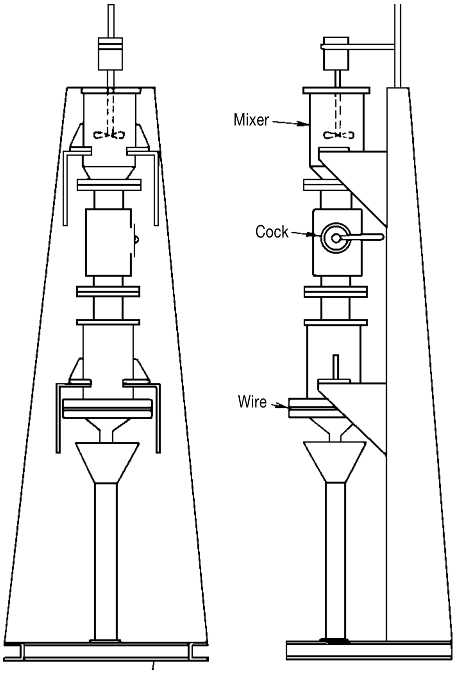


Fig. 6.16 Dynamic retention tester

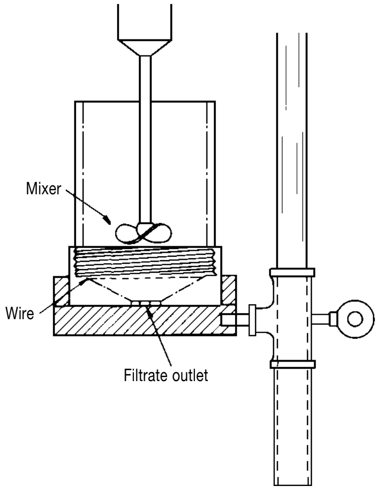


Fig. 6.17 Dynamic drainage jar

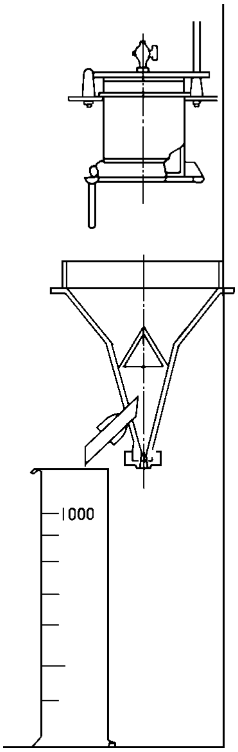


Fig. 6.18 Canadian standard freeness tester

Test results obtained this static method showed the insufficient correlation with the retention in the field. Therefore, dynamic test methods using the dynamic retention tester (DRT), the dynamic drainage jar (DDJ) and so on have employed recently.

Figures 6.16$^{1)}$ and 6.17$^{2)}$ show the outlines of those testing apparatus. In each testing method, a retention aid is added to the sample slurry and the sample is agitated. Then the SS and ash content of the filtrate are measured to evaluate the effect of the agent.

(b) Drainability test

The Canadian Standard Freeness (CSF) tester is generally used to evaluate the drainability of pulp. Figure 6.18 shows the outline of CSF tester. The CSF tester is useful for evaluating the drainability but not applicable for squeezing test. Therefore, in order to evaluate the both of drainability and squeezability, two kinds of tests, the web test and the press test, should be done.

(i) Web test

Figure 6.19$^{3)}$ shows the web test apparatus for evaluating the drainability. In the web test, the gravitational dehydration property assuming the initial dehydration condition on the wire is measured. After the suction dehydration carries out under a reducing pressure for a specified period, the wet paper is taken out and its moisture content is measured.

(ii) Press test

Figure 6.20$^{3)}$ shows the press test apparatus for

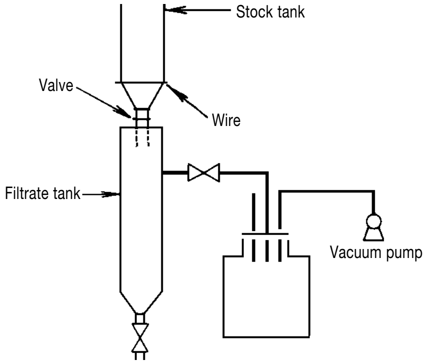


Fig. 6.19 Drainability test apparatus (web test)

evaluating the squeezability. In this test, wet paper is pressed under a specified pressure for a specified period and the moisture content of the paper is measured.

(6) Case studies of retention aids

(a) Increase in the retention of filler in a papermaking process

Table 6.4 shows the field data on the filler retention in a high quality papermaking process. These data show that the SS of the circulating white water has been clearly decreased because the one pass retention (OPR) has been improved by using a retention aid. As the result, the papermaking conditions have been drastically improved.

(b) Increase in the retention and papermaking speed in a coat base papermaking process

Table 6.5 shows a case study of a retention aid in a papermaking process of a coat base paper using a high speed twin-wire machine.

Table 6.4 Increase in filler retention by using a retention aid in a high quality papermaking plant

Place of sampling	Item of analysis	Control	With retention aid (0.015%)
Head box	SS (%)	3.04	2.85
	Ash (%)	0.67	0.61
	Ash/SS (%)	22.0	21.4
Machine inlet	SS (%)	1.01	0.78
	Ash (%)	0.35	0.22
	Ash/SS (%)	34.7	28.2
Tray	SS (%)	0.45	0.23
	Ash (%)	0.29	0.12
	Ash/SS (%)	64.4	52.2
	COD (mg/*l*)	78.0	50.0
Circulating water	SS (%)	0.64	0.35
Excess white water	SS (%)	0.53	0.30
Recovered SS (Settling tank inlet)	SS (%)	0.51	0.36
Settling tank overflow	SS (mg/*l*)	58	35

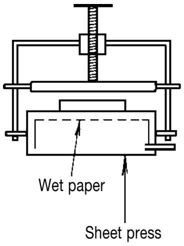


Fig. 6.20 Squeezability test apparatus (press test)

The use of the retention aid increased the filler OPR and reduced the SS of white water. As the result, the papermaking speed was increased and the machine operation was stabilized because of the reduction of SS concentration in the stock at the machine inlet.

(c) Increase in the productivity in a white board manufacturing process

White board is a multi-ply board consisting of 5 to 9 layers of paper. It is made by using cylinder-type paper machines, such as ultra-former.

As the CSF of the pulp used for the middle and back layers of white board is low, the increase in the drainability using retention aid is required to increase the papermaking speed and to reduce the amount of steam using for the drier.

Table 6.6 shows the profit obtained by using a retention aid in a white board manufacturing. These data show that the profit becomes greater when a board paper with the higher basis weight is manufactured.

6.3.4 Sizing Agents

The wood pulp fibers are hydrophilic and have the porous structure with many capillaries in their surfaces and insides. Therefore, the fibers easily absorb water and oils. In the papermaking pro

Table 6.5 Effect of a retention aid in a coat base paper manufacturing using a twin wire machine

Retention aid		Without	With
Filler OPR (%)		16.8	24.2
Machine speed (m/min)		720	800
Stock at machine inlet	SS (%)	1.23	1.02
	Ash (%)	0.47	0.31
White water at tray	SS (%)	0.63	0.45
	Ash (%)	0.39	0.24

Table 6.6 Profits obtained by using a retention aid in a white board manufacturing

Basis weight of white board (g/m³)	Increase in machine speed (%)	Reduction in steam consumption (%)	Profit (thousand yen/day)		
			Increase in sales profit	Reduction of steam cost	Total
260	0	2	0	16	16
310	0	2	0	16	16
350	1.5	1.5	51	12	63
400	3	2.9	102	23	125
450	4.5	4.3	153	24	187
500	5	4.8	170	34	204
550	5.5	5.2	187	42	229
600	6	5.7	204	46	250
700	7	6.5	238	52	290

Dosage of retention aid: 0.03% against pulp
Basis of profit calculation: 1) Sale price of white board; ¥120/kg
2) Sales profit; 28% of sale price
3) Unit cost of steam; ¥4,000/kg
4) Unit steam consumption; 2 ton/ton paper

cesses, an appropriate resistance against the permeation of those fluids has to be given to the fibers according to the uses of paper. The chemicals used for this purpose are called sizing agents. The sizing agents are divided into the internal and surface sizing agents, but the latter is generally applied.

The sizing agent is added to the machine chest or head box to control the permeation of various fluid, such as water and water-based inks, into the paper.

(1) Kinds of sizing agents

The sizing agents are classified into the following four types from their main components:

① Rosin-based sizing agents including reinforced rosin sizing agents,
② Petroleum-resin based sizing agents,
③ Wax sizing agents,
④ Reactive sizing agents.

They are also classified into the liquid type and the emulsion type.

In the neutral papermaking process using calcium carbonate as the filler, sizing agents are also used and they are called the neutral sizing agents. They are divided into two types of reactive sizing agents and cationic self-fixing sizing agents.

Among them, the following two kinds of sizing agents are mainly used:

① Aklyl-ketene dimer (AKD) type sizing agents,
② Alkenyl-succinic anhydride (ASA) type sizing agents.

The recent trend in the uses of sizing agents is a remarkable increase in the use of emulsion-type rosin sizing agents and ASA-type sizing agents.

(2) Factors affecting sizing efficiency

(a) Kinds of pulps

The sizing efficiency varies depending on the kinds of pulps. Table 6.7 shows a relationship between the kinds of pulps and the sizing efficiencies. Generally, the sizing effect becomes greater on unbleached pulp than on bleached pulp. Soft wood pulp is sized easier than hard wood one.

(b) Bleaching and washing of pulp

The sizing of high-purity pulp cooked and bleached sufficiently are generally not easy comparing with that of a pulp including substances with a low molecular weight, such as hemicellulose.

(c) Water temperature

The increase of water temperature reduces the sizing efficiency and increases the required dosage of sizing agent. The cause of this reduction in the sizing efficiency is considered that the flocs produced by the aluminum and rosin becomes larger, and the adsorption of the floc particles on pulp fibers becomes coarsely under higher water temperature.

Table 6.7 Relationship between the kinds of pulps and their sizing efficiencies

Kind of pulp	Freeness (ml)	Retention of sizing agent (%)	Size fastness (sec)
Groundwood pulp	260	69	42
Unbleached kraft pulp	370	59	21
Unbleached sulfite pulp	385	47	13
Lag pulp	370	68	4

Sizing conditions: Dosage of sizing agent; 2%
Stock pH; 4.5

As a countermeasure to this problem, emulsion-type sizing agents have been developed. The emulsion type sizing agent shows the better sizing effect at an elevated temperature than that of the fortified rosin type agents as shown in Figure 6.21.

(d) Hardness of water

Electrolytes in water affect the sizing efficiency and the increase of the hardness especially decreases the sizing efficiency.

Figure 6.22 shows the relationship between the hardness and the effects of sizing agents. The effect of emulsion type sizing agent is stable against the increase of hardness. In case of same total hardness, magnesium ion gives the worse influence on the sizing effect than calcium ion. Chloride ion is also worse on the sizing effect than sulfate ion.

(3) Fixing of sizing agents by using retention aids

Sizing agents tend to fix more tightly on short fibers than on long fibers. When the retention of fine fibers is poor, this will not only increases the consumption of sizing agent but also the sizing agent adsorbed on the fine fibers will be circulated. Then the deposit problems will occur in the system.

Table 6.8 shows the effects of retention aids on the sizing efficiencies of neutral sizing agents. The use of the retention aids improves the retention of the sizing agents and increases the size fastness by 4 to 7 seconds.

6.3.5 Antifoaming Agents

(1) Causes of foaming and foaming problems in the papermaking processes

In the papermaking process, the white water cascades down and is stirred in the save-all, the white water pit, etc. Then air is mixed into the water.

When air is mixed into a clean water like tap water, the size of air bubbles in the water is relatively large. Then bubbles soon float up to the water surface and disappear easily.

In the papermaking processes, various agents, such as sizing agents, aluminum sulfate and paper-strength agents, are added to the white water.

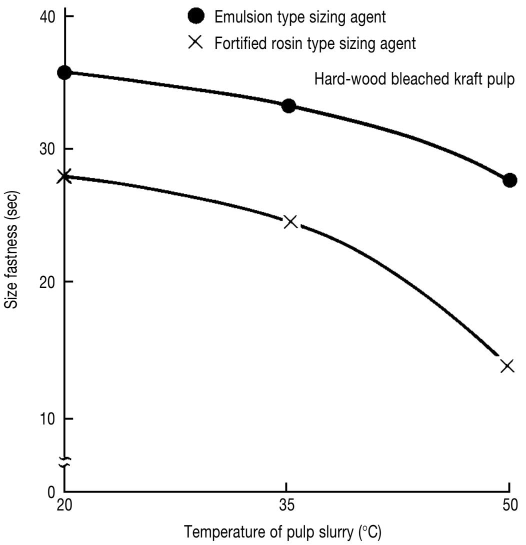


Fig. 6.21 Comparison of the effects of sizing agents at an elevated temperature

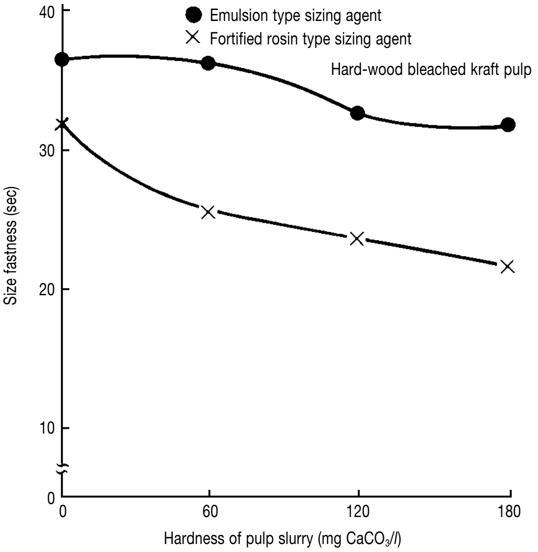


Fig. 6.22 Relationship between sizing effects and the hardness of pulp slurry

Table 6.8 Improvement of sizing efficiency by using retention aids

Sizing agent	Retention aid	Basis weight of paper (g/m²)	Ash content of paper (%)	Size fastness (sec)
Alkyl-ketene dimer type 0.2%	Control	57.1	9.4	26.5
	A: 0.02%	58.0	12.1	31.8
	B: 0.02%	57.8	11.9	30.6
Alkenyl-succinic anhydride type 0.2%	Control	57.4	9.6	35.5
	A: 0.02%	58.1	12.1	42.7
	B: 0.02%	58.0	12.0	42.2

Kind of pulp: Hard wood bleached kraft pulp

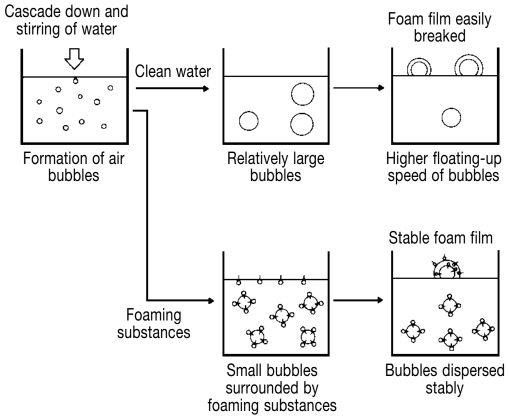


Fig. 6.23 Schematic model of foaming processes in a clean water and a contaminated water

Contaminants from the pulping process are also present in the white water. These substances make the bubbles in the white water very fine. Such fine bubbles are stably dispersed in the white water and they are difficult to break even after floating up to the surface of the white water.

Figure 6.23 shows a schematic model of the foaming processes in a clean and a contaminated waters. Various problems are caused by the stable foaming in the papermaking processes. Table 6.9 shows typical problems caused by foaming. Generally, it is considered that those problems may be caused by the foaming on the water surface. However, bubbles in the white water also cause serious troubles.

(2) Prevention of foaming problems

The prevention methods of foaming are divided into mechanical method and chemical method. As

Table 6.9 Problems caused by foaming in papermaking processes

Kind of foams	Phenomenon	Problems
Foams on water surface	Adhesion of foams and formation of scum on the wall of white water pit, etc.	Formation of fish eyes Paper breaks
	Carryover of foams from white water pit, etc.	Deterioration of working conditions Deterioration of machine efficiency
Fine dispersed bubbles in white water	Foaming in stock inlet and scum formation	Formation of fish eyes Paper breaks
	Adhering of bubbles to stock	Deterioration of sheet formation by un-uniform stock dispersion Bad wet web dehydration on wire causig bad sheet formation, paper breaks and increase of steam consumption in dryer Decrease of the binding power between board layers
	Bubbling on sheet wire	Formation of pin-holes

the effect of mechanical method, such as water spraying, is limited, the chemical method using antifoaming agents is generally applied for papermaking processes.

The functions of antifoaming agents are divided into foam killing and foam-inhibiting effects. The foam-killing is the action to break foams. The foam-inhibition is the effect to reduce the number of bubbles floating up to the water surface by unifying the bubbles dispersed in the water.

The effect of antifoaming agents is visually observed by the amount of foams on the water surface, but most antifoaming agents also decrease the amount of bubbles dispersed in the water. Therefore, a suitable antifoaming agent should be selected considering the effect to reduce the foaming in the both of water surface and the inside. Previously, the measurement of the bubble amount in white water was difficult, but recently, a monitoring equipment has been developed to measure it easily.

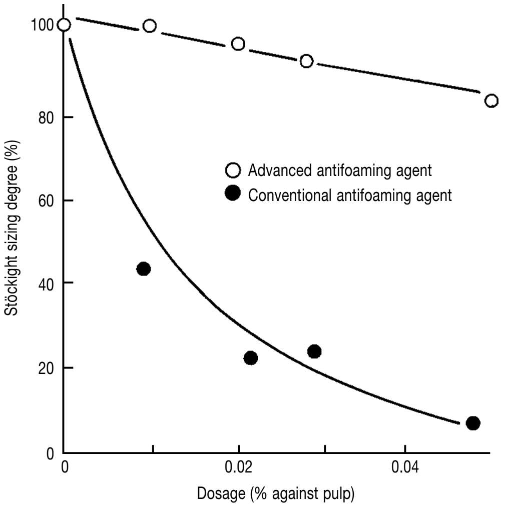


Fig. 6.24 Comparison of the influences of an advanced and a conventional antifoaming agents on sizing degree

(3) Kinds of antifoaming agents

As the detail of antifoaming agents is described in the section 10.7, the kinds and characteristics of typical antifoaming agents using for papermaking process are summarized in this section.

(a) Self-emulsifying type antifoaming agents

Antifoaming agents of this type are surfactants with low HLB, which are manufactured by reacting fatty acids or higher alcohols with polyethylene oxide or polypropylene oxide. The appearance of those antifoaming agents is an oily but they disperse and form the stable emulsions when they are added into water.

Most self-emulsifying type antifoaming agents show the better effects with the small dosages, compared with emulsion-type antifoaming agents. However, they tend to reduce the sizing degree in the case of an excess dosing.

Therefore, self-emulsifying type agents were previously used for paperboard making, which requires not so high sizing degree comparing with printing papers. However, such disadvantage of this type has been recently improved as shown in Figure 6.24, and their application for printing paper-making has been begun.

(b) Emulsion-type antifoaming agents

Emulsion-type antifoaming agents are made of surfactants with low HLB, waxes or silicon oils by emulsifying them in water with emulsifiers.

Antifoaming agents of this type are widely used for various papermaking processes including printing papers because they scarcely influence on the sizing and their cost performance is excellent.

(c) Mineral-oil type antifoaming agents

Antifoaming agents of this types include mineral oils as the main ingredient, and metallic soaps, silicon oils, silicon dioxide, fatty acid amides, surfactants, etc., are formulated to improve the antifoaming effect.

Those antifoaming agents are mainly used in the pulp washers.

(4) Factors affecting the effect of antifoaming agents

In this section, main factors affecting the effect of the self-emulsifying type antifoaming agents are discussed because they are advanced chemicals and their application has become popular in papermaking processes.

(a) HLB of antifoaming agent

As the active ingredient of self-emulsifying type antifoaming agents is nonionic surfactants, the performance greatly depends on the hydrophilic-lipophilic balance (HLB). Figure 6.25 shows a typical relationship between the HLB of an antifoaming agent and its antifoaming effect for white water. In the case of EO and PO addition compounds of a fatty acid with the same total EO and PO addition rate, the increase of EO addition ratio increases the HLB and the antifoaming effect maximizes at a specified HLB.

(b) Temperature

Figure 6.26 shows the influence of white water temperature on the antifoaming agents with vari

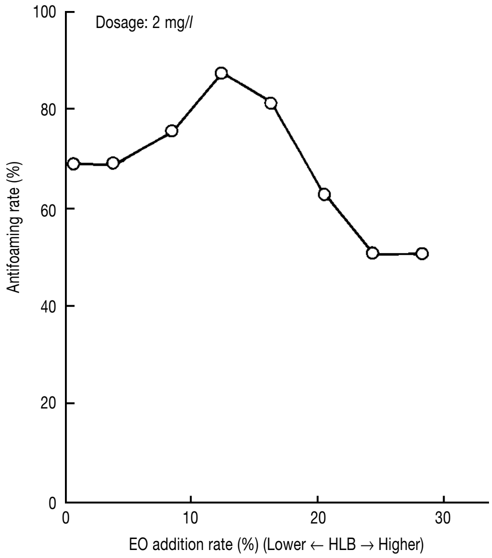


Fig. 6.25 **Relationship between the HLB of self-emulsifying type antifoaming agents and their effects for white water**

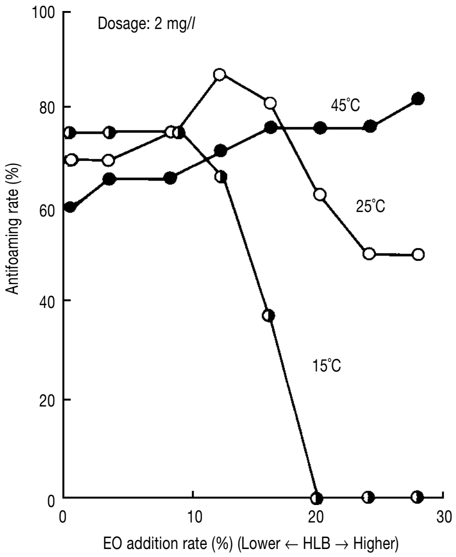


Fig. 6.26 **Relationship between the appropriate HLB of self-emulsifying type antifoaming agents and white water temperature**

ous HLB, which are same agents showing in Figure 6.25.

Appropriate HLB of the antifoaming agents becomes higher at the higher temperature and becomes lower at the lower temperature as shown in Figure 6.26. Therefore, the suitable antifoaming agent must be selected according to the process temperature.

6.4 Deposits on Papers and Their Prevention

In Japan, most of paper manufacturing companies have already realized the increase of their productivities by increasing the papermaking speed, by changing raw materials for pulp production and so on. Therefore, a present target of their improvement on papermaking is the improvement of paper quality, especially in case that a large ratio of DIP is used for papermaking.

From this point of view, the main problem related to papermaking is the generation of holes, spots and fish eyes shown in Photograph 6.1 (p. 6-32). These defects of paper not only decrease the product quality drastically, but also cause various problems during printing. The generation of holes also causes paper break to reduce the operational efficiencies and productivities of paper machines.

The holes, spots and fish eyes are caused by the various depositions on papers in the papermaking processes.

6.4.1 Kinds of Deposits

The word, "deposits", is used for the undesirable accumulated substances which are generated everywhere in the pulping and papermaking processes.

Deposits are classified by their compositions, as shown below:

Slime (biological fouling),
Pitch,
Scale,
Foam,
Size,
Aluminum sulfate gel,
Dirt.

Deposits are usually formed by a combined deposition of two or more of the above components.

Figure 6.27 shows the classifications of deposits and their typical compositions. They are roughly classified into organic, inorganic and mixed-types. Their compositions often vary depending on the sampling place, sampling time and operational conditions of the equipments.

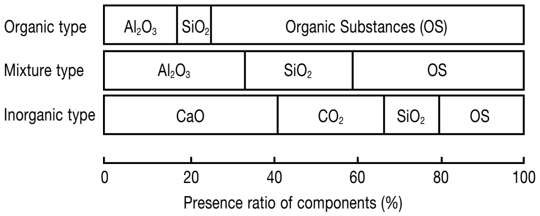


Fig. 6.27 Classification of deposits and their typical compositions

6.4.2 Causes of Deposit Problems

The occurrence of deposit problems has increased in the papermaking processes recently. The reasons are as follows:

(1) Change of raw materials

Pitch deposits consisting of various sticky substances have increased due to the change of raw material from soft wood to hard wood and the increase in the recycle of waste paper. Ink pitch caused by the components of ink has also become a major problem as the use of DIP increases.

(2) Changes in papermaking conditions

In urban areas of Japan, as the costs for water supply and wastewater discharge have increased, the employment of closed water circulation systems for the pulp and paper manufacturing processes is progressing.

The unit water requirement becomes 5 to 10 m^3 for 1 ton of paper product in many plants, and the deposit problems caused by a high concentration of inorganic salts are increasing. Figure 6.28 and Table 6.10 show the flow sheet of a white water recycling system and the analyses of white waters in a paper board manufacturing plant. The neutral papermaking method using calcium carbonate as the filler, has become quite popular for printing paper manufacturing because of the demand for preserving books longer. In the neutral papermaking process, a high rate of white water recycling is generally adopted. However, the generation of deposits consisting of the hydrolysis products of the neutral sizing agents has become the biggest problem in the neutral papermaking.

(3) Use of large-size and high-speed paper machines

Various types of twin-wire formers have employed to reduce the paper quality difference between the front and back sides and to stabilize the machine operational conditions. These machines increase the productivity, but reduce the retention of raw materials. As the result, SS in the white

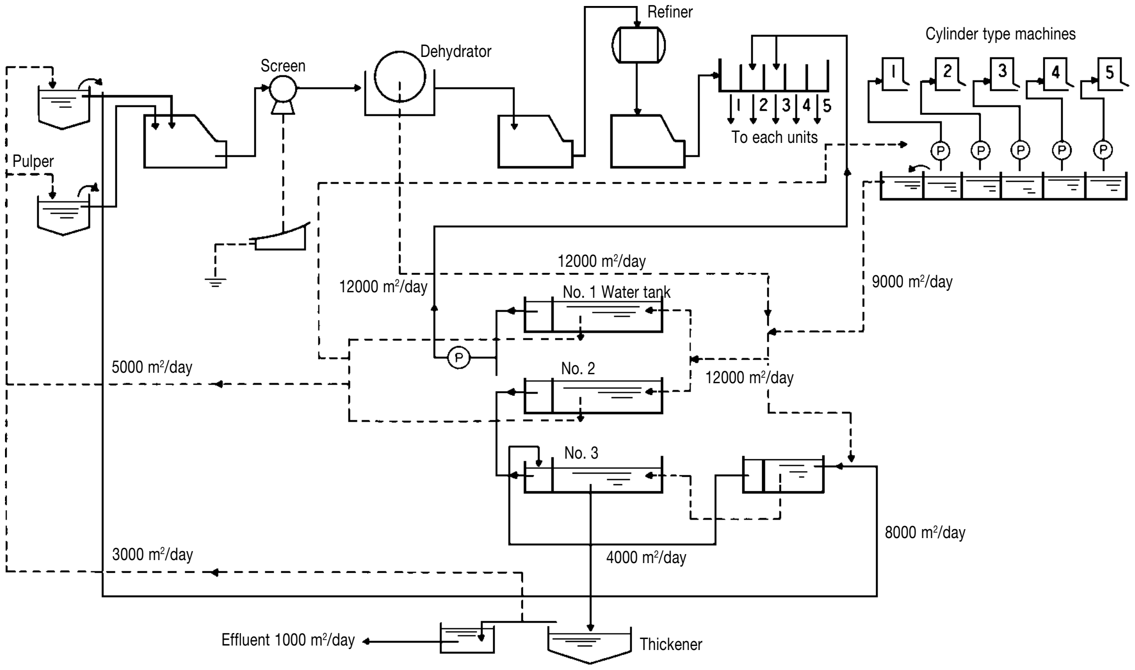


Fig. 6.28 Flow diagram of white water recovery and recycling system in a paperboard making plant

Table 6.10 Comparison of the unit water consumptions and white water qualities between a low and a high white water recycling rates in a paperboard manufacturing

White water recycling rate			Low	High
Unit water consumption (m^3/ton product)			35	10
White water	PH		6.2	4.8
	Electrical conductivity	(μS/cm)	660	3,670
	M-alkalinity	(mg $CaCO_3/l$)	68	49
	Total aluminum	(mg/l)	5.4	16.7
	Total iron	(mg/l)	0.6	2.5
	Ca^{2+}	(mg/l)	69	641
	Mg^{2+}	(mg/l)	3	32
	Al^{3+}	(mg/l)	1.2	8.2
	Fe^{3+}	(mg/l)	Below 0.1	0.7
	Cl^-	(mg/l)	22	85
	SO_4^{2-}	(mg/l)	221	1,460
	SiO_2	(mg/l)	5	7

water increase, and cause the various deposit troubles. Deposits which previously causes no problem, becomes to cause various problems in the papermaking process using the high-speed paper machines.

(4) Increase in the use of chemical additives

Internal sizing agents and so on are used to improve the sizing fastness, papers strength, formation and paper surface quality. The use of various surface sizing agents has also increased to improve the printability. This trend is expected to continue, as well as the diversification of product in the future. These chemicals have become the major cause of the deposit problems when the application of the chemicals is inadequate.

Table 6.11[4)] shows the kinds and dosages of those additives used for the neutral paper making process. Cationic paper strengthen agents adsorb on pulp and filler surfaces to increase the zeta potential of those particles. In that case, the fixing rate of the neutral sizing agent and the filler with the pulp fibers is worsened, and the amount of deposits consequently increases. The increase

Table 6.11 Kinds and dosages of additives using for neutral papermaking process

Kinds	Main ingredient	Dosage (% against pulp)
Sizing agent	Alkenyl-succinic anhydride	0.15
Coating agent	Cationic starch	0.5
Filler	Aluminum sulfate	0.2
Paper strengthen agent	Epichlorohydrin based polymer	0.2
	Polyacrylate	0.3
Retention aid	Polyacrylate	0.025

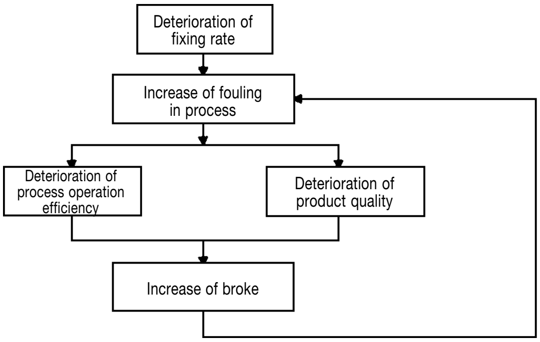


Fig. 6.29 Increase of broke by a deterioration of fixing rate

of deposits induces web break and the other problems. The increase of broke accelerates the contamination of the system, then causes the further generation of deposits. Figure 6.29[4)] shows these relationships.

6.4.3 Places of Deposit Generation and Kinds of Deposits

Figure 6.30 (p. 6-33) shows the places of deposit generation and the types of deposits in pulp and papermaking processes. To stabilize the overall operation of pulping and papermaking processes and to improve the product quality, the generation of deposits in each process has to be prevented by applying suitable measures.

When spots generate on the product, troubleshooting measures usually concentrate on the papermaking process. However, this kind of measure is difficult to solve the troubles perfectly because the foulings generating the spots are formed not only in the papermaking process but also in the pulping and pulp recovering processes. Countermeasures should be applied for the overall pulping and papermaking processes to solve the problems completely.

The kinds of deposits in each process are shown below:

(1) Pulping process

(a) DIP manufacturing process

Inorganic deposits consisting of mainly calcium carbonate adhere to the flotator wall and filter, and may cause product defects such as holes and fish eyes.

(b) Broke chest

Deposits in the broke chest are often caused by microorganism growth. The numbers of bacteria in pulp slurry are generally $10^5/\text{m}l$ in the broke chest and 10^7 to $10^8/\text{m}l$ in the coat broke chest respectively. Therefore, the biocidal treatment should be applied for the coat broke chest and it is also desirably applied for the body broke chest. Fiber, suspended solids and pitch are concentrated on the foams generated in the chest, and often form the scum on the side walls of the chest.

(c) Refiner chest

Pulp wood contains a large amount of resin acids which generates deposits consisting of pitch mainly in the pulper chest and refiner chest. These pitches decrease the productivity by clogging filters, and generate pitch spots on the products.

(d) Mixing chest and machine chest

Filler, aluminum sulfate and various additives are added into the mixing chest and machine chest. The filler forms flocs with the aluminum sulfate, cationic starch, paper strengthen agent, fibers, etc., and the flocs are sent into the wire. When the floc size becomes too large, it causes deposits. Deposits often generate at the water line of the chest and in the pipings. These large flocs sometimes form filler spots on the sheet.

Particularly, when the papermaking conditions are widely changed, deposits in the chest and its pipings often come off and mix with the white water. The increase of white water contamination causes web breaks, pinholes and so on.

(2) Papermaking process

(a) Machine inlet

Since slurry in the machine inlet is a mixture of raw pulp and white water, the contamination of white water may cause problems. The improvement of retention and the prevention of foaming in the papermaking process are particularly important. When the retention becomes low, the SS concentration of white water becomes higher and the contamination in the papermaking process will be increased. Particularly in the neutral papermaking process, if the retention of the neutral sizing agent is low, the sizing agent is hydrolyzed. Then they cause foaming and their deposits on the surface of the inlet wall. It is important to select an appropriate antifoaming agent for preventing the occurrence of pinholes and spots due to foaming. The spots formation caused by foam often occurs when foams are contained in the water. In this case, the application of an antifoaming agent which decreases the amount of air bubbles dispersing in the water is effective. Slime also generates in the slice lip and sometimes causes trouble. An attention must be paid for slime control.

(b) Foil and suction box

Deposits of slime mainly adhere at the bottom of the foil and suction box. Deposits composed of pitch adhere on the surface of the foil and on the top plate of the suction box. Entering of these deposits into the machine decreases the efficiency of dehydration on the wire and the productivity. Moreover, it shortens the service life of the wire.

(c) Press roll

When press wastes generate, they contaminate the felt and cause web break. Hydrolyis products of sizing agents, fillers and aluminum compounds are the major components of the deposits in the neutral papermaking process. To reduce the amount of deposits, it is important to improve the fixing of sizing agents. Since various cationic polymers are used as retention aids in the neutral papermaking process, the control of zeta potential of pulp flocs in the papermaking process is important to reduce the deposits.

(d) Wire, felt, save-all and white water silo

Many deposits consisting of filler, fiber and sizing agent combined with the aluminum hydroxide flocs are observed in the acidic papermaking process. In this case, main countermeasures are slime and deposit control, and the machine washing during the shut-down period. In the neutral papermaking process, the slime control is generally more difficult than that in the acidic papermaking process. However, when deposits adhere in the inside of the save-all and on the wall of the white-water silo, or when the number of bacteria in the white water exceeds $10^6/\text{m}l$, an improvement of slime treatment is essential. The application of comprehensive slime treatment for the pulping process and the white water recovery process must be done to eliminate machine problems completely.

(3) White water recovery process

(a) Clarifier

The filler retention sometimes becomes poor when a paper machine with a high papermaking speed is used. In that case, the clarifier operates under an overload and the system performance sometimes deteriorates.

To solve this problem, retention aids are usually used. In the case of sedimentation treatment, flocs combined with air bubbles sometimes float up and form the scums. When the scums adhere to the side walls of the clarifier, they cause slime problems and lower the quality of recovered water.

(b) Sand filter

When the recovered water is re-used, the SS value should be reduced 10 mg/l or lower. A sand filter is usually used to remove SS. Slime sometimes grows in the filter and decreases the filtration efficiency. When the recycled water is used as the shower water, slime generates in the shower nozzles and the strainers. These slimes often reduce the productivity of equipment.

(4) Deposits caused by additives

(a) Calcium carbonate

Calcium carbonate is generally used as the around 10% suspension using white water. The calcium carbonate may adhere as a scale in the injection line. If the scale comes off from the piping and goes through the screen, it will cause "filler spots" and deteriorates the product quality. The deposition of scale should be prevented by using dispersing agents.

(b) Dyestuffs

Generally, the dye solution tanks are periodically washed to prevent slime troubles. When the tank washing is impossible, slime treatment chemicals should be applied.

(c) Sizing agents

In the tanks of emulsion type sizing agents, the foaming due to the quality deterioration or the emulsion break due to the temperature increase sometimes occurs. These problems decrease the sizing efficiency and cause the adhesion of scum on the inner wall of the tank or the formation of slime.

(d) Cationic starch

Slime grows in the cooking equipment of the cationic starch, the service tank and the strainer.

(e) Paper strengthen agents and retention aids

The paper strengthen agents and the retention aids are generally used after dissolving with water. As these polymer-based chemicals are difficult to perfectly dissolve, the entering of the undissolved ones into the papermaking process will cause spots on the paper surface. When the quality of the water for the chemical dissolving is poor, fish eyes, flocs combined with SS and so on are formed. Then they cause the holes of products and web breaks. When the tanks and the injection systems of these chemicals are used for long periods of time, slime will be formed on their inner walls. These equipment must be periodically washed.

(5) Coating process

(a) Size-press solution

After paper comes out of the dryer, the surface sizing using starch, etc., is applied for the paper to improve the surface quality and to increase the surface strength. When the starch solution rots in the storage tank, it will cause the clogging of screen. Since the size-press solution is circulated and used repeatedly, slime formation in this line causes the spot of the product. Scums produced by foaming also cause the fish eyes on the product.

(b) Coating solution

Coating solution generally consists of pigment and adhesive, and various chemicals also added to this solution. Among these chemicals, adhesives, such as starch, latex and polyvinyl alcohol, often rot and cause deposit problems. Preservatives are generally added into them to prevent their rot.

6.4.4 Deposit Ihibitors

Various deposits generate in the paper and pulp manfuacturing processes and these deposits cause the holes, spots and fish eyes of papers, which deteriorate the product quaity. In order to prevent these problems, various chemicals have been used to cope with each cause.

(1) Deposit contol agents

(a) Kinds of deposit control agents

Recently, problems caused by inorganic deposits have increased, because the neutral papermaking and the white water recovery rate have been increased. The inorganic deposits consist of calcium slats, aluminum slats, silicates, barium salts and the other compounds. These deposits cause many problems and reduce the productivity in all areas of pulp and paper mills. Various deposit control agents are applied to prevent the inorganic deposits.

The deposit control agents are roughly classified into three groups as shown below.

① Dispesants (sodium lignin sulfonates, polymers, tannins, etc.),
② Scale inhibitors (polyphosphates, phosphonates, etc.),
③ Chelating agents (EDTA, NTA, etc.).

Some polymers and phosphonates have both functions of ①and ② These chemicals are widely applied as deposit control agents because they sufficiently prevent the inorganic deposits. Dispersants and chelating agents need their high concentrations to prevent the deposits sufficiently. Therefore, these dispersants and chelating agents are generally used as cleanig agents rather than as deposit control agents. Table 6.12 shows the cleaning test results of EDTA against barium sulfate scale.

(b) Prediction of inorganic deposits

Hardsoluble inorganic substances often deposit around the seed crystals of calcium carbonate deposited. This kind of deposits is prevented by controlling the precipitation of calcium carbonate.

Therefore, the deposition of inorganic substances is predicted by calculating the saturation degree of calcium carbonate in an aimed system. Gernerally, Saturation Index[5)] (Langelier Index) is used for predicting the possibility of calcium carbonate deposition.

The difference between the pH (pHa) of a water and the saturation pH (pHs) of calcium carbonate is called the Saturation Index (SI). The following equations show the relationship between the SI and the saturation condition of water with calcium carbonate.

Table 6.12 Cleaning effect of EDTA on barium sulfate scale

Cleaning agent	Dosage (%)	Temperature (°C)	Amount of dissolved $BaSO_4$ (mg/l)
EDTA	0.5	20	2,800
		40	2,900
EDTA	0.5	20	2,400
NaOH	0.5	40	2,900
NaOH	0.5	20	Below 100
		40	Below 100

SI = pHa - pHs .... (6.3)
SI > 0 Supersaturated water with calcium carbonate .... (6.4)
SI < 0 Unsaturated water with calcium carbonate .... (6.5)

The positive SI shows that calcium carbonate will deposit in the water. The calculation method of pHs is described in the section 3.3.1, (1).

(c) Selection of deposit control agents

Most of deposit control agents adsorb on the micro-crystals of calcium carbonate and disperse them or reduce their growth rates. As the result, the precipitation or deposition of large size calcium carbonate crystals is prevented.

As the deposition condition of calcium carbonate is different depending on the SI of water, the kind of effective deposit control agent and the required dosage is also different depending on the SI.

To select an appropriate deposit control agent and to determined the required dosage, KURITA has measured the Critical Saturation Index (CSI) of each deposit control agent by changing the dosage. The CSI is the maximum SI which the precipitation of calcium carbonate can be prevented by using some deposit control agent with a specified dosage. Therefore, the agent having higher CSI with the lower dosage is better deposit control agent. Figure 6.31[6)] shows the relationship between the CSI and the dosage of a phosphonate based deposit control agent. The CSI of this agent

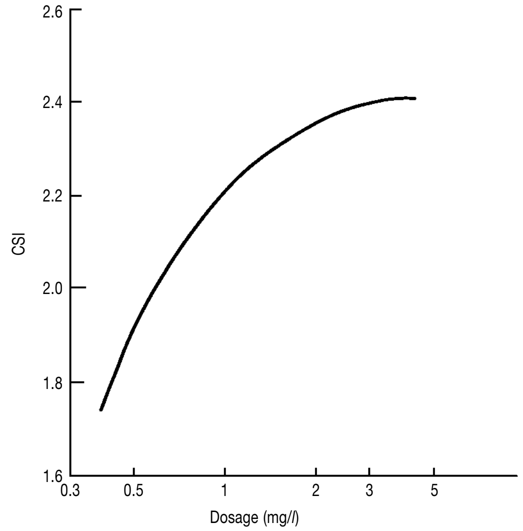


Fig. 6.31 Relationship between the CSI and the dosage of a phosphonate based deposit control agent

increases as the dosage increases. In case of water with the SI of below 2.2, only 1 mg/*l* of this agent can prevent the calcium carbonate precipitation. When the SI of water becomes 2.4, the dosage of 5 mg/*l* is required to prevent the precipitation.

As the same procedure, an appropriate deposit control agent and the required dosage are determined from the SI of water and the CSI of the agent.

(2) Pitch control agents

(a) Pitches and pitch problems

Pitches are classified into the natural sticky resins contained in the wood using as the raw material of pulp and the synthetic viscous substances in recycled waste paper. Table 6.13 shows the classification of pitches found in pulp and paper manufacturing processes.

The adhesion of resin pitch to paper causes various problems, such as paper break, and the formations of pinholes and spots. Many studies reported on the compositions of resin pitches7), 8), the changes of pitch components during the wood-seasoning period9) and the behavior10) of resins in the cooking and bleaching processes.

Recently, as the recycle of waste papers increases, the occurrence of pitch troubles increases because the synthetic resins coming from waste papers adhere on the wires, felts and so on using in the papermaking processes.

(b) Basic concepts of pitch control

To prevent pitch troubles sufficiently, comprehensive measures must be applied by considering the operational conditions of the entire process of pulp and paper production. The use of only pitch control agent is not sufficient to solve pitch problems. Table 6.14 shows the basic concepts and the actual measures for pitch control.

(c) Pitch control method

(i) Newsprint papermaking process

In the news print papermaking process, resins including in GP and TMP, and inks coming from DIP manufacturing process combine together to form the large and sticky particles. Then these particles adhere on the wires, felts, driers, canvases, etc., of papermaking machines, and cause problems, such as web break and spot formation on the products.

As the result, the productivity is greatly decreased and the product quality is lowered.

Table 6.13 Kinds of pitches

Kinds of pitches			Adhesion
Pitches	Natural pitches	Resins from raw wood	Weaker
	Artificial pitches	Synthetic resins and waxes from waste magazines	↓
		Printing inks from waste newspapers	
		Rubber and acrylic resin based adhesives from waste corrugated cardboard	Stronger

Table 6.14 Basic concepts and actual measures for pitch control

Concepts	Measures
Prevention of the entering of pitch into papermaking process	Washing of pulp Separation and removal of pitches
Prevention of pitch aggregation	Use of surfactants and/or polymer dispersants
Dispersion of pitches and the fixing of them as their micro-particles within papers	Use of alum, talc, clay, polymer dispersants, etc.
Removal of pitches from equipments using for papermaking	Cleaning by using kerosene, gasoline, surfactants, etc.

In this system, alum and surfactants are used for preventing the pitch problems. Alum forms the aluminum hydroxide flocs having positive electrical charges and the flocs combine with resin pitches with the negative electrical charges. Then the flocs are fixed on the pulp fibers before the formation of large and sticky pitch particles.

The surfactants permeate into the ink pitches and disperse them as the small and not-sticky particles.

The combined treatment of alum with surfactants sufficiently controls pitch troubles in this process.

(ii) Base board and toilet paper making processes

Pitch problems of the paper machines for the base board of corrugated fiberboard and toilet paper making are caused by sticky synthetic substances composing of the adhesives used for the adhesive tapes including in the waste papers, and used to bind the backs of books. In these processes, the combination of chemical and mechanical treatments is required to solve the pitch problems. Copolymers having hydrophilic and hydrophobic functional groups are used as the pitch control agents. Screens with the mesh of 100 or more are generally used for the mechanical removal of pitches.

(3) Slime control agents

The deposit composed of microorganisms mainly is called "slime". Slime control agents (biocides) are used to prevent slime problems caused by the adhesion of slime.

(a) Microorganisms forming slime

The microorganisms forming slime are bacteria, fungi and yeasts. Bacteria are found in all kinds of slime. Table 6.15 shows typical microorganisms forming slime in pulp and papermaking processes.

(b) Source of microorganisms coming into papermaking processes

The microorganisms come into papermaking processes from everywhere, including the water, the raw materials, the additives and so on. The broke treatment process, the waste paper treatment process, the pulp recovery process and the dissolving tanks of additives, such as dyes and polymers, have higher bacteria counts and become the sources of contamination with microorganisms in the papermaking processes.

(c) Formation of slime and its problems

Microorganisms coming into the papermaking process grow and adhere on the wall surfaces in the system. They also grow on the surfaces of various suspended solids, such as pulps and fillers, and form flocculated slime flocs in locations where they easily adhere, such as the inlet, saveall and white water silo. This slime comes off and causes the fish eyes and web break. Figure 6.32 shows the process of slime formation and its coming off.

The types of slime and the kinds of slime troubles vary depending on the differences of paper quality and papermaking conditions, such as temperature and pH. Table 6.16 shows the relationship among paper qualities, the types of slime

Table 6.15 Kinds of microorganisms forming slime in pulp and papermaking processes

Bacteria	Fungi
Achromobacter gullalus	Aspergillus fumigatus
Aerobacter aerogenes	Fusarium
Aerobacter cloacas	Geotrichum candidum
Bacillus megaterium	Monilia candida
B. subtilis	Penicillium chrysogenum
Beggiatoa	Trichoderma lignorum
Cellulomonas iugis	
Clostridium butyricum	
Desulphovibrio desulphuricans	
Flavobacterium aquatile	
Gallionella	
Leptothrix	
Micrococcus albus	
Micrococcus aquilis	
Micrococcus conglomeratus	
Micrococcus varians	
Paracolabactrum aerogenoides	
Pseudomonas fluorescens	
Sphaerotilus	
Sporocytophaga myxococcoides	

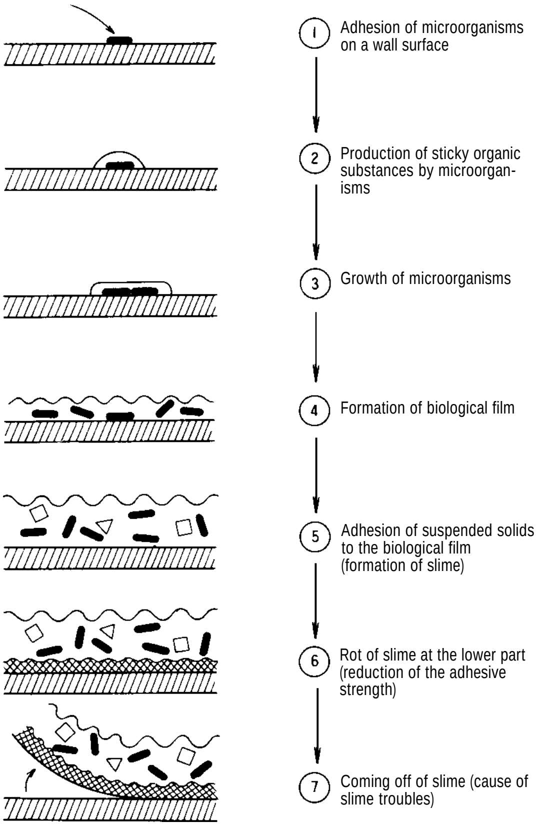


Fig. 6.32 Process of slime formation and its coming off

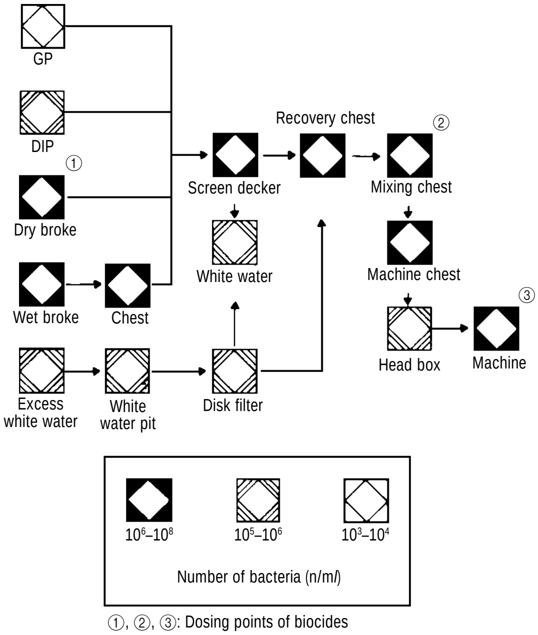


Fig. 6.33 A typical relationship between bacteria accounts and dosing points of biocides in a pulp and paper mill

and the kinds of troubles.

(d) Application of slime control agents

When a slime control agent is applied for a machine, the operational conditions of machine have to be checked and analyzed to confirm the characteristics of machine and the slime adhesion conditions.

(i) Investigation of growth condition of microorganisms

The number of bacteria in each section from the stock preparation to the papermaking processes is measured to confirm the sources of microbial contamination in the system.

Figure 6.33 shows an example of bacteria account in a papermaking mill. The parts where the numbers of bacteria are 10^6 to 10^8/m*l*, become the sources of microbial contamination and should be treated by using suitable slime control agents.

(ii) Selection of slime control agents

Kinds of pulp and additives, water temperature, pH, etc., are confirmed, and a suitable slime control agent should be selected for the aimed system.

(iii) Determination of water balance in the system and the dosage of slime control agent

The retention time of the system should be confirmed from the quantity of inflow water and holding water volume for each process. Then the dosage and injection period of slime control agent have to be determined. In papermaking processes, as the slime control agents are consumed by suspended solids, such as pulp, the agents have to be continuously injected during a specified period to keep the required dosage for obtaining a sufficient biocidal effect.

Figure 6.34 shows a relationship between the injection period and the concentration of a slime control agent.

The water balance is generally determined by adding a tracer in the system and analyzing the change in the concentration.

As the slime adhesion condition varies depending on the operational conditions of the system, especially water temperature, the dosing method of agent has to be changed according to the operational conditions to obtain the stable biocidal effect.

Table 6.16 Relationship among paper qualities, the types of slime and the kinds of slime troubles

Paper quality	Art base paper, coat base paper, printing paper, drawing paper, typewriter paper, kraft paper, white board, machine glazed paper, etc.	Newsprint paper, groundwood paper, etc.	White cardboard, manila board, chipboard, color board, corrugating medium, semi-corrugating board, external liner, internal liner, etc.
Type of machine	• Fourdrinier machine • Combination machine	• Fourdrinier machine • Twin-wire former	• Cylinder machine • Ultra former
Papermaking conditions	• Use of highly purified pulp (less nutrient for microorganism) • Use of various additives (influencing on the quality and quantity of nutrient) • Low or neutral pH of white water	• Use of moderately purified pulp (presence of wood components as nutrient) • Low whitewater pH	• Use of waste paper stock including a plenty of nutrient • Neutral white water pH
Types of slime	• Pink slime • Slime composed of bacteria mainly	• Slime composed of fungi and yeasts mainly • Slime composed of bacteria mainly	• Slime composed of fungi and yeasts mainly, sometimes including bacteria • Slime composed of filamentous bacteria mainly sometimes including general bacteria • Slime composed of bacteria mainly
Kind of slime trouble	• Quality deterioration by spots • Paper break • Increase in the frequency of machine washing	• Paper break • Paper quality deterioration by fish eyes • Increase in the frequency of machine washing	• Paper quality deterioration by fish eyes • Increase in the frequency of machine washing

(iv) Kinds of slime control agents and their effects

Most effective and economic slime control method is the use of slime control agents. Table 6.17 shows the kinds of typical slime control agents using for pulp and paper manufacturing processes.

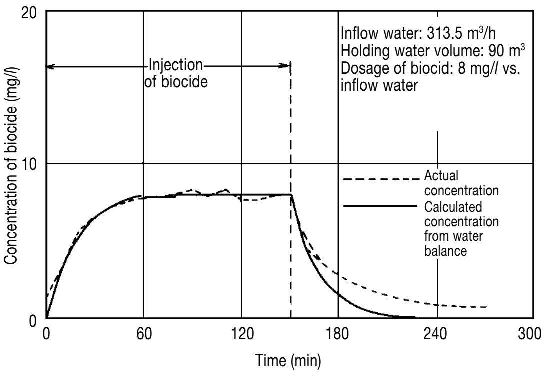


Fig. 6.34 A typical relationship between the injection period and the concentration of a biocide

These chemicals have both the biocidal and biostatic effects, and prevent the slime problems. Figures 6.35 and 6.36 show the biocidal and biostatic effects of slime control agents.

(v) Succession and alternative use of slime control agents

When one kind of biocide is used for a long period of time, the major kind of bacteria producing slime will be changed and the bacteria which resist to the biocide become the major. This is called "succession". Then the initial effectiveness of the biocide is no longer obtainable. To prevent this kind of decrease in biocidal effect, the alternative use of two to three kinds of biocides is generally adopted.

(vi) Monitoring of slime control effect

To obtain a sufficient and stable slime control effect, it is required to periodically measure the number of bacteria in the system. Recently, ATP meter* has become available to measure the num

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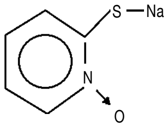
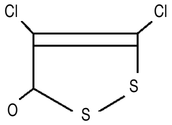
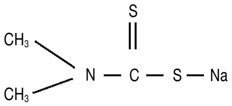
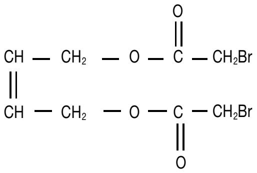
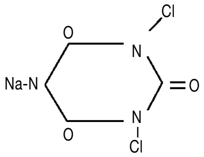
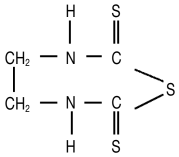
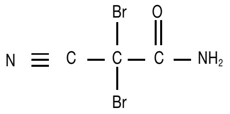
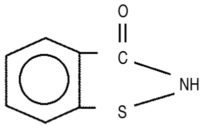
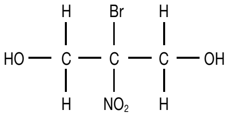
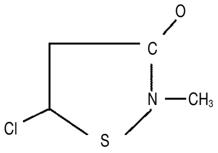
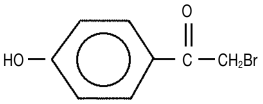
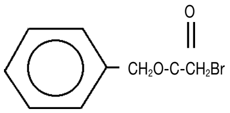
* Meter measuring the number of bacteria by extracting the adenosine triphosphatase (ATP) of bacteria and determining the concentration.

Table 6.17 Typical slime control agents using for pulp and paper-manufacturing processes

Organic nitrogen and sulfur compound	Organic bromine compound	Organic nitrogen compound	Organic sulfur compound
Methylenbisthiocyanate $CH_2(SCN)_2$	Methylenbisbromoacetate $CH_2(OCOCH_2Br)_2$	2-Pyridinethiol-1-oxide-Na-salt 	5-Oxy-3,4-dichloro-1,2-dithiole 
Na-dimethyldithiocarbamate 	Bis-1,4-bromoacetoxy-2-butene 	Na-dichloroisocyanurate 	
Ethylenetiuram-monosulfide 	2,2-Dibromo-3-nitrilopropionamide  $N \equiv C-\overset{Br}{\underset{Br}{C}}-\overset{O}{\overset{\Vert}{C}}-NH_2$		
1,2-Benzoisothiazoline-3-one 	2-Bromo-2-nitropropane-1,3-diol  $HO-\overset{H}{\underset{H}{C}}-\overset{Br}{\underset{NO_2}{C}}-\overset{H}{\underset{H}{C}}-OH$		
5-Chloro-2-methyl-4-isothiazoline-3-one 	2-Bromo-4'-hydroxyacetophenone 		
	Benzyl bromoacetate 		

ber of bacteria within a short period of time.

It is desirable to carry out the periodic biocidal and biostatic tests using the white water and slurry from the system in order to confirm the effect of the biocide or to select the optimum biocide if it is required.

(vii) Countermeasures for neutral papermaking process

The number of machines for neutral papermaking of high quality papers, such as art paper and coat paper, has been increased in Japan. In this process, the operational conditions, such as the neutral pH, the presence of starch from the coat broke and the high recovery rate of water, are appropriate for the growth of microorganisms. Therefore, the number of bacteria in the system easily rises to 10^8/m*l* and causes severer slime troubles comparing with acidic papermaking pro-

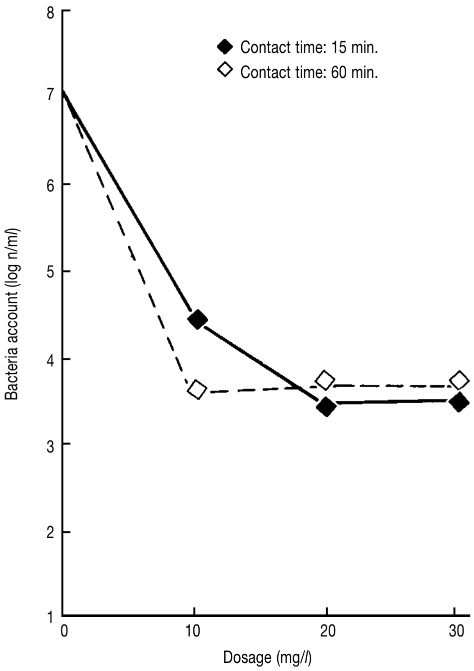


Fig. 6.35 Biocidal effect of an organic bromine compound in a white water

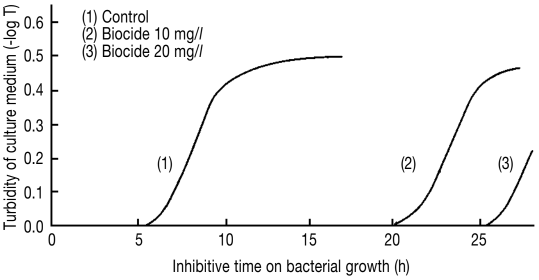


Fig. 6.36 Biostatic effect of an organic nitrogen and sulfer compound in a white water

cess as shown in Table 6.18.

Therefore, the following cares must be paid for the application of slime control agents in the neutral papermaking process.

① Apply a biocide to reduce the number of bacteria.

② Use a biostatic chemical together with the biocide to maintain the lower level of bacterial number.

③ Increase the dosing frequency of slime control agents and shorten the injection period. At the same time, shorten the dosing intervals.

Table 6.18 Comparison of bacterial growth conditions between acidic and neutral papermaking processes

Process	Acidic papermaking	Neutral papermaking
White water pH	4–7	7–8
Number of bacteria (n/ml)	10^4–10^7	10^7–10^8
Required period for bacterial growth without biocide (h)	3–12	0.5–3.0

In fact, a treatment consisting of 1 hour of chemical injection and 2 hours of the injection stoppage is better than a treatment of 4 hours of the injection and 8 hours of no injection. Slime control agents formulating biocides with biostatic agents have been developed for neutral papermaking processes.

(viii) Safety measures for the use of slime control agents

Recently, slime control agents with the lower toxicities have been in the market, however, these biocides are essentially toxic for human being. Therefore, it is necessary to take suitable precautions for storing, handling and using of these agents. The protective clothes, goggles and rubber gloves have to be worn for handling them. For selecting a suitable biocide, it is necessary to be careful about not only the acute toxicity but also the skin irritation, the chronic toxicity, biodegradability, the influence on activated sludge in wastewater treatment plant and so on.

In addition, the use and handling of slime control agents are restricted by various laws and regulations in each country. Therefore, all of these aspects must be considered prior to using these agents.

(4) The other slime control methods

(a) Washing of contaminated parts in each process

For each part, such as chests, pipings and tanks of additives in pulping, conditioning and papermaking processes, the amount of slime and the number of bacteria should be periodically checked and measured. Then the contaminated parts with microorganisms have to be washed to prevent the slime troubles.

(b) Design changing of processes

Anaerobic bacteria and fungi are easily grown in the dead spaces of the raw material chest, piping and so on. These bacteria and fungi become a source of microbial contamination of various processes. These areas soon become contaminated even after being washed. Also, even if a slime control agent is added, it hardly reaches these dead spaces. Therefore, it is necessary to improve the structure to eliminate or minimize the dead spaces, and to promote the smooth water flow.

6.4.5 Preservatives

(1) Use of starch and its putrefaction problems

Various starches are used as surface sizing agents, binders for coating, adhesives for paperboard and so on in papermaking processes.

Figure 6.37 shows the preparation process of starch glue. In most cases, starch solution is heated to make the glue. The putrefaction of starch occurs in the starch slurry before the cooking and in the glue liquid after the cooking.

When starch rots, the pH of the glue liquid, the viscosity of the paste and its adhesiveness decrease. Even if the bulk of glue has not rotten, the glue attached to the tank wall and dead spaces in the pipings where the glue liquid is not frequently replaced by new one, has often rotten locally.

The rotten glue causes the clogging of strainers and nozzles, and deposit problems, such as the fish eyes of papers, as shown in Table 6.19.

(2) Starch putrefaction and its prevention[11)]

(a) Putrefaction

When starch is left without any special care, it may be soon acidified. After the number of bacteria in the starch has increased, the pH will start to drop, and later a rotten odor will be released. This phenomenon differs from the growth of slime in the papermaking system, and will occur under anaerobic and high temperature (50 to 60° C) conditions.

Table 6.19 Troubles caused by the putrefaction of starch

- Clogging of strainers and nozzles
- Fish eyes → Deterioration of paper quality and increase of broke
- Generation of unpleasant smell → Deterioration of working environment
- Decrease of adhesivity of glue → Deterioration of paper quality
- Disposal of rotten glue → Increase in wastewater treatment cost and reduction in the efficiency of wastewater treatment plant by bulking
- Increase of cleaning and washing of apparatus → Increase in the maintenance cost

⇓

Reduction in the advantages of starch glue

(b) Factors influencing on the effects of preservatives

Generally, preservatives are added into the starch to prevent the putrefaction. The biocides using as slime control agents and antimicrobial agents are used as the preservatives. Factors influencing on the effect of preservatives are as follows.

(i) Kinds of starch

Tapioca starch is more perishable than corn starch. Therefore, a higher dosage of preservative is required for tapioca starch. Oxidized starch is less perishable than ordinary starch. Recently, the use of house-made starch glue has been increased in pulp and paper mills. The house-made starch glue easily rots because the starch processing is often insufficient.

(ii) Temperature

Starch slurry is kept at room temperature and in most cases the glue liquid temperature is 50 to 60° C. Generally, preservatives show the stronger biocidal effects as the temperature rises. Therefore, even a smaller dosage of preservative shows

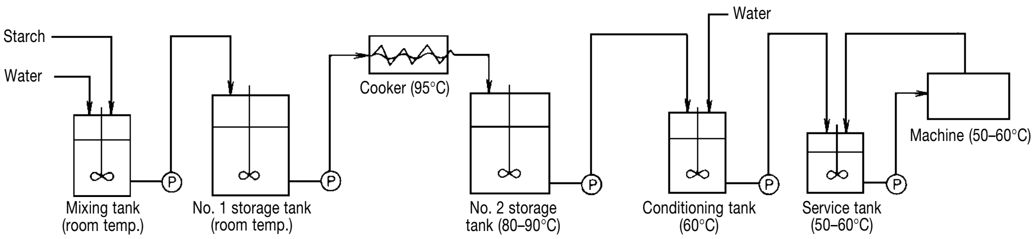


Fig. 6.37 Typical preparation process of starch glue

the sufficient result in the glue liquid.

(iii) pH

The pH of the glue liquid is generally neutral in a system where the glue is used as the surface sizing agent or adhesive for paperboard, but the pH is 9 to 11 in a system where the glue is used as the coating liquid. As an appropriate pH range of each preservative is different, the pH of glue is very important factor for selecting suitable preservatives.

(iv) Dosing point of preservatives

Generally, preservatives are separately dosed into the mixing tanks of starch and the conditioning tank of the glue. When a preservative is added into the mixing tank of the starch and it is desired to maintain the antiseptic effect after heating the starch slurry to make the glue, a preservative having the sufficient heat stability must be selected.

(v) Resistance of microorganisms

When a preservative has been used for a long time in a system including much nutrient, such as a starch glue conditioning system, bacteria having the resistance against the preservative becomes the dominant bacteria and the effectiveness of the preservative will be decreased.

To avoid the development of the resistance of bacteria, the alternative use of several kinds of preservatives must be required.

(c) Case study of using preservative

Figure 6.38 shows the effect of a preservative adding to the starch glue liquid used as the surface-sizing agent. Before using the preservative, the pH of the glue decreased to around 5 and the number of bacteria reached around $10^7/\mathrm{m}l$. After 50 mg/l of the preservative was added to the glue, the pH rose to around 8 and the number of bacteria decreased to $10^5/\mathrm{m}l$ or less.

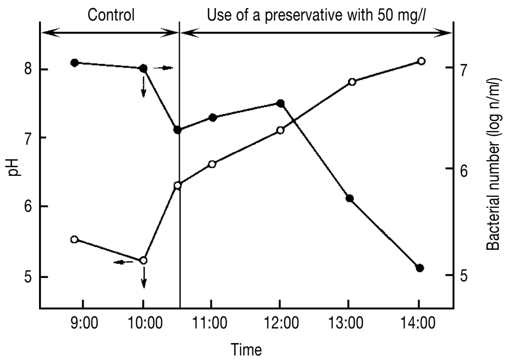


Fig. 6.38 Effect of a preservative on a starch glue liquid in the storage tank

(d) The other uses of preservatives

Besides the starch glue, various synthetic substances, such as paper-strengthen agents, retention aids, latexes and dispersants, are also rotted by the microorganism growth in papermaking processes. In order to prevent these problems, preservatives are generally used.

6.4.6 The Other Additives for Deposit Control

(1) Antifoaming agents

(a) Foaming and deposit formation

Various organic chemicals are used in the papermaking processes and they easily cause foaming.

Especially, sizing agents, paper strengthen agents and internal sizing agents often cause the foaming.

When foaming occurs in the stock conditioning process and the papermaking process, particularly in the wire part, sizing agents, paper strengthen agents, starch, pitches, fine pulp fibers and fillers are adsorbed on the surfaces of foams. Foams on the water surface will disappear in the course of time, but the substances adsorbed on the foams will remain as the scum on the water surface. This scum is generally sticky and its surface is hydrophobic. Therefore, the scum may adhere to the wall surfaces with a low water flow rate in the system. Once this scum adheres to the wall surface, it becomes a hotbed for microorganisms and causes slime and deposit problems. When the amounts of these deposits become larger, they may come off the wall surfaces by impacts, such as a change in the water flow rate. The deposits coming off cause the fish eyes and spots on the papers. Figure 6.39[4)] shows this process of foaming, scum formation and its coming off.

(b) Prevention of scum and deposit formation by foaming

To prevent the formation of scum and deposits caused by foaming, it is important to reduce the suspended solids in white water by controlling the papermaking conditions to fix the sizing agent, paper strengthen agents, starch, fine pulp fibers and fillers on the pulp fibers. Antifoaming agents are also used to minimize the scum and deposit formation by foaming.

The following must be carefully noted for applying antifoaming agents:

① Determination of the cause of foaming,

② Selection of an appropriate antifoaming agent according to the foaming condition,

③ Selection of an antifoaming agent having no

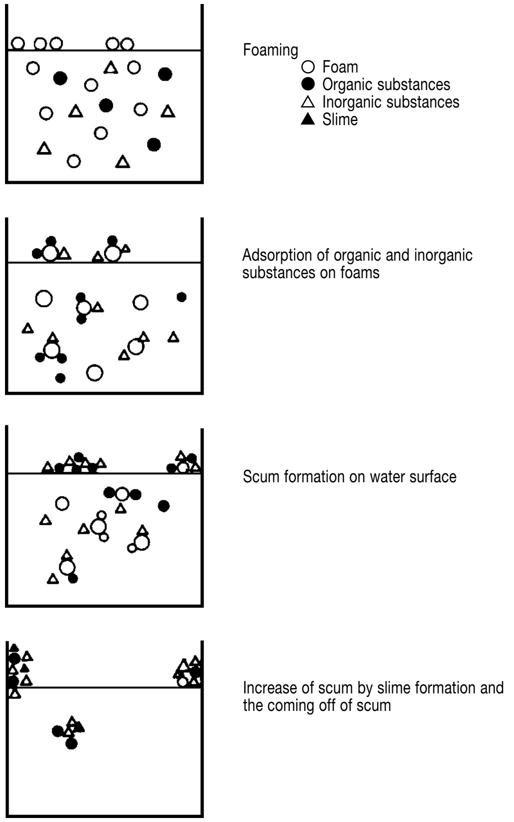


Fig. 6.39 Scum formation by foaming and the coming off of scum

bad-influence on paper quality, especially on the sizing effect,

④ Selection of an antifoaming agent having the degassing ability for a closed-type inlet.

(2) Size-fixing agents

(a) Problems caused by unfixed sizing agents

Since both rosin sizing agents and neutral sizing agents have the surface-activities, most of them cause foaming in water.

Recently, the fixing rate of sizing agent becomes worse due to the higher temperature in papermaking process and worse water quality by water recycling. The remaining sizing agent which is not fixed fiber, becomes the main cause of the foaming problems. As the fixing rate of neutral sizing agent is particularly bad, the unfixed sizing agent cause not only deposit problems in the wire parts but also the contamination of the smoother and press roll in the press part.

(b) Reduction in the amount of unfixed sizing agents

A retention aid having size fixing effect should be used to prevent the deposits caused by unfixed sizing agents.

Table 6.20[4)] shows the size-fixing effect of a retention aid. The use of this retention aid increases the Stöckight sizing degree. It means the reduction in the amount of unfixed sizing agent in the white water.

Thus the deposit problems caused by unfixed sizing agents are minimized by using a suitable retention aid.

6.4.7 Total Treatment for Deposit Control

The compositions of deposits differ depending on the operational conditions of papermaking process, the quality of the product and so on. Therefore, an appropriate measure for the deposit control has to be selected according to the composition of deposits, the operational conditions and so on. Table 6.21 shows the typical relationships among paper qualities, the causes of deposits and the kinds of adequate additives using for deposit control.

To effectively prevent the deposit problems by using those chemicals and, to improve the productivity and the product quality, the followings should be carried out.

① Analysis for determing the compositions of deposits and spots on the product should be done to confirm the substances causing the deposit problems.

② Water analysis, the measurement of zeta potential of suspended solids in white water, the measurement of the bacterial number and so on should be done to determine the causes of the deposit formation.

③ Appropriate additives for deposit control are selected on the basis of the results of ①and ② then the dosages and the dosing points of additives have to be determined.

Table 6.20 Size-fixing effect of a retention aid

Dosage of retention aid (% vs. pulp)	Gramage (g/m^2)	Stöckight sizing degree (sec)	Ash content of paper (%)
0	76.1	6.7	9.2
0.01	76.1	7.6	14.6
0.02	76.6	10.0	15.3
0.03	76.8	11.2	15.5

Table 6.21 Relationship among paper qualities, the causes of deposits and additives for deposit control

Paper mill	Paper quality	Cause of deposits	Additives for deposit control
A	Coat base paper	Growth of fungi Adhesion of pitch Adhesion of starch for sizing	Slime control agent Pitch control agent Antifoaming agent
B	High quality printing paper	Adhesion of sizing agent Growth of slime	Antifoaming agent Slime control agent
C	High quality printing paper	Adhesion of neutral sizing agent	Size-fixing agent Antifoaming agent
D	High quality printing paper	Foaming by surface sizing agent Rotting of the sizing agent	Antifoaming agent Preservative
E	Coat base paper	Formation of scum with foaming caused by sizing agent Growth of slime	Antifoaming agent Size-fixing agent Slime control agent
F	High quality printing paper	Formation of scum with foaming caused by sizing agent	Antifoaming agent Size-fixing agent

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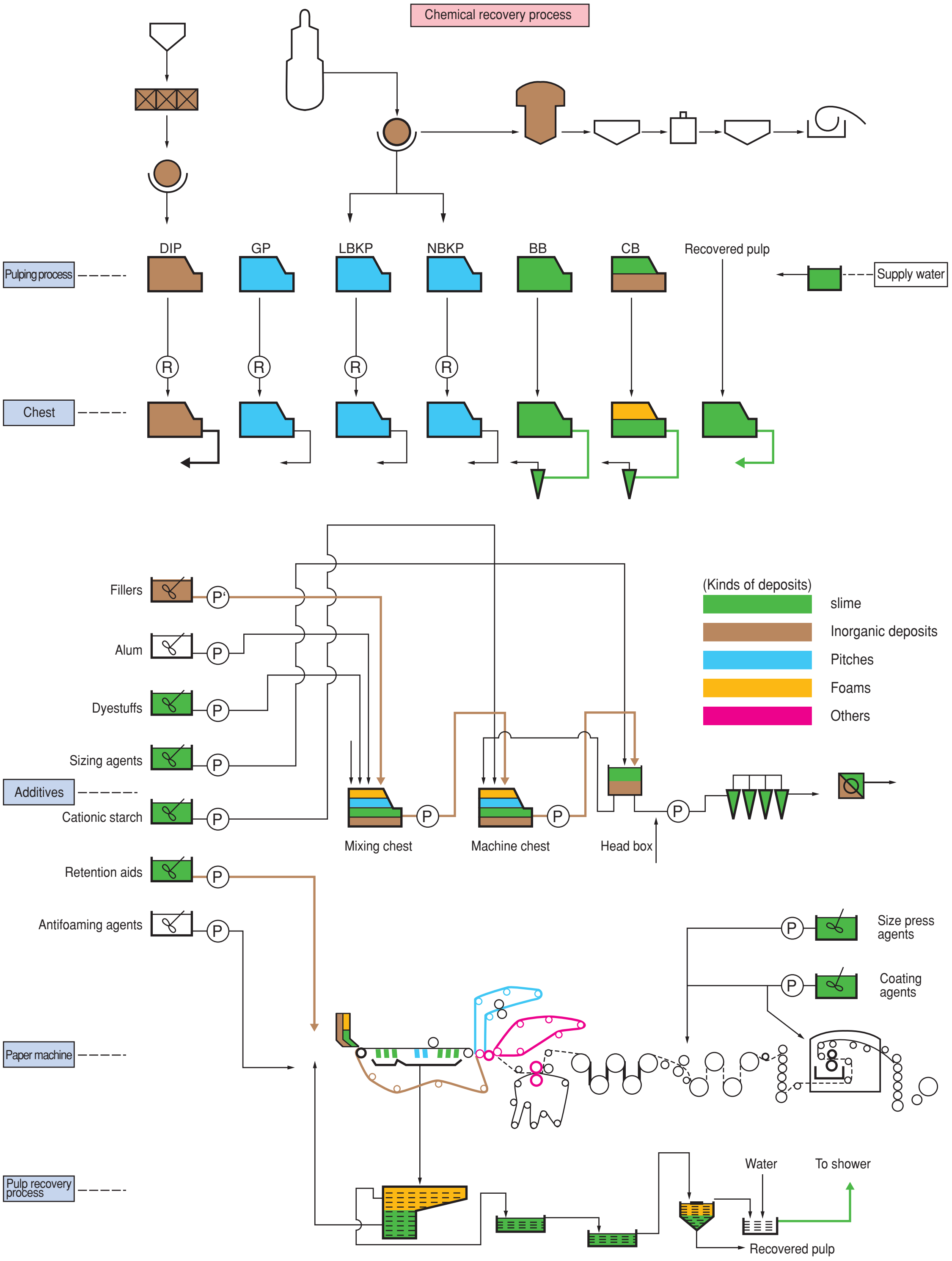


Fig. 6.30 Places of deposit generation and the kinds of deposits

7. Chemicals for Petroleum Refining and Petrochemical Processes

7.1 Kinds and Properties of Crude Oils

Crude oils are generally viscous and darkbrown liquids. The main components are liquid hydrocarbons with the carbon numbers ranging between 3 to 40. They also include petroleum gas and solid components, such as solid paraffins and asphalt. Their compositions and properties widely vary with the areas of production.

Crude oils are generally classified according to their compositions. Typical classifications of crude oils are as follows:

① By the content of light fractions,
   Light crude: higher content of light fractions
   Heavy crude: lower content of light fractions,
② By the sulfur content,
   Sweet crude: lower sulfur content
   Sour crude: higher sulfur content,
③ By the kinds of main hydrocarbons,
   Paraffin-base crude
   Naphthene-base crude
   Mixed-base crude.

As Japan has extremely poor crude oil production, most of crude oils are imported from the Middle East countries, Indonesia, China and so on. The amount of imported crude oils to Japan was approximately 258 million k*l* in 1996.

Table 7.1 shows the properties of main crude oils imported to Japan.

Table 7.1 (1) Properties of typical crude oils imported to Japan (Data of Petroleum Association of Japan)

	Country	Saudi Arabia				Neutral zone	Iran	
	Crude Oil	Arabian light	Arabian heavy	Arabian medium	Arabian extra-light (Berni)	Khafji	Iranian light	Iranian heavy
Properties of crude oil	Specific gravity (15/4°C)	0.852	0.887	0.8712	0.8412	0.884	0.855	0.871
	A.P.I. degree	33.5	27.7	30.8	36.6	28.5	33.9	31.5
	Vapor pressure (kg/cm^2, 37.8°C)	0.35	–	0.51	0.165	0.535	0.52	–
	Viscosity (cSt, 30°C)	6.90	22.4	13.96	4.252 (37.8°C)	–	4.7 (50°C)	6.5 (50°C)
	Pour point (°C)	-15 >	-20 >	-35 >	–	-35	-15 >	-12.5
	Wax (W%)	–	2.2	–	–	2.7	6	–
	Sulfur (W%)	1.72	2.70	2.50	1.16	2.85	1.40	1.71
	Nitrogen (W%)	0.09	–	0.13	–	0.15	–	0.22
	Carbon residue (W%)	3.1	7.2	5.72	–	8.04	3.4	5.20
	Water and sediment (V%)	0.05	0.3	0.2	0.05	Trace	–	0.15
	Water (V%)	0.05	0.2	0.1	Trace	Trace	–	0.1 >
	Salts (W%)	3	0.0110	0.001	–	0.0026	–	0.0039
	Heavy metals (mg/*l*)							
	V	12	–	42	–	55	–	63
	Ni	4	–	12	–	16	–	16

Table 7.1 (2) Properties of typical crude oils imported to Japan (Data of Petroleum Association of Japan)

	Country	U.A.E.	Indonesia			Brunei	Mexico	China
	Crude Oil	Murban	Sumatra light	Duri	Klamono	Light seria	Maya	Daqing
Properties of crude oil	Specific gravity (15/4°C)	0.828	0.8500	0.925	0.942	0.851	0.9224	0.859
	A.P.I. degree	39.2	34.9	22.0	18.7	34.7	21.8	33.1
	Vapor pressure (kg/cm^2, 37.8°C)	0.306	0.18	–	0.01	0.35	0.35	0.09
	Viscosity (cSt, 30°C)	2.5	11.3 (50°C)	14.5 (50°C)	34.7	2.2 (50°C)	123	19.0 (50°C)
	Pour point (°C)	-30	+35	+10	-15.0	+ 5	-15	+32.5
	Wax (W%)	–	14.0	9	–	3.1	2.3	19.5
	Sulfur (W%)	0.80	0.10	0.25	0.97	0.06	3.4	0.11
	Nitrogen (W%)	0.04	0.09	–	–	–	0.3	0.15
	Carbon residue (W%)	1.40	2.78	7.0	5.98	0.3	11.8	2.4
	Water and sediment (V%)	0.05	0.10	–	–	–	0.4	0.2
	Water (V%)	Trace	Trace	0.4	–	–	0.3	0.2
	Salts (W%)	42	0.001	10 mg/*l*	–	–	0.005	0.0005
	Heavy metals (mg/*l*)							
	V	–	3	–	–	–	250	1 >
	Ni	–	13	–	–	–	50	3

7.2 Outline of Production Processes

7.2.1 Petroleum Refining Processes

The outlines of the refining processes are shown in Figures 7.1 and 7.2(p.7-21).

Crude oil is unloaded from a tanker into crude oil tanks where water is precipitated and removed by settling as much as possible. The crude oil is charged to desalters through several heat exchangers.

Salts and metallic impurities in the crude oil are removed by using the desalters because they reduce the heat transfer efficiencies of heat exchangers and furnaces by their scaling, and corrode the atmospheric distillation plant and so on. A desalted crude oil is heated further through several heat exchangers and furnaces. Then it is fed into a distillation unit. In the unit, the crude oil is separated into gas, naphtha, gas oil and residual oil by the differences between their boiling points.

The gas is divided into LPG and off gas in a LPG recovery plant. After removing hydrogen sulfide through a washing systems, the LPG is marketed and the off gas is used as the site-use fuel.

The light naphtha is desulfurized by a hydrodesulfurization process and blended with a gasoline.

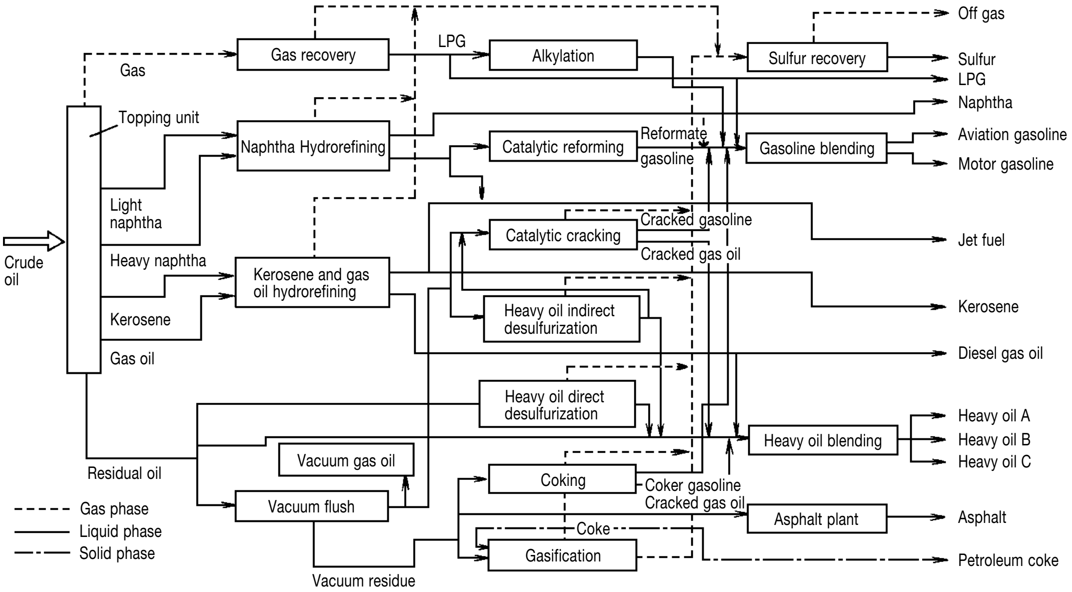
The heavy naphtha is treated by a hydrodesulfurization plant to remove the sulfur compounds and processed in catalytic reforming-units to blended with a high octane gasoline.

The kerosene and gas oil are also treated by a hydrodesulfurization plant to remove the sulfur compounds. The kerosene is marketed as a product or mixed with a refined naphtha to prepare a jet fuel. The gas oil is sold as a diesel fuel.

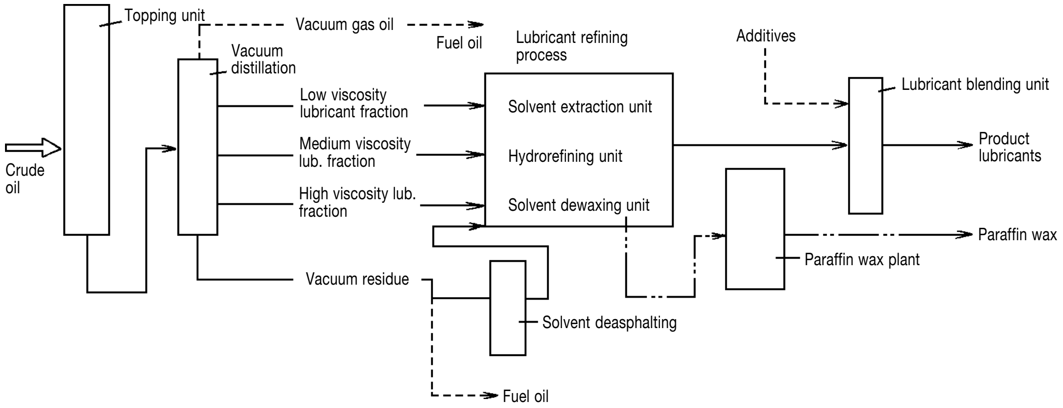
The residual oil is used as a heavy fuel oil without further treatment, or desulfurized by a vacuum-gas-oil-hydro-desulfurization unit or an atmospheric-residue-hydro-desulfurization unit to blend with a commercial heavy fuel oil. Sometimes, the vacuum gas oil is cracked by a catalytic cracking unit to yield a cracked gasoline of high octane number. The cracked gasoline is blended with a reformate or the other fractions to produce a commercial gasoline.

Heavy fuel oils are prepared by mixing heavy oil fractions from the crude unit and vacuum unit, gas oil fractions from the crude unit and the catalytic cracking unit, and the desulfurized heavy oil from the desulfurization unit.

The production of lubricating oils from residual



a) Petroleum refining process



b) Lubricant production process

Fig. 7.1 Typical petroleum refining processes

oils is performed as follows. Three or four fractions with different viscosities from the vacuum distillation unit are refined through a solvent extraction unit, a hydrorefining unit and a solvent dewaxing unit. Commercial lubricating oils are manufactured by blending these refined oils to obtain their required viscosities. Additives are formulated if it is required.

7.2.2 Ethylene and Propylene Production Processes

An example of ethylene production process is shown in Figure 7.3.

The process consists of three sections of the thermal cracking, cooling and fractionation. Ethylene is produced by cracking naphtha, sometimes gas oil or natural gas. Since this cracking reaction is endothermic, it is performed in coexistence with steam, called "Dilution Steam", using as a heat source and a retarder of polymerization.

The thermal cracking is usually carried out under the conditions at the naphtha/steam ratio of 1 to 2/1, the temperature of about 850° C and the retention time in the furnace of less than 0.5 second.

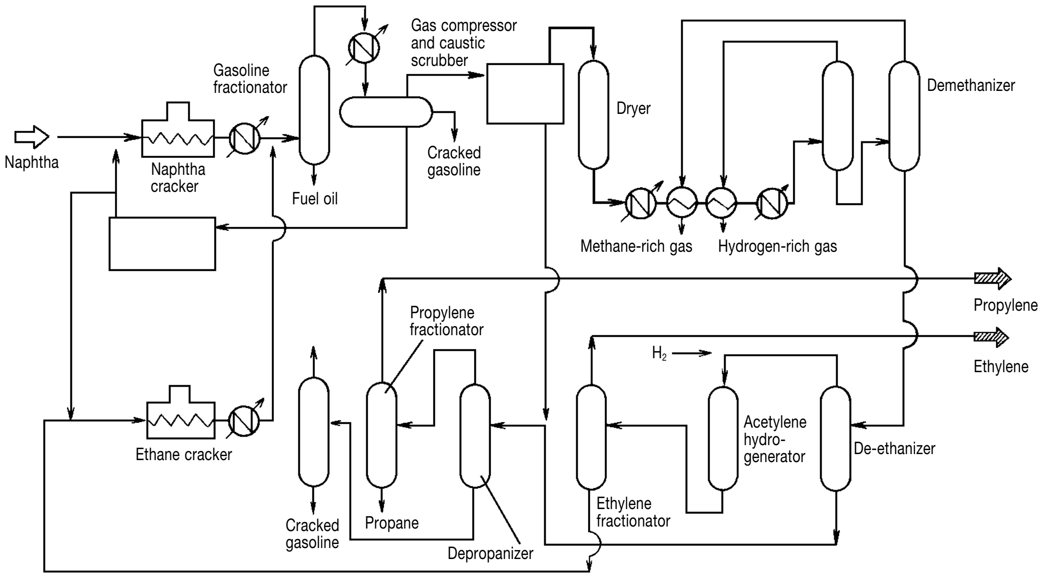


Fig. 7.3 Flow diagram of an ethylene and propylene production process (Lumus method)

The cracked gas from the furnace is quenched to prevent secondary reactions and to separate gasoline, etc. As hydrocarbons with four or more carbon numbers still remain in the gas, it is liquefied by compression to separate those hydrocarbons. The compressing pressure is about 30 to 40 kg/cm^2. In this process, acidic gases, such as hydrogen sulfide and carbon dioxide, are removed by caustic washing and amine scrubbing.

The purified gas is dried by using a synthetic zeolite, etc., and separated into each product by a cryogenic separation.

The yields of ethylene and propylene are 20 to 25% and about 15% respectively. Cracked gasoline, butane and butadiene are also obtained.

7.3 Chemicals for Petroleum Refining Processes

7.3.1 Desalting of Crude Oils and Demulsifiers

(1) Impurities in crude oils

Crude oils include various kinds of impurities. They are divided into oil soluble and oil insoluble substances. The former includes sulfur, nitrogen, organo-metallic compounds and so on. The latter mainly consists of water, salts and sludge. The oil soluble impurities are relatively difficult to remove. The oil insoluble impurities are easily to remove but cause corrosion problems in distillation towers, etc. Therefore, they have to be removed before the crude oil processing.

Water content in the crude oils imported to Japan is generally 200 to 20,000 mg/*l*. The water is dispersed into crude oils as fine particles forming a stable water-in-oil type emulsion. In most cases, salts in crude oils are present in the water droplets and their concentration sometimes reaches around ten percent.

Most of the salts is sodium chloride and the others are magnesium and calcium chlorides. These chlorides deposit in the heat exchanger tubes and sometimes clog them in the crude oil preheating process before the distillation towers. In addition, they are thermally decomposed and yield hydrochloric acid which causes severe corrosion in the distillation tower and the downstream units. Magnesium chloride particularly yields the acid at relatively low temperature.1)

(2) Desalting process

Among various desalting methods, electrical desalting processes are generally employed. In the electrical desalter, water is mixed with a crude oil and separated again in a high voltage electrical field. In this process, a several mg/*l* of demulsifier is commonly used to promote the water and oil separation.

The flow sheet of a crude oil desalting process is shown in Figure 7.4. After dosing a demulsifier into a crude oil from the suction side of a crude oil charge pump, the crude oil is agitated by the pump

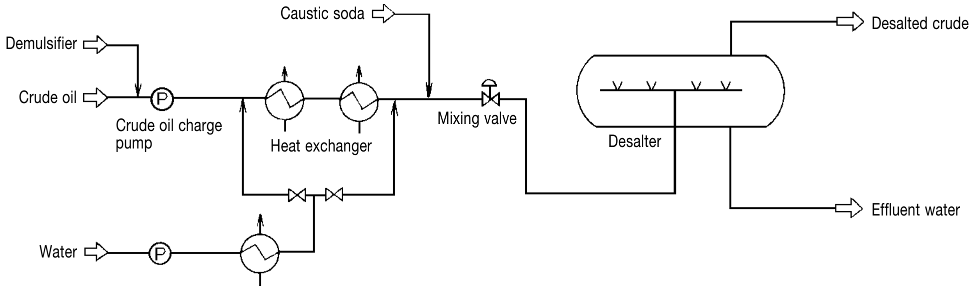


Fig. 7.4 Flow sheet of a crude oil desalting process

impellers and then preheated in the heat exchangers. The wash water of about five percent against the crude oil is injected and they are emulsified through the mixing valve to send to the desalter. The emulsifying degree is controlled by adjusting the opening of the valve and monitored by measuring the pressure difference between the inlet and outlet of the valve. In the electrical desalter with the pressure of 5 to 10 kg/cm^2 and the temperature of 110 to 140° C, the alternating current electric field of 10,000 to 30,000 volts applies for the emulsion to aggregate the water droplets dispersed in the crude oil. Then the aggregated water drops gravitationally sink to the bottom.

Figure 7.5[2)] shows a schematic state of water separation in an electrical desalter. The separated water is continuously discharged into a wastewater treatment plant. When the pH of discharged water becomes acidic, caustic soda is usually dosed into the wash water to prevent the corrosion of desalter. Depending on a required desalting rate, a single or double stage desalting is employed. The desalting rate of a single stage desalting is generally 70% to 95%.

Though the main purposes of desalting are the desalting and the dehydration of crude oil, it also removes inorganic micro-particles in the crude oil. The removal of the inorganic micro-particles is effective to prevent the fouling of heat exchangers in the crude oil preheating lines and heavy oil direct desulfurization unit, and to keep the efficiency of catalyst in fluid catalytic cracking units.

(3) Appropriate conditions for the desalting

The following conditions are required to appropriately carry out the desalting of crude oils.

(a) Mixing of crude oil with wash water

A key point of desalting is an appropriate mixing condition of a crude oil with the wash water to obtain a sufficient desalting rate. The appropriate condition varies depending on the properties of crude oils. For increasing the desalting efficiency, a relatively strong mixing is better for light crude oils and a relatively weak mixing is better for heavy crude oils.

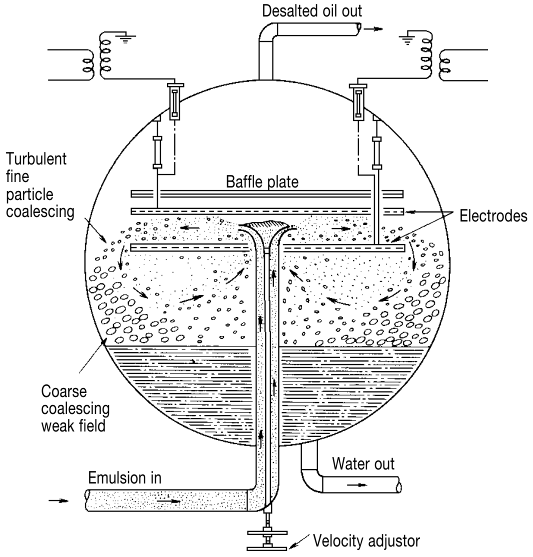


Fig. 7.5 Water separation in an electrical desalter

(b) Heating

Heating promotes the demulsification and the formation of large water droplets from the emulsion of crude oil with water. Heating also lowers the viscosity of crude oil and promotes the separation of water from crude oil.

(c) Electric field

A micro-droplet of water wrapped with stable oil film is polarized by applying an electric field and pulled by the both electrodes of desalter. As the result, the oil film is broken and water droplets aggregate to form a large water drop. The larger electric field, the better for the demulsification.

(d) Retention time

The water droplets aggregated in the electric field gradually grow and are gravitationally separated from the oil. Therefore, a sufficient retention time in a desalter is required for an efficient water and oil separation. The heavier crude oil requires the longer retention time in the desalter.

(e) Use of demulsifiers

Generally, surface-active agents are used as demulsifiers for crude oil desalting. The demulsifiers adsorb on the oil films surrounding water droplets and break the oil films. Then water droplets aggregate to form large water drops enough to gravitationally separate them from crude oil.

Nonionic surfactants having both of lipophilic and hydrophilic groups are mainly used as demulsifiers. Typical ones are polyglycol copolymers, polyglycol esters and phenol resin derivatives.

The stability of emulsified water droplets varies depending on the properties of crude oils.

Particularly, the properties of emulsions are widely different between paraffin-rich and asphaltene-rich ones. It is ideal to employ the best demulsifier for each crude oil, but it is difficult when the mixture of various kinds of crude oils is treated or the kinds of crude oils are frequently changed. Therefore, the mixtures of surface-active agents having different properties are generally used as demulsifiers effective for various kinds of crude oils.

Generally, demulsifiers are diluted with an organic solvent and injected into crude oils.

(4) Treatment of crude oils with difficulties in the desalting

It was mentioned above that the stability of emulsions differs depending on the kinds of crude oils. For example, Maya crude produced in Mexico is difficult to desalt because of the high carbon residue content and the stable emulsification.

Such crude oils are usually treated by mixing with the other crude oils to minimize the bad influence on the desalting.

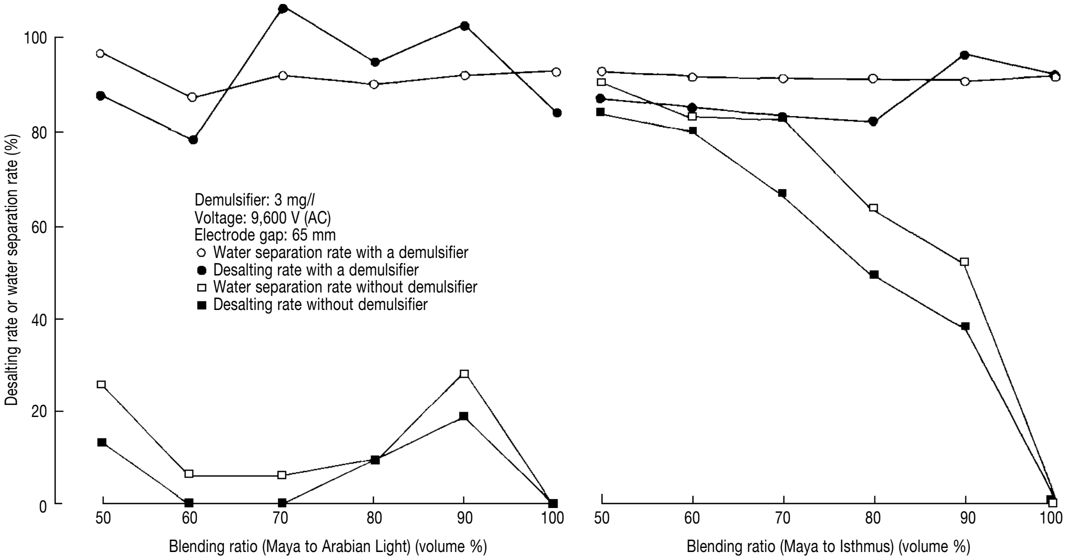
Figure 7.6 shows the desalting rates and the water separation rates in an electric desalter, when Maya crude is mixed with Arabian light or Isthumus crude. In the case of Arabian light mixing, the desalting is almost impossible without demulsifier. While in the case of Isthumus crude, the desalting and water separation are sufficiently carried out without demulsifier at their mixing rate of around 1 by 1. The use of a suitable demulsifier shows the sufficient desalting and water separation effects on the both mixed crude oils.

(5) Test methods for crude oil desalting

(a) Settling test

The settling test is a simple and convenient method for the crude oil desalting.

Three to ten percent of water is added to a crude



(a) Blending with Arabian Light crude **(b) Blending with Isthmus crude**

Fig. 7.6 Influence of Maya crude blending ratio to the other crudes on the desalting effect

oil to form the emulsion. Then a demulsifier is dosed into the emulsion and mixed. The sample is kept at a specified temperature and the amount of separated water is periodically measured.

This test gives useful informations such as the comparative effects of different demulsifiers with their different dosages and the water separating properties of crudes. However, in this test, the required dosages of demulsifiers become higher than those in actual disalters because of the difference in the desalting conditions.

(b) Electric desalting test

In this test, an electric field is applied for an emulsion prepared by mixing water with a crude oil. Then the amount of separated water and the desalting rate are measured. During the test, the sample is continuously stirred by using a mixer.

Generally, this test is carried out under an ambient temperature and an atmospheric pressure. However, using some type of testing apparatus, the test under an elevated temperature and pressure can be carried out.

Photograph 7.1 (p.7-23) shows the Electric Dehydration and Desalting Apparatus (EDDA) applying the electric field.

This is a potable type and easily used in the sites.

7.3.2 Fouling in Petroleum Refining and Petrochemical Processes, and Antifouling Agents

(1) Kinds and properties of fouling

The foulings found in petroleum refining and petrochemical processes are generally classified into following six categories:

① Deposition of asphaltene in the preheaters of topping units, vacuum distillation units and fluid catalytic cracking units (FCC) or the residual oil lines of topping units and vacuum distillation units,

② Fouling with polymers formed by the oxidation-polymerization of unsaturated hydrocarbons in the treating units of naphtha, kerosene or gas oils, especially in hydro-desulfurization units and the preheater trains of FCC units,

③ Fouling with polymers formed by the thermal polymerization of various monomers in their production processes, such as depropanizers in ethylene plants, acrylonitrile plants and ethylene dichloride plants,

④ Coking substance which is a kind of carbon formed by the oxidizing and dehydration reactions of organic polymers and rubber like materials at a high temperature in the naphtha crackers of ethylene plant, the ethylene dichloride thermal crackers of vinyl chloride monomer plants, the furnaces of crude units and vacuum units, delayed cokers, etc.,

⑤ Inorganic matters, such as salts included in crude oils, and corrosion products formed in crude oil refining processes or petrochemical plants,

⑥ Sludge formed by an incompatibility when different kinds of crude oils and distillates are mixed together.

(2) Troubles caused by fouling

Places subjected by fouling in petroleum refining and petrochemical plants are divided into following two categories:

① Transfer lines of the process fluids such as pipe lines, pumps and strainers,

② Heat transfer sections for process fluids such as heat exchangers, reboilers, furnaces, strippers and fractionating columns.

Foulings in those equipments reduce the flow rates of process fluids and the heat transfer efficiencies. They sometimes cause the cloggings of pipings and heat exchanger tubes. As the result, the following problems are caused:

① Reduction of a process productivity due to the reduction in the flow of a process fluid,

② Occurrence of unscheduled process shutdown by the clogging of pipings, heat exchangers, etc.,

③ Fluctuation of process operation conditions and a difficulty of the operation control,

④ Increase in the maintenance cost due to the frequent plant shutdown maintenance,

⑤ Increase in the energy cost due to the reduction of thermal efficiencies of furnaces, heat exchangers, etc.

(3) Types and functions of antifouling agents

For preventing those problems, the use of antifouling agents is generally employed because mechanical measures, such as increase in fouling allowance of heat exchangers and, installation of spare furnaces and heat exchangers, require much investment.

Table 7.2 shows the types and functions of the antifouling agents. For selecting a suitable antifouling agent, the mechanism of fouling formation in an aimed process should be presumed from the compositions of the fouling and the process fluid. Then chemicals having required fouling prevention mechanisms are chosen.

Table 7.2 Types and functions of antifouling agents

Mechanism for fouling control	Type of antifouling agent	Kinds of chemicals
Prevention of fouling formation	Antioxidant	Polyalkylpolyamines, Phenols, Phenylene diamines, Aromatic amines, Phosphate esters
	Metal deactivator	Azomethines, Polyamines, Salicylidenes
	Corrosion inhibitor	Polyalkylpolyamines, Alkylimidazolines
	Coking inhibitor	Dithiols, Polyalkenylsuccinic imides
Prevention of fouling adherence	Detergent	Alkylphenol metallic salts, Alkylbenzene sulfonates
	Dispersant	Polyalkenylsuccinic imides, Polymethacrylates

Figure 7.7 shows an example of relationship between the fouling formation mechanisms and kinds of suitable antifouling agents. In this case, hydrocarbons are oxidized and polymerized by oxygen and heat to form large size polymer sludges. Therefore, the use of antioxidant type and dispersant type antifouling agents is effective.

(4) Fouling and its prevention in crude oil preheating trains

(a) Fouling problems

Figure 7.8 shows the flow diagram of a crude oil preheating train. The preheating train consists of around ten heat exchangers. It preheats the crude oil by the heat removing from each fraction of atmospheric distillation unit.

Problems caused by fouling in the preheating trains are as follows:

① Increase in the frequency of heat exchanger cleaning,

② Increase in the fuel consumption for the preheating furnace due to the reduction of the feed temperature,

③ Shortening of the continuous operation period of the train.

(b) Fouling formation mechanisms and fouling compositions

To inspect the crude oil preheating train, it is opened after purging the flammable crude oil into the distillation unit by using steam. Therefore, the fouling sampled after the steam purge has a different composition comparing with fouling under the process operation. Generally, the sample includes heavier substances than the original ones.

Therefore, it is difficult to determine the mechanism of fouling formation from the fouling analysis.

However, the fouling formation mechanisms are generally considered as follows:

① Deposition or precipitation of inorganic substances, such as salts and corrosion products,

② Separation and adhesion of asphaltenes in crude oils,

③ Adhesion of the mixture of asphaltenes with inorganic substances to the surfaces of preheater tubes, etc.

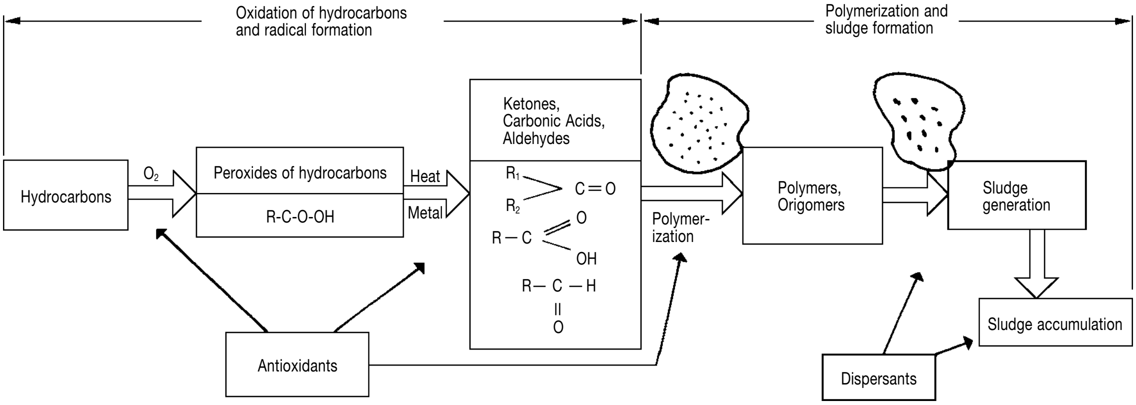


Fig. 7.7 Relationship between the fouling formation mechanisms and the kinds of suitable antifouling agents

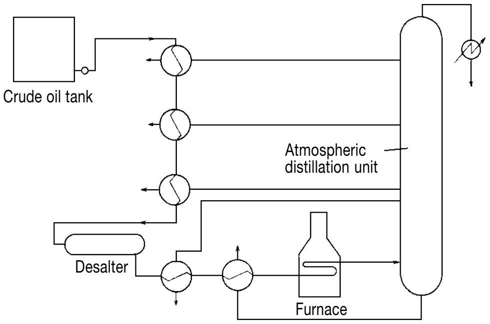


Fig. 7.8 Flow diagram of a crude oil preheating train

The asphaltenes are essentially insoluble in crude oils. But they are stably dispersed in colloidal states in some crude oils, by covering the surfaces with petroleum resins. The stable colloidal state is broken by heating the crude oil, and asphaltenes are deposited.

(c) Antifouling agents

Since the inhibition of fouling formation is very difficult, antifouling agents minimizing the fouling adhesion on metal surfaces are generally used for crude oil preheating systems. Dispersants are generally used as the main ingredient of the antifouling agents. Antioxidants, metal-inactivators, coking inhibitors and so on are often used together with dispersants.

The dosages of antifouling agents are generally in the range of 5 to 50 mg/*l*.

(d) Test methods for antifouling agents

Many test methods have been used for evaluating antifouling agents. The ASTM-CRC Fuel Coker (ASTM D 1660) was widely employed in the 1960's. After that, the Jet Fuel Thermal Oxidation Tester (JFTOT) (ASTM D 3241) has been used. In the present, this method has been improved to detect the fouling on a heating tube as the change of the overall heat transfer coefficient or the fouling resistance.

A testing apparatus showing in Photograph 7.2 (p.7-23) is called "Heating Block Tester" and used to evaluate the antifouling agents for crude preheaters. In this test method, a crude oil is supplied to the heating blocks with three cylindrical heaters and heated. The heating conditions of three heating blocks simulate the conditions of the preheater before desalters, the preheater after desalters and the heating furnace, respectively.

(e) Evaluation of antifouling agents in field

Important points for evaluating the effects of antifouling agents in actual plants are as follows:

① Comparison of chemical effect under the same operational conditions,
② Accumulation of quantitative data,
③ Calculation of economical advantage for the antifouling effect.

Table 7.3[3),4)] shows the typical evaluation method for the effects of antifouling agents in the site.

The most quantitative evaluation method is the measurement of the changes in the overall heat transfer coefficient (U value) in each heat exchanger.

The measurement of the heat transfer efficiency includes the measurement of the fouling factors of heat exchangers.

Table 7.3 Conventional evaluation methods for the effects of antifouling agents in the site

Evaluation for each heat exchanger	1) Inspection of heat exchanger	It is difficult to examine the real fouling condition of heat exchanger under the operation because it is opened after purging the crude oil with steam.
	2) Measurement of change in the overall heat transfer coefficient	Quantitative data are obtained and the comparison of the fouling control effect is possible under the same operational conditions. However, the economical evaluation of the fouling control effect is difficult.
	3) Measurement of change in the crude oil temperature difference between the inlet and outlet	Ditto
Evaluation for whole crude preheater train	1) Measurement of change in the crude oil temperature at the inlet of heating furnace	Inadequate method because the change in the operational conditions may give larger influence on the temperature than fouling.
	2) Measurement of fuel oil consumption per unit amount of treated crude oil	Inadequate method because the change in the operational conditions of distillation unit and kinds of crude oils may give a larger influence on the consumption than fouling.

When the fouling condition of a heat exchanger is evaluated by using the U value, the U values under the same operational conditions have to be selected to minimize the influence of changes in the operational conditions on the U values. Then the changes in the U values are compared for evaluating the different fouling control methods.

The U value of a heat exchanger is calculated by using the equation (7.1).

$$U = \frac{Q}{A \cdot F \cdot Tlm} \tag{7.1}$$

where

U = overall heat transfer coefficient (kcal/$m^2 \cdot h \cdot ^\circ C$)

Q = heat flux (kcal/h)

A = heat transfer area (m^2)

Tlm = logarithmic mean temperature difference (°C)

F = temperature correction factor depending on the types of heat exchangers

The U value is reduced by the fouling of heat exchanger and the fouling factor is obtained from the change in the U value.

$$r = \frac{1}{U_f} - \frac{1}{U_0} \tag{7.2}$$

where

r = fouling factor ($m^2 \cdot h \cdot ^\circ C$/kcal)

U_f = overall heat transfer coefficient with fouling (kcal/$m^2 \cdot h \cdot ^\circ C$)

U_0 = overall heat transfer coefficient without fouling (kcal/$m^2 \cdot h \cdot ^\circ C$)

The fouling condition of crude oil preheater is quantitatively shown by the fouling factor and the increase in the fouling factor reduces the crude oil temperature at the inlet of the heating furnace. This temperature reduction increases the fuel consumption in the heating furnace.

Therefore, the change in the crude oil temperature at the furnace inlet is calculated from the change in the heat transfer efficiency of each preheater as follows:

① The change in the heat transfer efficiency of each preheater with fouling is determined by calculating the U value and/or the fouling factor.

② The change in the crude oil temperature at each preheater outlet is calculated from the U value and/or the fouling factor. Then the change in the crude oil temperature at the inlet of heating furnace is obtained.

③ The change of the crude oil temperature at the furnace inlet gives the change in the fuel consumption in the furnace.

Figure 7.9 shows a typical change in the crude oil temperature calculated by this method in a refinery with the capacity of 80,000 barrels per day. In this case, the increase in the dosage of an antifouling agent from 2 to 10 mg/*l* perfectly prevents the fouling of preheaters and keeps the constant crude oil temperature at the heating furnace inlet. In this refinery, the reduction of crude oil temperature by 1°C at the furnace inlet increases the fuel cost for the furnace by 1 million yens per month.

(5) Fouling and its prevention in fluid catalytic cracking (FCC) units

In the FCC units, the slurry oil recycle line of the main fractionator is most severely fouled. Recently, antifouling agents for this unit has been developed and effectively applied.

Figure 7.10 shows a typical application result of an antifouling agent for a FCC unit with the slurry recycle rate of 70,000 barrels per day. The bottom temperature of the main fractionator is 360 to 371°C and the slurry viscosity is 6 to 14 cSt at 100°C.

Before the application of the antifouling agent, the heat exchangers in the slurry recycle line were severely fouled and the cleaning of heat exchangers was required once every month. The addition

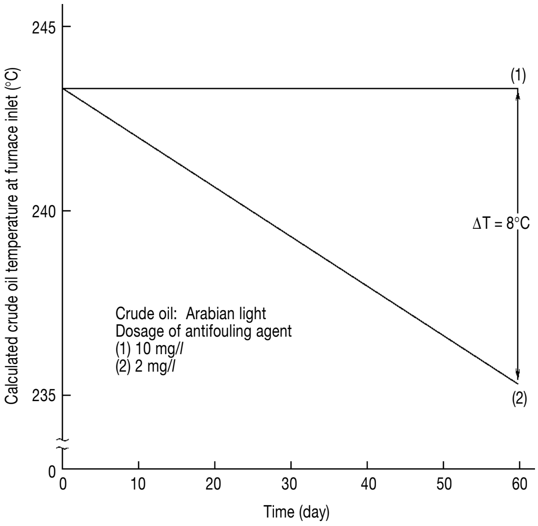


Fig. 7.9 **Reduction in crude oil temperature at a heating furnace inlet by the preheater fouling and the effect of an antifouling agent**

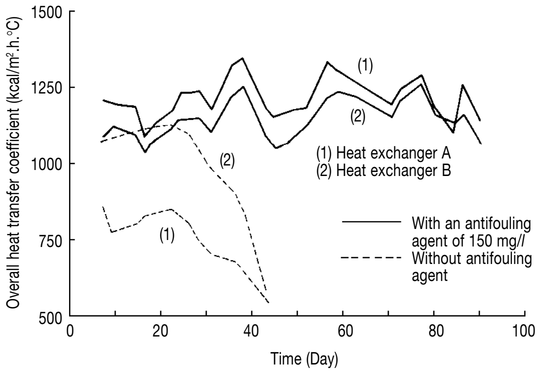


Fig. 7.10 Effect of an antifouling agent in the slurry recycle line of a FCC unit

of the antifouling agent with the dosage of 150 mg/*l* against slurry recycling rate almost perfectly prevented the fouling of heat exchangers and kept their thermal efficiency as shown in Figure 7.10. The thermal recovery rate at the waste heat boilers was widely improved.

(6) Fouling and its prevention in depropanizers of ethylene plants

In the depropanizer, the hydrocarbon mixture of C3 or more is separated into the fractions of C3 and C4 or more. Fouling adheres to the bottom of fractionator and the reboilers. The fouling is white or dark brown gummy substances and reduces the thermal efficiencies of the reboilers.

The fouling substances are formed by the thermal polymerization reaction of unsaturated hydrocarbons, especially dienes. Those unsaturated hydrocarbons include propylene, propadiene, butadiene and so on.

Antioxidants, dispersants or their mixed formulations are usually used as antifouling agents for depropanizers.

Table 7.4 shows the inhibition effects of antifouling agents on the polymerization of butadiene. The combination of the antioxidant A and the dispersant A shows the better inhibition than that of the antioxidant B only.

Photograph 7.3 (p.7-23) shows the testing apparatus for evaluating the antifouling agents for depropanizers. This testing apparatus is called "Dynamic Tester".

(7) Fouling and its prevention in the other processes

Recently, naphtha, kerosene and so on are imported to Japan as raw materials for hydro-desulfurization units and FCC units. As these raw materials include unsaturated hydrocarbons and oxygen, their polymerization reaction by oxygen causes severe fouling problems in those processes. Heat exchangers in those units sometimes clog with fouling during the process operation of 2 to 3 months.

Table 7.4 Effects of antifouling agents on the polymerization of butadiene

Antifouling agent	Dosage (mg/*l*)	Polymer formation rate (%)	Antifouling rate (%)
None	–	52.8	–
Antioxidant A and Dispersant A	30	17.1	67.6
	50	8.2	84.5
	90	2.8	94.7
Antioxidant B	70	21.0	60.2
	120	18.5	65.0

Table 7.5 shows the saturated dissolved oxygen concentrations of each fractions of crude oil.

Figure 7.11 shows the relationship between the concentration of dissolved oxygen in a gas oil and the fouling rate of a heat exchanger. The higher concentration of dissolved oxygen causes the severer fouling. Antifouling agents for these processes are mainly the formulations of antioxidants and dispersants. Their dosages are usually 20 to 50 ml/*l*. In some cases, the dosage is increased as the concentration of dissolved oxygen increases.

7.3.3 Corrosion Inhibitors

(1) Corrosion and its control in crude oil atmospheric distillation units

In the atmospheric distillation units, impurities in crude oils cause the severe corrosion problems. Those impurities form acids, such as hydrochloric acid, by their hydrolysis reactions in the preheating trains and the heating furnaces.

These acids transfer into the vapor phase in the distillation tower and dissolves into the condensed

Table 7.5 Saturated dissolved oxygen concentrations in crude oil fractions

Fraction	Dissolved oxygen (mg/kg)
Naphtha	80
Kerosene	76
Gas oil	60
Heavy gas oil	28

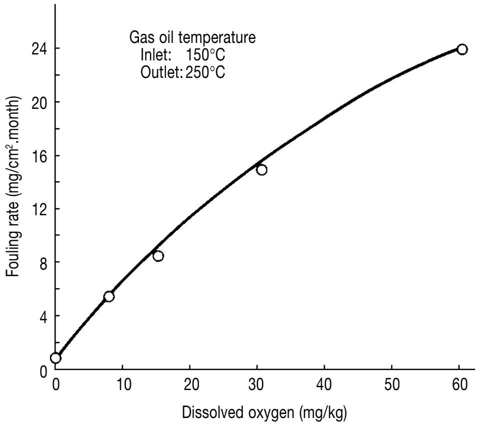


Fig. 7.11 Relationship between the concentration of dissolved oxygen in a gas oil and the fouling rate of the heat exchanger

water when the vapor condenses in the overhead line of the tower. Then the acids cause the corrosion problems of the overhead lines.

(a) Corrosive substances

(i) Hydrogen chloride (hydrochloric acid)

Crude oils commonly contain inorganic salts like NaCl, $MgCl_2$, $CaCl_2$ and so on.

When crude oils are heated, the $MgCl_2$ and $CaCl_2$ are hydrolyzed to form hydrogen chloride at 120° C and 180° C respectively. The NaCl is stable and hardly hydrolyzed. This hydrogen chloride attacks the overhead lines. Especially, the initial condensation zone where the vapor firstly condenses, is severely corroded.

(ii) Hydrogen sulfide

Hydrogen sulfide is generated by thermal decomposition of organic sulfur compounds, such as mercaptans and thiophenes, in crude oils.

In the overhead lines, the hydrogen sulfide dissolves into condensed water and corrodes the apparatus.

Hydrogen sulfide is weaker acid than hydrochloric acid, but it causes severe sulfide attack of metals5). Hydrogen sulfide dissolves into water at much lower temperatures than hydrogen chloride. It is reported that hydrogen sulfide scarcely dissolves into water at the temperature of above 65° C in the overhead lines6).

(iii) Organic acids

Naphthenic acids are one kind of organic acids including in crude oils. Naphthenic crude oils, such as Venezuela and some Southeast Asian crude oils, include a large amount of naphthenic acids.

The corrosivity of crude oil containing naphthenic acids correlates to the total acid number of the crude oil. A special countermeasure is required to prevent the napthenic acid corrosion in the case that the total acid number exceeds 2.0. The naphthenic acids show the severe corrosivity in the temperature range of 230 to 290° C. The metallic corrosion by naphthenic acids is characterized by remaining no corrosion product at the corroded parts with the shape of sharp knife edges.

Lower fatty acids, such as formic acid, acetic acid and propionic acid, are also detected in the drain water of the overhead lines. These organic acids dissolve into the condensed water and cause corrosion problems.

The kinds and concentrations of those organic acids in the condensed water should be analyzed to select a suitable corrosion control method. The analysis is conducted by using a calboxylic acid analyzer.

Figure 7.12 shows an example of the carboxylic acid analysis of a condensed water in an overhead line.

(iv) Others

Carbon dioxide is one of the corrosion substances in crude oils. A part of carbon dioxide is originally included in crude oils, and the other part has been dissolving into crude oils during the transportation. In some case, the carbon dioxide of 200 mg/*l* as CO_2 is found in the drain water of topping unit overhead lines.

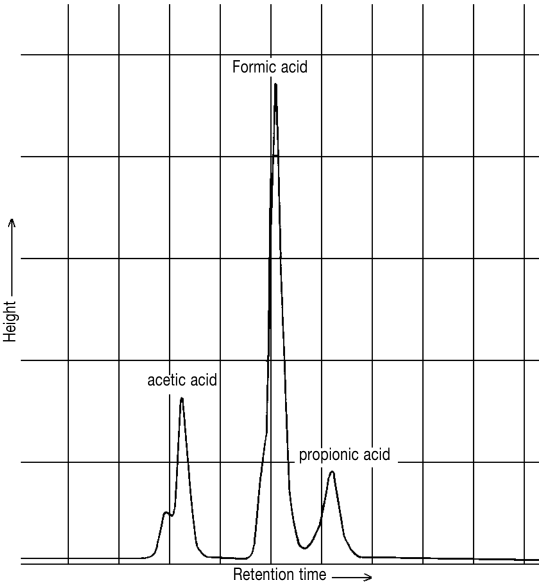


Fig. 7.12 An analysis of carboxylic acids in the drain of overhead line in an atmospheric distillation unit

Oxygen entering into distillation process gives the great influences on the corrosion. Oxygen dissolves into crude oils in the tanks during their storages for a long time. When water using for crude oil desalting includes oxygen, the oxygen transfers into crude oils in the desalting process.

(b) Outline of corrosion control methods

Following methods are generally applied to prevent the corrosion problems in atmospheric distillation units:

① Removal of inorganic salts from crude oils, especially $CaCl_2$ and $MgCl_2$,

② Addition of caustic soda into crude oils to minimize the amount of hydrochloric acid transferring into crude oils,

The addition of caustic soda has a probability to cause the caustic embrittlement of metals and a deterioration in the performance of catalysts in the down flow processes of topping units. Therefore, the overdosing of caustic soda has to be avoided.

③ Use of neutralizers in the atmospheric overhead lines and in atmospheric distillation tower,

Neutralizing amines are usually used as the neutralizers for topping units. These amines prevent the pH reduction of condensed water in the overhead lines to minimize the corrosion problems. However, a sufficient care is required to prevent the fouling problems caused by the deposition of the neutralizing reaction products.

④ Use of corrosion inhibitors,

Filming amines are usually used as corrosion inhibitors for the topping units.

(c) Application methods and effects of neutralizers

(i) pH reduction in the initial condensation zone

The overhead line of an atmospheric distillation unit is outlined in Figure 7.13. In this system, acids, mainly hydrochloric acid, severely attack the metals, especially at the initial condensation zones of condensers. In the initial condensation zone, since most of hydrochloric acid in the vapor dissolves into the condensed water, it extremely reduces the pH and causes severe corrosion.

Even using ammonia as a neutralizer, the neutralization at the initial condensation zone is difficult because most of ammonia remains in the vapor phase at the initial condensation zone. Kondo, et al.[6], reported the pH at the initial condensation zone when the final drain pH was controlled at 7.0 by using ammonia. Figure 7.14 shows their test results. The pH of initial condensation zone lowers up to 3 to 4. Cornish[7] measured the pH of initial condensation zone in a field and reported that it was 2.0 when the final drain pH was controlled at 7.0 by using ammonia.

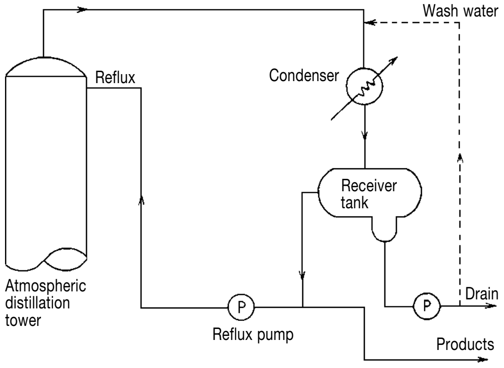


Fig. 7.13 **Flow diagram of the overhead line of an atmospheric distillation unit**

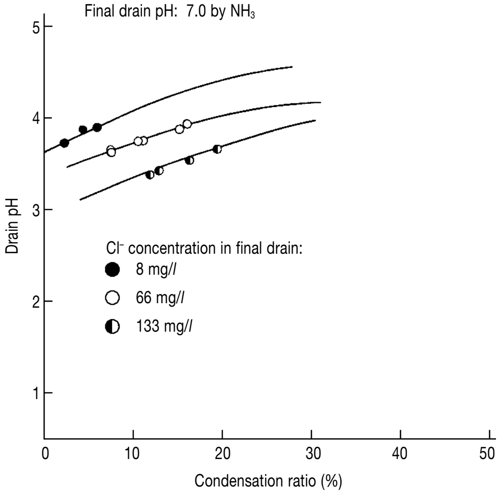


Fig. 7.14 **Relationship between condensation ratio and the drain pH**

(ii) Estimation of pH at the initial condensation zone

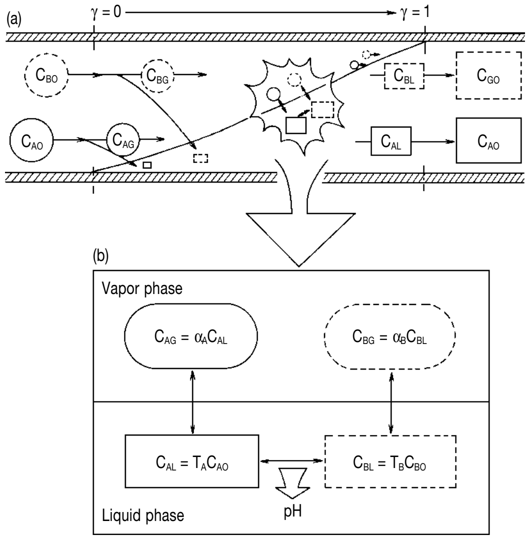
The determination of the pH at the initial condensation zone is essential to solve the corrosion problems in the overhead lines. However, the pH measurement is very difficult in the fields.

Therefore, Kishi, et. al.[8], have developed a program to compute the pH at the initial condensation zone from the analysis data of final drain for determining suitable neutralizers and the injection method. This pH calculation program is based on the distribution ratios of chemical substances between vapor and liquid phases, and the dissociation equilibriums of acids and bases in the liquid phase. The calculation method is outlined as follows.

Figure 7.15 shows a schematic model of the distribution equilibriums of acids and bases between vapor and liquid phases in a condensation system.

The C_{AO} and C_{BO} show the initial concentrations of an acid and a base in the initial vapor phase ($\gamma = 0$). The C_{AO} and C_{BO} are equal to their concentrations in the final condensation zone ($\gamma = 1$).

The liquid pH at a condensation ratio γ is determined by the distribution ratios of acids and bases in the vapor and liquid phases, and their dissociation equilibrium conditions in the liquid phase at that temperature. It is assumed that each acid and base independently behave in the vapor phase, and their distribution equilibriums between vapor and liquid phases are also independent. In that case, the concentrations of each acid and base in the vapor and liquid phases are determined by each apparent distribution ratio (α_A or α_B) between the vapor and liquid phases. Then, when each acid or base has the dissociation equilibrium condition independently, the pH of liquid is determined by the total amounts of H^+ and OH^- dissociated.



C_{AO}: Initial concentration of acid in vapor phase
C_{AG}: Concentration of acid in vapor phase at a partial condensation zone
C_{AL}: Concentration of acid in liquid phase at a partial condensation zone
C_{BO}: Initial concentration of base in vapor phase
C_{BG}: Concentration of base in vapor phase at a partial condensation zone
C_{BL}: Concentration of base in liquid phase at a partial condensation zone
γ: Condensation ratio
α_A: Apparent vapor-liquid distribution ratio of acid
α_B: Apparent vapor-liquid distribution ratio of base
T_A: Correction factor for acid
T_B: Correction factor for base

Fig. 7.15 A schematic model of the distribution equilibriums of acids and bases between vapor and liquid phases in a condensation system

The above pH estimation method is expressed by using functional equations described below.

The concentrations of each acid and base in the liquid phase are shown by the equations (7.3) and (7.4) respectively.

$$C_{AL} = f_1\,[\gamma, C_{AO}, K_A, \alpha_A, (H^+)] \tag{7.3}$$
$$C_{BL} = f_2\,[\gamma, C_{BO}, K_B, \alpha_B, (H^+)] \tag{7.4}$$

where

K_A, K_B = dissociation constants of acid and base

The hydrogen ion concentration and pH in the liquid phase are obtained from the equations (7.5) and (7.6).

$$(H^+) = f_3(C_{AL}, C_{BL}, K_A, K_B) \tag{7.5}$$
$$\text{pH} = -\log(H^+) \tag{7.6}$$

The K_A, K_B, α_A and α_B change depending on the temperature of an aimed system.

Figure 7.16 shows the pH calculation results from the analysis data of final drain in the overhead line of an atmospheric distillation unit. In this case, ammonia only and the mixture of ammonia with a neutralizing amine are used as the neutralizers, and the final condensate pH is controlled at 6.5. However, the pH at the initial condensation zone are widely different and the mixture shows the better neutralizing effect. This pH difference is caused by the difference in the distribution ratios of ammonia and the amine at the initial condensation zone.

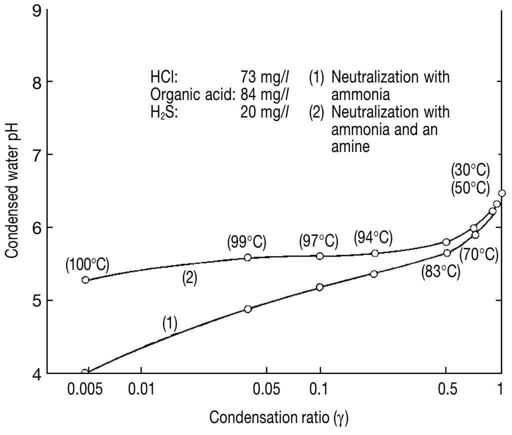


Fig. 7.16 Relationship between the condensation ratio and the pH of condensed water under different neutralizing treatments

To effectively control the corrosion problems in the overhead lines, it is important to sufficiently increase the condensate pH at the initial condensation zone and to keep an appropriate condensate pH from the initial to the final condensation zones.

As each acid or each neutralizer has the different distribution ratio, this computer calculation program is very useful to select suitable neutralizers and to determine an appropriate formulation and the required dosage.

Generally, the neutralizers are injected into the overhead lines before the condensers. The use of neutralizers is an effective corrosion prevention method, however, the accumulation of neutralized salts may cause a pipe clogging, an under deposit corrosion and so on. To prevent those secondary problems, water washing of the overhead line is carried out for removing the salts.

(d) Application methods and effects of corrosion inhibitors

In the overhead lines, oil soluble film forming inhibitors are generally applied as the corrosion inhibitors. The main ingredients of these filming inhibitors are amines, imidazolines and their derivatives.

Those inhibitors form their adsorption layers on metal surfaces and prevent the corrosion by disturbing the contact of corrosive substances with the metal surfaces. Their inhibition effects are improved by increasing the condensed water pH as shown in Figure 7.17[9)]. Therefore, neutralizers are generally used together with the filming inhibitors in the overhead lines of atmospheric distillation units.

However, an excess increase of condensate pH sometimes causes the deposition problems of corrosion products in the systems. To minimize the deposition problems and to obtain the sufficient corrosion inhibition, the pH of final drain is generally controlled in the range of 6.0 to 6.5 under the combined treatment of filming inhibitors together with neutralizers.

Those filming inhibitors are dissolved with solvents, such as naphtha, and injected into the overhead lines far from condensers.

(2) Corrosion and its control in fluid catalytic cracking (FCC) units

Figure 7.18 shows the flow diagram of a FCC unit. The corrosion problems mainly occur at the overhead lines of main fractionators, gas compressor systems and so on.

(a) Causes of corrosion

In the cracking process, ammonia, hydrogen sulfide and cyanides are generated. In the overhead lines, the ammonia increases the condensed water pH up to 7 to 10. Then the dissociated hydrogen sulfide and cyanide ions cause the metallic corrosion. The equations 7.7 and 7.8 show the corrosion reactions of iron by those ions.

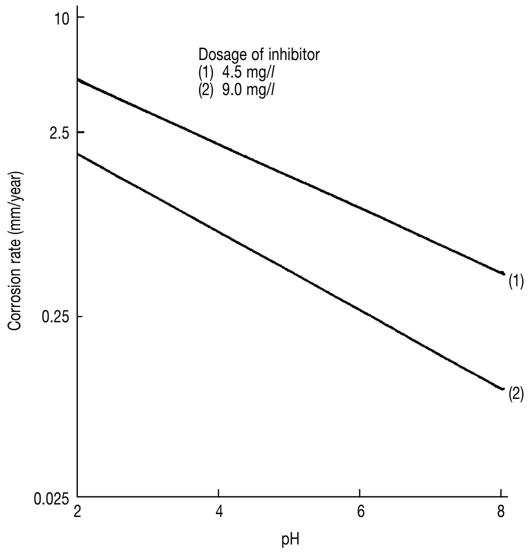


Fig. 7.17 Relationship between the effect of a filming inhibitor on carbon steel and the condensate pH in the overhead line of an atmospheric distillation unit

$$2Fe + 2H^+ + 2HS^- \rightarrow 2FeS + 2H_2 \qquad (7.7)$$
$$FeS + 6CN^- \rightarrow Fe(CN)_6^{4-} + S^{2-} \qquad (7.8)$$

The corrosion product, FeS, adheres on the metal surface but it shows no corrosion protection because it is porous in the pH range of 6.6 to 8.8[10)]. The presence of CN^- ion accelerates the corrosion because it dissolves the FeS.

Moreover, hydrogen formed by the reaction (7.7) diffuses into the inside of metal and causes the hydrogen embrittlement.

(b) Corrosion control methods

In the FCC units, water washing and the use of filming inhibitors are generally applied for controlling the corrosion caused by hydrogen sulfide and cyanides.

(i) Water washing

The water washing is generally applied for the overhead lines of the main fractionators and the gas compressor systems. The amount of wash water is 2% or more for the amount of process fluid. The water washing minimizes the corrosion by the following two ways:

① Dilution of corrosive substances, hydrogen sulfide and cyanides, in the water phase in

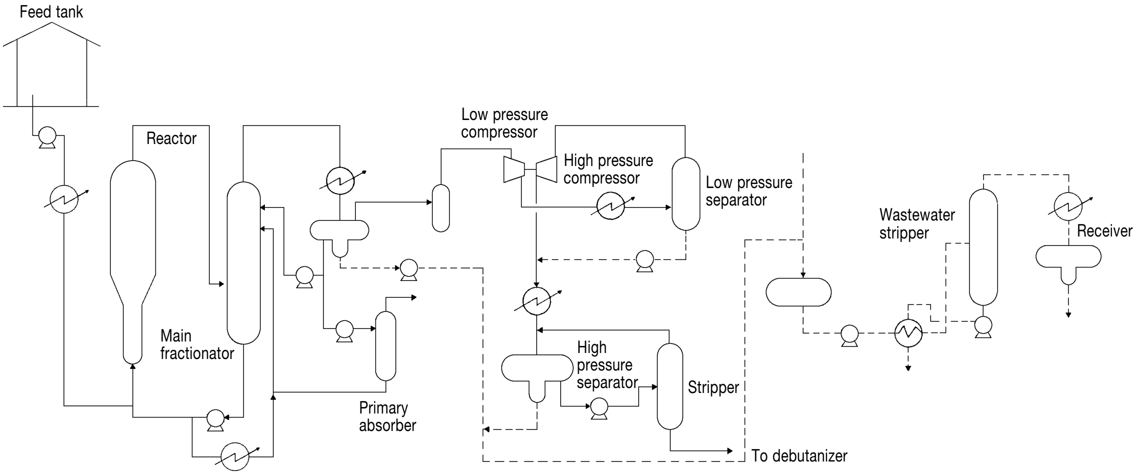


Fig. 7.18 Flow diagram of a fluid catalytic cracking unit

the system,

② Flushing of accumulated corrosion products in the system to minimize the under deposit corrosion.

(ii) Use of filming inhibitors

As the only water washing is not enough to prevent the corrosion problems in the FCC units, the filming inhibitors are generally applied together with the water washing.

The filming inhibitors are divided into two types of oil soluble and water soluble ones.

The oil soluble inhibitor is fed into a line before condensers in the overhead system of main fractionator, then it protects the overhead system and primary absorber system from their corrosion. However, the oil soluble ones deteriorate the oil and water separation at the downstreams when they are excessively dosed.

To solve this problem, water soluble inhibitors have been applied for the FCC units recently. They scarcely influence the oil and water separation and easily form the protective film on the metal surfaces where contact with corrosive water phase including hydrogen sulfide and cyanates. The dosages of them are 50 to 200 mg/*l* and they effectively control the corrosion of the overhead lines in FCC units.

(3) Corrosion and its control in dilution steam generators (DSG) of ethylene plants

The DSG is also called Waste Water Vaporizer (WWV). Figure 7.19 shows the flow diagram of a DSG system. The DSG is a kind of boiler which the process condensate in the ethylene plant is recycled as the feedwater.

As the feedwater includes organic acids, such as acetic acid, the DSG system is severely corroded. Generally, caustic soda and/or neutralizing amine are used to neutralize the organic acids and to minimize the corrosion of this system. The use of caustic soda is an effective corrosion control method and economic. However, the carryover of caustic soda to steam phase has a probability to cause the alkaline corrosion of the cracking furnaces using the steam. Therefore, the dosage of caustic soda is minimized and neutralizing amines are generally used together with caustic soda.

Generally, the pH of boiler water is controlled at around 9 at a room temperature. However, the pH of boiler water sometimes reduces below 6 at a high temperature because of the differences in the dissociation conditions of acids and alkalis between low and high temperatures. Therefore, the selection of suitable neutralizers and the determination of their dosage have to be carried out taking the high temperature pH into consideration.

(4) Test methods for corrosion inhibitors

(a) Laboratory test methods

(i) Corrosion test apparatus for initial condensation zone

The outline of a test apparatus is shown in Figure 7.20. Photograph 7.4 (p.7-23) shows the test condensers of this apparatus. This apparatus simulates the initial condensation zone of overhead condenser in distillation units and so on.

The corrosion conditions and the effects of corrosion inhibitors in those overhead lines are determined by using this test apparatus.

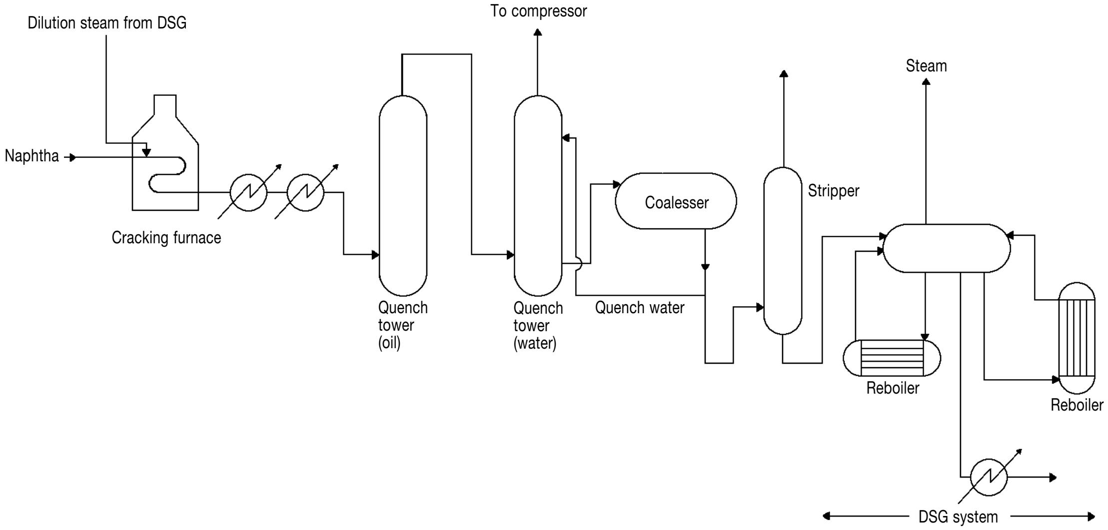


Fig. 7.19 Flow diagram of a dilution steam generator (DSG) system

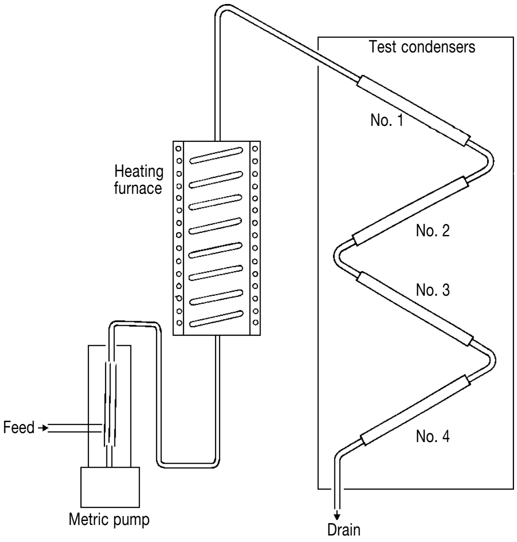


Fig. 7.20 A corrosion test apparatus for the initial condensation zone of fractionators

A typical test condition and the test results of this apparatus are shown in Table 7.6 and Figure 7.21. Under no chemical treatment, the corrosion rate is the largest at the No. 1 condenser where is the initial condensation zone. Then the corrosion rate becomes smaller from the No. 2 condenser to the No.4 condenser as the condensation rate increases. The use of neutralizers reduces the corrosion rate but they show the different effects even the pH of final drain is controlled in the same level.

Table 7.6 Typical testing conditions of neutralizers for the overhead lines of distillation units

Test fluid		pH : 3.0 HCl : 35 mg/l CH_3COOH: 100 mg/l H_2S : 0.4 mg/l
Feed rate		360 ml/h
Dissolved oxygen		None (by N_2 gas sealing)
Test tube	Material	Carbon steel (JIS: STB-35)
	Surface area	60 cm^2
Test period		20 h

In this case, the neutralizer C with the dosage of 170 mg/l shows the stable corrosion inhibition from the initial to final condensation zones.

(ii) Up-down corrosion test apparatus

Figure 7.22 shows the outlines of an up-down corrosion test apparatus. Specified amounts of oil and water are added into the glass cylinder and a test coupon is moved up and down through the water and the oil layers. Then, the corrosion rate is measured.

This test apparatus is used for evaluating the oil soluble and water soluble filming inhibitors for the overhead line of atmospheric distillation units, FCC units and so on. Table 7.7 and Figure 7.23 show a typical test condition and test results of this apparatus. The use of suitable inhibitors effectively reduces the corrosion rate of carbon steel.

(b) Corrosion monitoring in fields

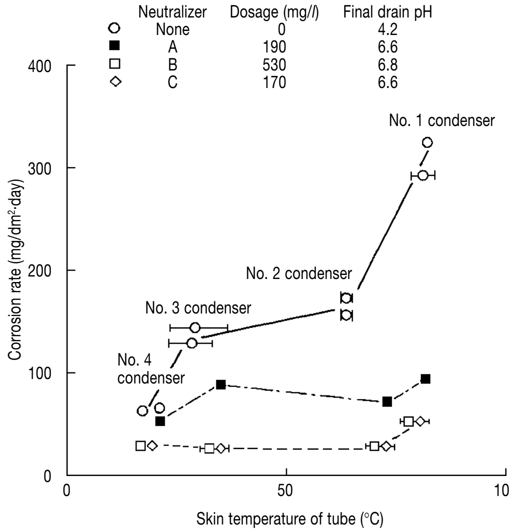


Fig. 7.21 Corrosion inhibition effects of neutralizers in an initial condensation zone

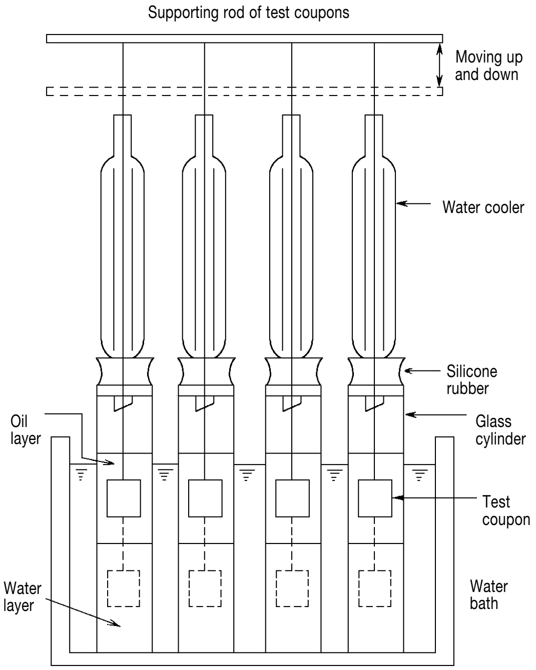


Fig. 7.22 Up-down corrosion test apparatus

Table 7.7 Typical test conditions of up-down test apparatus for evaluating filming inhibitors

Test fluid quality		Oil : Kerosene Water : Nacl 5% H_2S 480–550 mg/*l*
Volume of fluid		Oil : 400 m*l* Water : 500 m*l*
Temperature		80 °C
Dissolved oxygen		None (by N_2 gas sealing)
Test coupon	Material	Carbon steel (JIS: SPCC)
	Surface area	31 cm^2
Test period		20 h

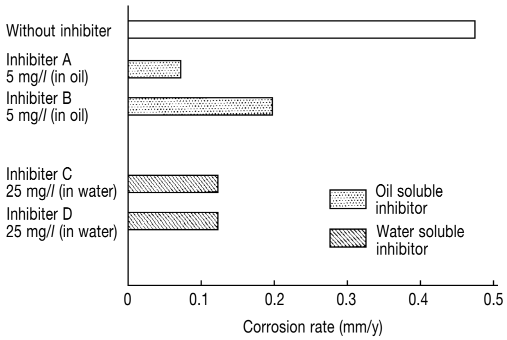


Fig. 7.23 Corrosion inhibition effects of various filming inhibitors under an up-down corrosion test

Various corrosion monitoring methods are applied for evaluating the corrosion conditions in field. As each method has the advantages and disadvantages, suitable methods have to be selected by taking the operational conditions of aimed process into consideration.

Table 7.8 summarizes the advantages, disadvantages and so on of typical corrosion monitoring methods applied in fields.

7.3.4 Metal Inactivators (Passivators) for the Catalysts of FCC Units

(1) Prevention methods for the deterioration of catalyst performance

Synthetic zeolites are generally used as catalysts for the FCC units. Heavy metals including in the feed for FCC units deposit on the catalyst, then they deteriorate the activity of the catalyst and/or induce unnecessary side reactions.

To minimize the bad influences of heavy metals on the catalysts, the following three methods are applied:

① Improvement of catalysts to increase the resistance against heavy metals,

② Removal of heavy metals from the feed for FCC units,

Table 7.8 Corrosion monitoring methods applied for refineries and petrochemical plants

Monitoring method	Outline of method	Application	Advantage	Disadvantage
Water analysis [Analysis of metallic ion concentrations in drain, etc.]	• To analyze the concentration of metallic ions in drain, which are corrosion products, for estimating the corrosion condition of the system • The estimation of drain pH at the initial condensation zone from the analysis of drain composition	System possible to take samples of drain, etc.	Easy and economic Correct pH estimation in the initial condensation zone by using computer	Incorrect result in case that corrosion products deposit in the system Difficult to monitor local corrosion
Hydrogen probe method	To electrochemically measure the amount of hydrogen generated by corrosion reaction for estimating the probability of hydrogen embrittlement	System which the hydrogen probe is installed	Acculate estimation method for hydrogen embrittlement and hydrogen induced cracking	Impossible to measure corrosion rate
Test coupon method	To install test coupons into the inside of system for measuring corrosion rate from the weight loss and observing the corrosion condition	Systems possible to install test coupons	Measurement of correct corrosion rate Possible to observe the shape of corrosion	Difficult to install test coupons in some systems
Electric resistance method	Corrosion rate measurement from the change in the cross section area of a test probe	Systems possible to install test probes	Continuous and instantaneous corrosion rate measurement	Difficult to install test probes in some systems Difficult to monitor local corrosion

③ Use of metal passivators which react with heavy metals to inactivate them.

The use of metal passivators has become popular. Antimony and its compounds are generally applied for inactivating nickel in the feed.

(2) Function of metal passivators

The nickel in the feed deposits on the catalyst in the reactor of FCC unit and accelerates the dehydrogenation reaction in the cracking process. As the results, the production of gasoline and kerosene is reduced. The increase in the hydrogen formation disturbs the safe and efficient process operation.

Antimony based metal passivators react with nickel and form their alloys on the catalyst to minimize the bad influence of nickel[11].

(3) Application methods and effects of metal passivators

Various organic and inorganic antimony compounds are used as the metal passivators. Recently, the inorganic ones become popular and the suspension of antimony pentaoxide in an organic

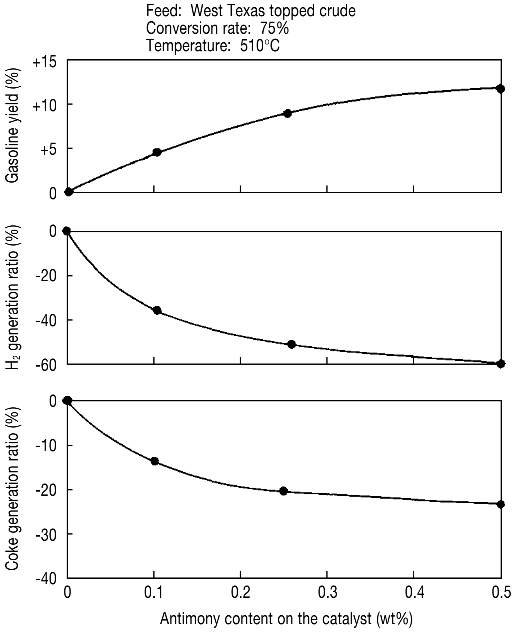


Fig. 7.24 The effect of a metal passivator in a FCC unit

solvent is generally injected into the feed of FCC units. The dosage is 0.5 to 1.0 mole equivalent against the nickel concentration in the FCC feed. The diameter of antimony pentaoxide particle in the suspension is generally 9 to 30 μm.

A typical effect of a metal passivator is shown in Figure 7.24[12]. The use of the passivator apparently reduces the generation of hydrogen and coke. As the result, the production of gasoline is increased.

7.3.5 The Other Chemicals

(1) Dispersants for iron sulfides

Water including a high concentration of hydrogen sulfide and iron sulfides is discharged from various petroleum refining processes, such as naphtha stabilizers, desulfurizers and FCC units. When those effluents are treated by sour water strippers, etc., to remove the hydrogen sulfide, the iron sulfides precipitate together with oils and adhere to the treatment plants. This fouling reduces the performance of sour water strippers and so on. To prevent those fouling, some kinds of surface-active agents are applied as dispersants which disperse the oils into water and minimize the precipitation of iron sulfides.

Photograph 7.5 (p.7-24) shows the effect of a dispersant. The use of the dispersant apparently prevents the precipitation of iron sulfides.

(2) Antifouling agents for polymer base fouling

The process condensate of ethylene plants is used as the feedwater for the DSG. As this feedwater includes unsaturated hydrocarbons, they polymerize and form fouling including polystyrene and so on in the system.

Some kinds of water soluble polymers disperse this fouling and prevent the adhesion to the system. Photograph 7.6 (p.7-24) shows a laboratory test result of a dispersant. The use of the dispersant reduces the fouling amount adhered on the stirrer in the test apparatus.

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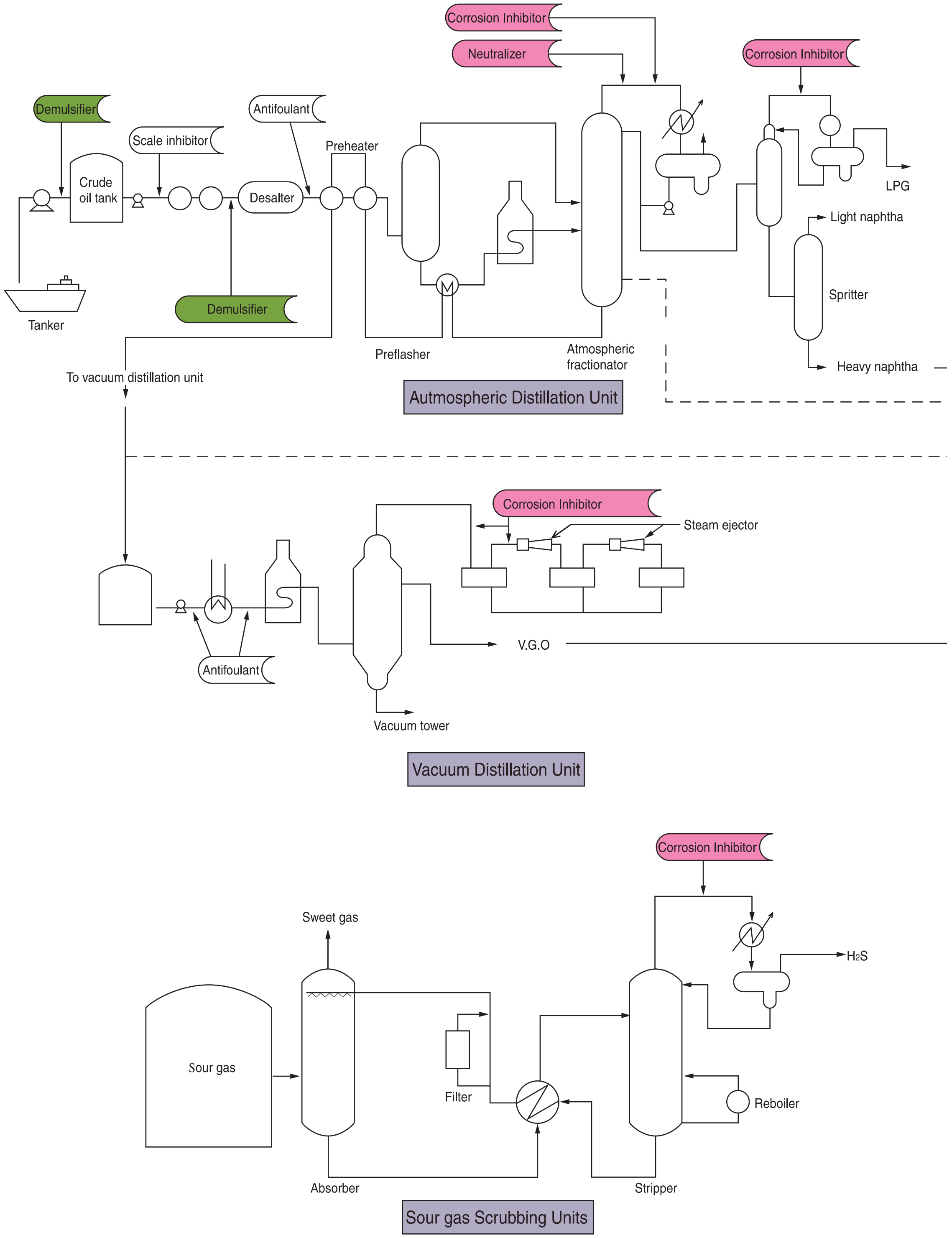
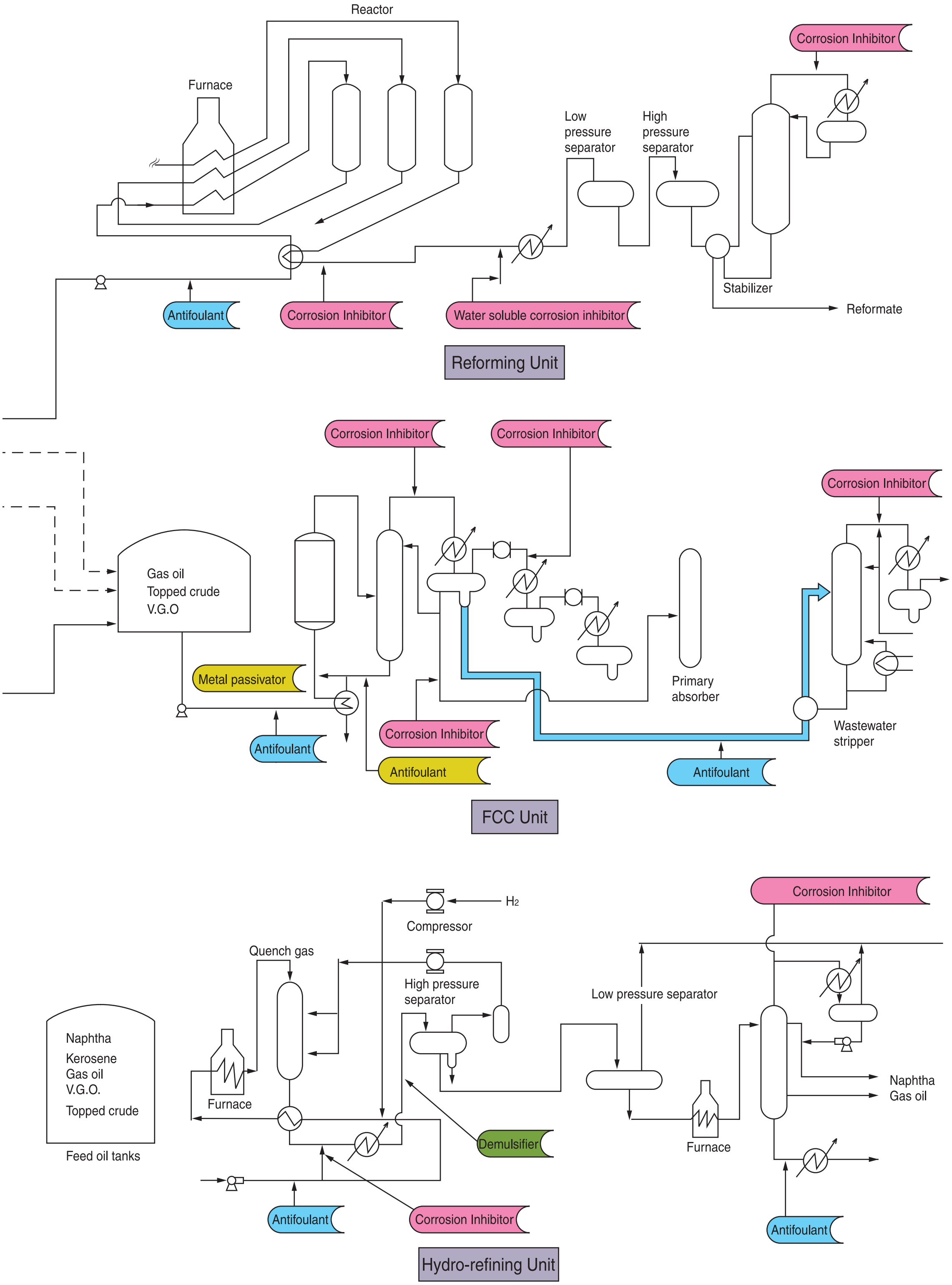


Fig.7.2 Petroleum refining processes and the chemical injection points


Reactor
Furnace
Corrosion Inhibitor
Low pressure separator
High pressure separator
Stabilizer
Reformate
Antifoulant
Corrosion Inhibitor
Water soluble corrosion inhibitor
Reforming Unit
Corrosion Inhibitor
Corrosion Inhibitor
Corrosion Inhibitor
Gas oil
Topped crude
V.G.O
Metal passivator
Antifoulant
Corrosion Inhibitor
Antifoulant
Primary absorber
Antifoulant
Wastewater stripper
FCC Unit
Corrosion Inhibitor
H2
Compressor
Quench gas
High pressure separator
Low pressure separator
Naphtha
Kerosene
Gas oil
V.G.O.
Topped crude
Feed oil tanks
Furnace
Demulsifier
Furnace
Naphtha
Gas oil
Antifoulant
Corrosion Inhibitor
Antifoulant
Hydro-refining Unit

8. Water Treatment for Iron and Steel Making Plants

8.1 Introduction

Recently, the progress of the iron and steel industry has been remarkable. The industry has established a system for manufacturing large quantities of low-cost steel products and greatly contributes to a stable supply of basic materials for all industries and the construction of public facilities.

However, annual worldwide demand for steel has leveled off in the past 10 years, stabilizing at about 650 million tons. Thus, the iron and steel industry is in a fiercely competitive environment.

Iron and steel making enterprises are competing each other for the technology development. Especially, they are aiming to reduce the production cost in the field of ordinary steels and to produce higher quality products in the field of high-grade steels such as steel plates for automobile industries.

For the next-generation of iron manufacturing technology, smeling reduction processes have been investigated to replace the blast furnace and converter method using in the present. However, it will take a long time to utilize a new process. Therefore, the present iron manufacutring processes may continue during this decade.

A large quantity of water is used at integrated iron and steel works based on the blast furnace process. The water consumption is 100 to 200 m^3 per ton of crude steel. A crude steel production plant with the capacity of 5 million tons per year may use 1.5 million m^3 to 2.5 million m^3 of water a day. Using advanced water treatment technologies, many iron and steel works have made efforts for saving water, and their water recovery rates have reached as high as 95%. In these plants, the quantity of industrial water-intake is only 100,000 to 200,000 m^3 a day.

Waters using in iron and steel production plants are classified into indirect cooling water, direct cooling water and gas cleaning water. Since iron and steel making processes are under high-temperature conditions, special cares are required to prevent problems caused by water. Especially, increase in the water recovery rate accelerates the problem occurrence.

This chapter describes the usage of water in iron and steel making processes, and the water treatmente chemicals.

8.2 Outline of Iron and Steel Making Processes, and the Water Treatment Chemicals

An outline of iron and steel making processes is shown in Figure 8.1.

A large amount of water is used for various purposes in these processes from the raw material handling processes to final production processes. The waters using in iron and steel mills are divided into following three categories:

① Indirect cooling water for cooling equipments and process gases or liquids,
② Direct cooling water for cooling products and slag,
③ Gas cleaning water.

These waters are generally recycled or recirculated to save water. Then problems caused by water, such as corrosion, scaling and biological fouling, occur in those water recirculation systems and reduce the efficiency of iron and steel production. Various water treatment chemicals, such as corrosion inhibitors, scale inhibitors and biocides, are used to prevent those problems and to realize the safe and efficient operation of production processes.

Since the operational conditions and the water qualities are widely different in each water recirculation system, suitable water treatment chemicals and their application methods have to be carefully determined according to the operational conditions of each system.

Figure 8.2 (p. 8-21) shows a flow diagram of iron and steel making processes, and typical systems where water treatment chemicals are used. The

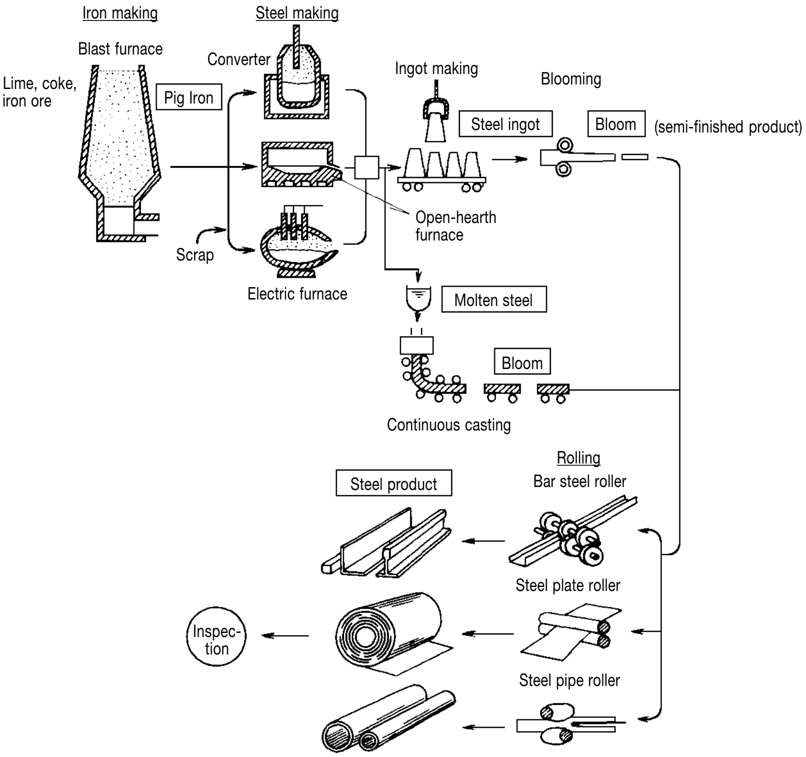


Fig. 8.1 Iron and steel making processes

usages of water and water treatment chemicals in each production process are mentioned below.

8.2.1 Raw Material Yards

The raw material yard requires water spraying to prevent iron ore and coal dusts from the blowing-away. This water spraying increases the moisture contents of coal and iron ore, resulting in the increase of the energy consumption in the downflow processes, such as coke plant.

Dust blow-away preventives are used to minimize the dust blowing-away and the moisture contents of them.

Flocculants are used for the yard wastewater treatment.

8.2.2 Sintering Plants and Coke Plants

In sintering plants, water is used as sintering dust collecting water, feedwater to the wasteheat boiler and so on.

The sintering dust collection methods include the wet and dry methods. In the case of wet method, the pH and calcium hardness of the dust collecting water become higher to cause calcium carbonate scale in the system, because the dust includes lime using as a raw material. Scale inhibitors are used for preventing the scale troubles.

For the wasteheat boilers, boiler compounds and so on are applied to prevent the corrosion and scale troubles.

In coke plants, water is used for cooling cokes, gas and facilities.

Previously, cokes were cooled by spraying water. Recently, the coke dry quench method (CDQ) has been mainly used and the heat is recovered by using wasteheat boilers.

In the indirect cooling water system for the gas and equipments, corrosion inhibitors, scale inhibitors and biocides are used for preventing problems caused by water.

Wastewater discharged from coke plants includes the ammonia liquor. The ammonia liquor is treated by using the activated sludge method. The excess sludges are dewatered by dehydrators and the cake is returned to coke ovens or incinerated. Dewatering agents are used for reducing the water content of the cake.

8.2.3 Chemical Plants

Gas generated in coke plants is finally utilized as fuel. Through the gas refining processes, various substances in the gas are separated and recovered as useful substances.

Firstly, the gas is desulfurized at the desulfurization tower. In the tower, antifoaming agents are used to prevent foaming caused by the contact of gas with the treatment liquid.

Since the gas includes the ammonia of 6 to 10 g/Nm^3, it is treated to remove ammonia in the ammonia stripper. The recovered ammonia is utilized to produce ammonium sulfate, etc.

As calcium fluoride scale and tar pitch adhere to the ammonia stripper, scale inhibitors and antifoulants are used.

After the ammonia removal, light oils in the gas are recovered. The recovered light oils are separated and refined into benzene, toluene and xylene at fractionators.

The overhead lines of fractionators including condensers are corroded by organic acids. Organic corrosion inhibitors are applied to prevent this corrosion.

8.2.4 Iron Making Process (Blast Furnaces)

In the iron making process, water is used for indirectly cooling the blast furnace body, tuyere and hot blast valves. The blast furnace slag is directly cooled by spraying water. Water is also used for cleaning the blast furnace gas (BFG).

The cooling of the furnace body, tuyere and hot blast valves is done to protect these equipments from their overheating. These cooling water systems have extremely high heat loads and are liable to meet corrosion and scale problems. Corrosion and scale inhibitors are applied to prevent these problems.

In the BFG cleaning system, the water is sprayed and contacts with the BFG to cool it and to remove the dust in the gas. Since the cleaning water contains a large quantity of suspended solids, the water is recycled after the sedimentation treatment in thickeners. Flocculants are used for the thickeners. The treated cleaning water still includes a sufficient concentration of calcium and zinc ions to deposit calcium carbonate and basic zinc hydroxide scales in the supply water line and spray nozzles. Scale inhibitors are used for controlling those scales.

As the BFG has the pressure of 2 to 3 kg/cm^2, the thermal energy is recovered as electricity by using the top-pressure recovery turbine facility (TRT). Scale inhibitors are used for preventing the turbine blades from scale problems. Recently, a dry gas cleaning system is adopted for improving the energy recovery rate at TRT. In this system, the drain containing hydrochloric acid is generated in the gas line behind the TRT, and it causes the corrosion of the piping. To prevent this corrosion, water is sprayed into the piping immediately after the TRT, however, the alkali consumption for the neutralization increases.

Blast furnace slag is recovered either as aggregates by cooling at a dry pit or as raw material of blast furnace cement by quenching at a slag granulate equipment. Since the slag is cooled by sprayed water after primary cooling with air, calcium oxide in the slag dissolves into cooling water. As the cooling water is recirculated and calcium carbonate scale deposits in the system, scale inhibitors are used. In the case of granulated slag, as the slag becomes glassy due to the quenching, the calcium in the slag scarcely dissolves into water. Therefore, no calcium carbonate scale is deposited.

8.2.5 Steel Making Process (Converters and Continuous Casting Plants)

In converter factories, water is used for indirectly cooling the lances and the hoods, and directly cooling the converter slag. Water is also used for cleaning the converter gas.

In the lance and hood cooling water system, the heat flux on the heat transfer surface is very high at 200,000 to 500,000 kcal/m^2·h. Thus severe corrosion and scale problems occur in this system. Accordingly, scale inhibitors and corrosion inhibitors are used. Recently, the employment of a closed cooling water system for preventing the scaling problems or an evaporation cooling system (a kind of boiler system) for recovering the thermal energy of the gas has become popular as the hood cooling system.

The converter gas is treated by gas combustion methods or non-combustion methods. At present, most of the gasses are treated by non-combustion type facilities. The most popular system is the oxygen converter gas recovery system (OG system) which was developed in Japan.

Since the gas cleaning water contains a high concentration of suspended solids, it is recycled after removing the suspended solids by thickeners. Flocculants are used in the thickeners. Scale inhibitors are used to prevent calcium carbonate scale deposited in the gas cleaning water recirculation systems.

For high-grade steel production, various secondary refining equipents, such as vacuum degassing facilities, are installed in converter factories. In these facilities, water is used for cooling the furnace body and exhaust gas, and for cleaning the exhaust gas. Water treatment chemicals are applied for the corrosion and scale prevention in each system.

In continuous casting plants, water is used for cooling the casting molds indirectly and for solidifying steel by water spraying after the casting.

Previously, open recirculating cooling water systems were generally applied for mold cooling systems. However, scaling problems often occurred in the systems, because the heat fluxes of molds, especially billet molds, are very high. Recently, the employment of closed cooling water systems has become popular for the mold cooling to minimize the scale problems. Corrosion and scale inhibitors are used for the open recirculating cooling water systems, and corrosion inhibitors are applied for the closed systems.

In the direct cooling water system, the circulation water includes a high concentration of suspended solids after spraying. In the system, settling ponds (scale pits) and filters are installed to remove the suspended solids. In the system, scaling with calcium fluoride and corrosion by the pH reduction of circulating water often occur, because an acidic continuous casting powder including fluorides comes into the spray water. In addition, the corrosion increases the iron content of the water and causes the clogging of spray nozzles with iron hydroxides. Corrosion and scale inhibitors are used to prevent these problems.

8.2.6 Hot Rolling Mills

Waters used at hot rolling mills are divided into the indirect cooling water for cooling furnace and various equipment, and the direct cooling water for cooling rolls and steel products. In the indirect cooling water systems, corrosion inhibitors and scale inhibitors are used for preventing the corrosion and scale problems. Since the direct cooling water is contaminated with mill scales and lubricating oils, it is treated by clarifiers and filters for the recycling. Coagulants, such as polyaluminium chloride (PAC), are added for promoting the oil removal.

8.2.7 Cold Rolling Mills

Water used in the cold rolling mills includes the indirect cooling water for various machineries and oil coolers, and the cleaning water for the surfaces of products, such as steel plates, pipes, bars and wire rods.

In the indirect cooling water system, corrosion and scale inhibitors are used.

Since the surface cleaning water contacts with products directly, the water quality becomes different in each process. The water is contaminated with acids, alkalis, oils, fats and so on. Therefore, the effluents have to be treated by using appropriate methods including neutralization, oxidation, oil separation, flocculation and sedimentation. Neutralizing agents, coagulants and flocculants are used for the wastewater treatment.

8.3 Problems in Indirect Cooling Water Systems and Their Countermeasures

Table 8.1 shows the classification of cooling water systems installed in iron and steel works. An appropriate cooling method and the kind of make-up water are determined according to the operational conditions of equipments to be cooled. Among them, the hot blast valves, tuyeres, lances, hoods and molds have very high skin temperatures and heat fluxes on their heat transfer surfaces. For example, the heat flux of hood cooling water system reaches 200,000 to 500,000 kcal/m^2·h during the blowing. These heat fluxes are extreamely high comparing with the heat flux of 50,000 kcal/m^2·h or less at heat exchangers in refineries and petrochemical plants.

As the detail of chemical cooling water treatment is described in the Chapter 3, cooling water treatment methods for the equipments having the high skin temperatures and high heat fluxes are discussed in this section.

8.3.1 Blast Furnace Body Cooling Systems

Cooling staves or cooling boxes are employed to cool and protect the firebricks and the iron surface of blast furnace.

The cooling box shown in Figure 8.3 is placed in the brick layers for cooling them. The cooling stave shown in Figure 8.4 is installed to cover the outside of bricks. Therefore, the stave provides the better sealing ability against the furnace gas and is more suitable for a high pressure operation

Table 8.1 Classification of indirect cooling water systems in iron and steel works

A. Department	B. Plant	C. Equipment to be cooled	D. Cooling system	E. Water used
Iron Production	Coke	Gas cooler	Cooling tower	Industrial water
	Sintering	Machine, etc.	Cooling tower	Industrial water
	Pelletizing	Blower, etc.	Cooling tower	Industrial water
	Blast furnace	Furnace body — Stave type	Boiler method (evaporation cooling method)	Deaerated demineralized water, demineralized water
			Closed recirculating	Industrial water
			Cooling tower	Industrial water
		Furnace body — Cooling plate type	Cooling tower	Industrial water
		Tuyere	Cooling tower	Industrial water
		Hot blast valve	Cooling tower	Industrial water
			Closed recirculating	Industrial water, softened water, demineralized water
		Furnace bottom	Cooling tower	Industrial water
		Blower, compressor, etc.	Cooling tower	Industrial water
Steel Production	Converter	Lance	Cooling tower	Industrial water, softened water
			Closed recirculating	Industrial water, softened water, demineralized water
		Hood	Boiler method (evaporation cooling method)	Deaerated demineralized water
			Closed recirculating	Industrial water, softened water, demineralized water
			Cooling tower	Industrial water
		Machinery, equipment, etc.	Cooling tower	Industrial water
	Continuous casting	Mold	Cooling tower	Industrial water
			Closed recirculating	Industrial water, softened water, demineralized water
Rolling mills	Blooming	Roll	Cooling tower	Industrial water
	Hot rolling	Heating furnace	Cooling tower	Industrial water
	Cold rolling	Gas, common machinery, etc.	Cooling tower	Industrial water
Power plant, etc.	Power plant	Condenser	Cooling tower	Industrial water
		Bearing, etc.	Closed recirculating	Industrial water, softened water, demineralized water
	Oxygen	Chilling separator, common machinery, equipment, etc.	Cooling tower	Industrial water

of blast furnace comparing with the cooling box. Accordingly, the cooling staves are widely employed for cooling blast furnace bodies in the present.

Since the cooling staves are made of carbon steel, their corrosion should be controlled by applying suitable corrosion inhibition methods.

For cooling the staves, following three systems are employed:

① Evaporation cooling system using a boiler of feeding deaerated demineralized water,
② Closed recirculating cooling water system having secondary coolers,
③ Open recirculating cooling water system (cooling tower system).

In the case of evaporation cooling system, the boiler is treated by using oxygen scavengers, boiler compounds and so on as same as general boilers.

In the closed recirculating cooling system , nitrite based corrosion inhibitors are generally applied together with biocides for nitrification bacteria.

In the cooling tower system, phosphate or phosphate-zinc based corrosion inhibitors, scale inhibitors and biocides are used.

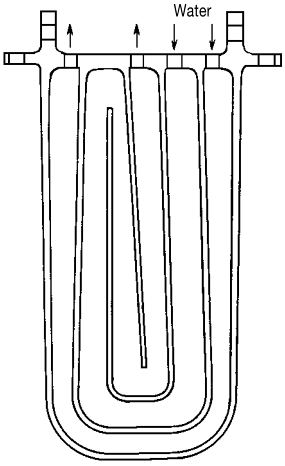


Fig. 8.3 Cooling box (six-pass type)

The cooling boxes are generally cooled by using cooling tower system and are treated by corrosion inhibitors, scale inhibitors and boicides.

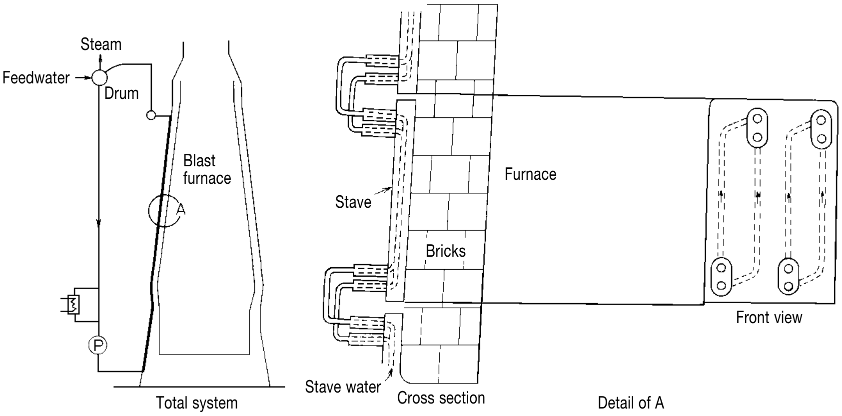


Fig. 8.4 Cooling staves and their installation at a blast furnace

Since the cooling boxes are made of copper, the copper corrosion inhibition is required in this system.

As the cooling condition of the blast furnace body affects the reactions in the furnace inside, the reduction of cooling efficiency relates to the productivity of the furnace. Therefore, the application of an appropriate water treatment is essential to provide the safe and efficient operation of the furnace.

8.3.2 Tuyere Cooling Systems

A tuyere is a copper made water cooling nozzle blowing the hot blast from a hot stove into the blast furnace. Figure 8.5 shows the structure of a tuyere.

As the top of tuyere is exposed to the extremely high temperature of the hot blast and the inside of blast furnace, the heat transfer condition is very severe. Therefore, a small amount of scale adhesion on the heat transfer surface of tuyere remarkably reduces the cooling efficiency and shortens the life of tuyere by accelerating the hot metal attack.

As the tuyeres are periodically exchanged, they are sometimes cooled by using cooling tower system which operates under a low cycles of concentration without water treatment chemicals. However, the use of suitable corrosion and scale inhibitors extends the survice lives of the tuyeres and the other equipments in the cooling water system.

8.3.3 Hot Blast Valve Cooling Systems

Generally, three to four hot stoves are installed for a blast furnace and each stove is intermittently operated to send the hot blast to the furnace. A hot blast valve of each hot stove is opened for sending the hot blast and closed during the heat accumulation.

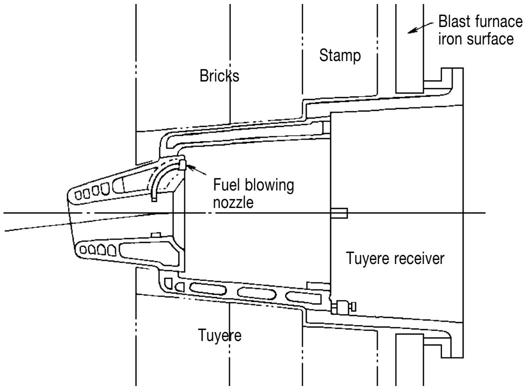


Fig. 8.5 Structure of a tuyere

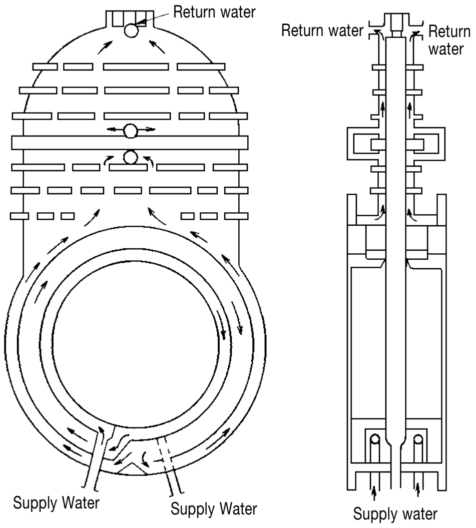
The hot blast valve is made of copper and carbon steel. The structure and the cooling water flow are shown in Figure 8.6.

The hot blast valves are usually cooled by using perfect closed or general closed systems. Cooling tower systems are sometimes used for cooling them.

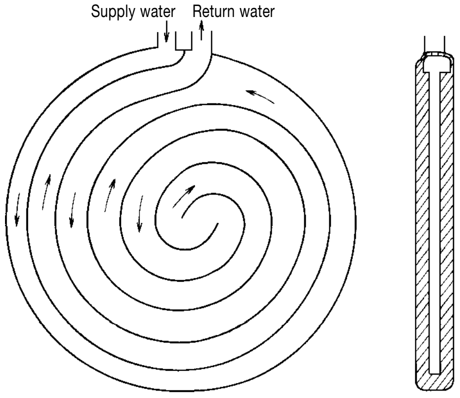
In the perfect closed system, demineralized water is used and treated by using oxygen scavengers, phosphates and alkalis like a general boiler water treatment.

In the case of general closed recirculating cooling water systems, nitrite based corrosion inhibitors and biocides are used.

In the cooling tower systems, the cracking of valve due to scaling may be generated under no scale inhibitor treatment. Therefore, the use of



(a) The structure and cooling water flow of a hot blast valve box



(b) The structure and cooling water flow of a hot blast valve

Fig. 8.6 Structure of a hot blast valve and the box

the inhibitors is inevitable.

8.3.4 Lance and Hood Cooling Systems of Converters

In Japan, the oxygen converter gas recovery system (OG system) is generally employed for recovering the converter gas as a fuel gas. Figure 8.7 shows a flow diagram of the OG system.

In the OG system, the equipments to be cooled are the lance blowing oxygen into the converter, and the hood consisting of the skirt, upperhood, lower-hood and the radiation area.

The structure and cooling water flow of a lance are shown in Figure 8.8. The lance has a triple tube structure made of carbon steel and the nozzle of the top part is made of copper. Oxygen is blown into the converter from the nozzle through the center tube. The cooling water is supplied to the middle pass and discharged from the upper side of the outer pass. The nozzle is received a large radiation heat from a molten steel and the splash of steel. Since the reduction in the cooling efficiency causes the break of the nozzle by the melting metal, the scale inhibition is inevitable for this system.

The hood is made of carbon steel and cooled by using following three methods:

① Evaporation cooling system using a boiler of feeding deaerated demineralized water,
② Closed recirculating cooling water system having secondary coolers,
③ Open recirculating cooling water system (cooling tower system).

As the heat flux of the hood cooling is very high and 200,000 to 500,000 $\text{kcal/m}^2\cdot\text{h}$, the evaporation cooling system or the closed cooling water system is generally used to prevent the scale problems of the hood.

In the case of cooling tower system, corrosion and scale inhibitors are used for keeping the heat transfer efficiency.

8.3.5 Mold Cooling Systems of Continuous Casting Plants

Continuous casting is a method of producing slab, bloom or billet directly from molten steel. Continuous casting plants are classified into slab , bloom and billet plants according to the sizes of steel products.

Figure 8.9 shows the outline of a continuous casting plants. The outflow of molten steel is adjusted through the tundish nozzle, and it enters the copper mold cooled by the indirect cooling water.

The steel is cooled through the mold and the surface of 10 to 20 mm in the thickness is solidified. After drawing out from the mold, the steel is perfectly solidified by spraying water. Then the size of the steel is adjusted by pinch rolls and is cut by the cutter to make products.

In the continuous casting plat, indirect cooling water cools molds, rolls and machineries. Generally, cooling tower system are employed in this plant, and they are treated by using corrosion and scale inhibitors. However, in the case of billet

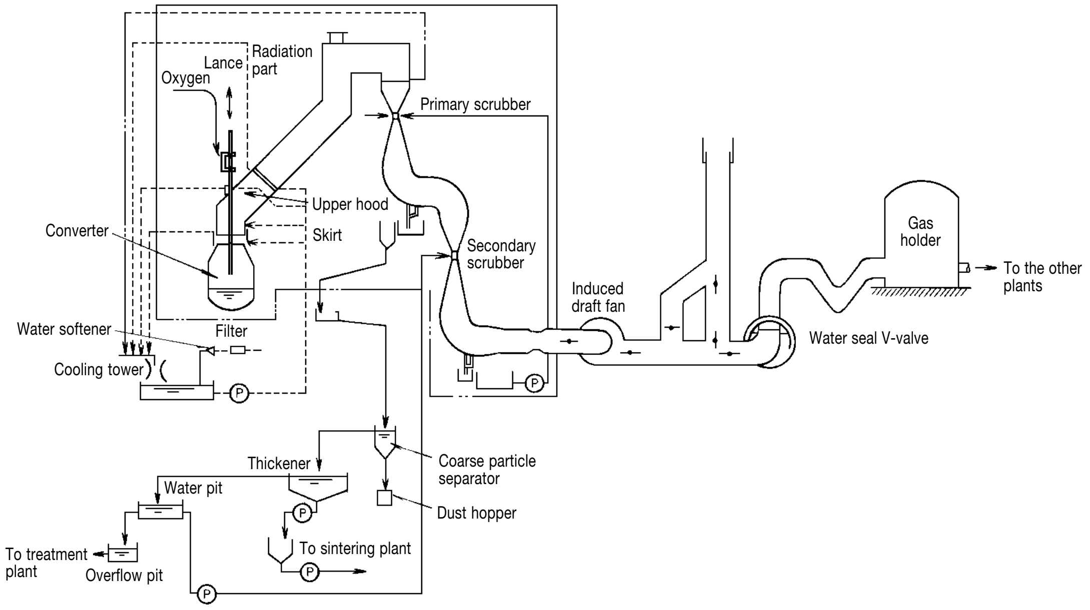
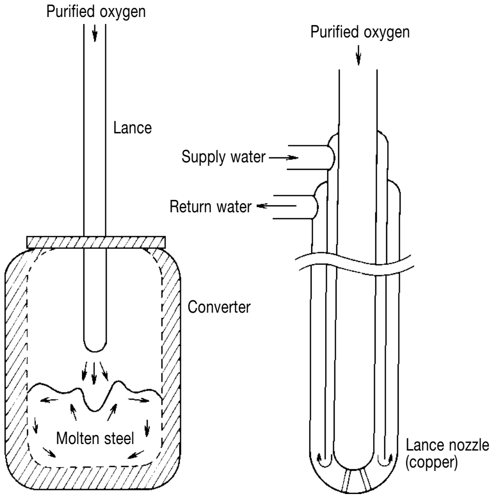


Fig. 8.7 Flow diagram of a oxygen converter gas recovery system (OG system)



(a) Setting of a lance into a converter

(b) Structure and cooling water flow of a lance

Fig. 8.8 Setting and structure of a lance

mold which is the smallest copper made mold with the size of 10 to 15 cm square, about 0.5 cm thick and about 100 cm long, even a small amount of scaling causes the deformation of mold. Therefore, a sufficient care should be paid for the cooling water quality and the chemical water treatment to prevent the scale problems.

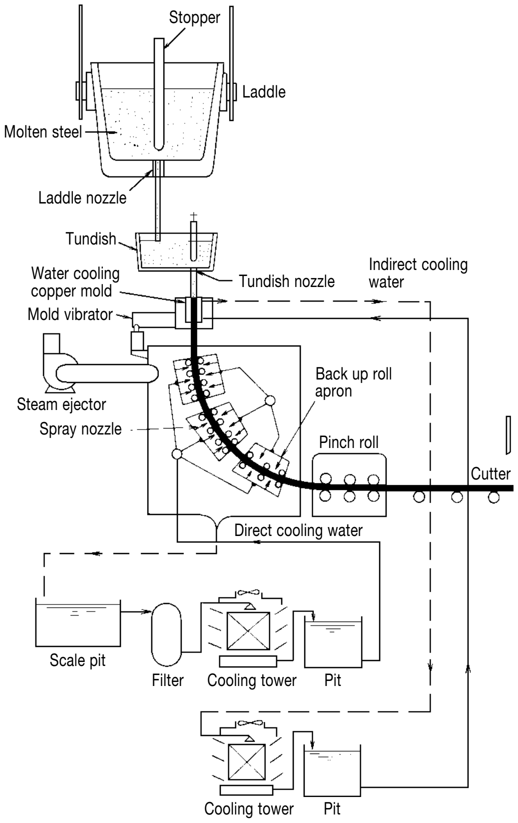


Fig. 8.9 Outline of a continuous casting plant

The best method for the scale inhibition is the employment of a closed cooling water system for the billet mold cooling.

8.4 Problems in Direct Cooling Water Systems and Their Countermeasures

Direct cooling water systems in iron and steel mills are the water spraying system of continuous casting plants, the cooling water system of rolling mills and so on. Main problems in the direct cooling water systems are the corrosion of machineries, etc., and the clogging of spray nozzles.

8.4.1 Spray Water Systems of Continuous Casting Plants

In the spray water system of continuous casting plant, water is directly sprayed to the steel products at the secondary cooling zone after the mold for cooling and solidifying them. The outline of this spray water system is shown in Figure 8.9.

After spraying water, the suspended solid concentration of the water becomes a very high. Then the suspended solids are removed by using scale pits, sedimentation ponds, filters, etc. Corrosion problems and the cloggings of spray nozzles occur in this system. The corrosion problems of rolls, machineries and so on occur when the pH of cooling water is reduced and/or the salt concentration is increased. The machineries surrounding the spray zone are repeatedly wetted and dried, then, the salts in the spray water are concentrated on the metallic surfaces. Accordingly those machineries are severely corroded. This type of corrosion is decreased by using corrosion inhibitors, however, the use of corrosion resistance metals, coating, lining, etc., is required for the sufficient corrosion inhibition. The pH reduction of cooling water is sometimes caused by applying a molding powder which is used as a lubricant between the mold and molten steel. The main components of the powders are calcium salts and silica, but fluorides are formulated with them at the 1.5 to 10% to reduce the melting point of powder. Since the fluorides dissolve into the cooling water and yield hydrofluoric acid, the higher formulation ratio gives the lower pH to cause the corrosion.

The use of corrosion inhibitors together with pH control agents effectively controls the corrosion problems. However, the corrosion inhibitors are considerably consumed in this system, because the suspended solids combine with the inhibitors and removed by the filter and so on. Accordingly, the consumption of the inhibitor in the direct cooling water system is much higher than that in the indirect cooling water system.

The clogging of spray nozzle is happened by various causes. The factors causing the clogging vary depending on each facility and its operational conditions. Table 8.2 summarizes the causes of spray nozzle clogging and the countermeasures.

To prevent the nozzle clogging, firstly the concentration of suspended solids in spray water has to be minimized by using strainers with suitable mesh, and by controlling the clarifier and filter operation appropriately. Then the use of chemicals, such as corrosion inhibitors, scale inhibitors and biocides, may show the sufficient effects.

Table 8.2 Causes and countermeasures of spray nozzle clogging

Causes	Countermeasures
Mill scale leaked from settling pond and filter	Improvement on operational conditions of settling pond and filter Use of suitable flocculants
Corrosion products from carbon steel piping	Use of corrosion resistance materials Use of corrosion inhibitors
Grease leaked from filter	Improvement on operational conditions of filter Replacement or cleaning of filter media
Slime growth in system	Application of chlorination, non-oxidizing biocides, etc.
Scale composed of calcium carbonate, etc.	Improvement of water quality, such as, reduction of the cycles of concentration, etc. Use of scale inhibitors
Coagulants and flocculants leaked from settling pond and filter	Improvement on operational conditions of equipment Reduction of chemical dosages

8.4.2 Spray Water Systems of Rolling Mills

In the rolling mills, water is sprayed for cooling the rolls and finish products. As the water is contaminated with mill scales and oils, it is treated by sedimentation and filtration. Figure 8.10 represents the water flow diagram of a hot rolling mill. Troubles in the direct cooling water system are similar to those in the continuous casting plants, such as the corrosion of rolls, products, etc., and the clogging of spray nozzles.

The countermeasures for the corrosion and nozzle clogging are the same as those for the spray water system in the continuous casting plants. Water treatment chemicals are considerably consumed by suspended solids and so on in this system.

8.5 Troubles and Countermeasures in Gas Cleaning Water Systems

In iron and steel works, gas cleaning water is used for cleaning the exhaust gasses of sintering plant, blast furnace, converter and so on. The gas cleaning water must be cleaned as much as possible and the proper flow must be maintained in order to supply the clean gas stably.

Even though dust in the gas cleaning water is removed by sedimentaion treatment, the zinc and calcium ions in the water deposit as the scales in the system. The scaling lowers the water flow rate and the gas cleanliness.

This section describes scale troubles in the blast furnace gas and the converter gas cleaning water systems, and their countermeasures.

8.5.1 Blast Furnace Gas Cleaning Water Systems

(1) Outline of system

The blast furnace gas (BFG) of 1,400 to 1,700 Nm^3 is produced per ton of pig iron in a blast furnace.

The BFG contains large quantities of combustible gasses, such as CO and H_2, and has the calorific value of about 800 kcal/Nm^3 as shown in Table 8.3. This corresponds to about one-third of the energy of fuel charged into the blast furnace. To effectively utilize this energy, the BFG is recov-

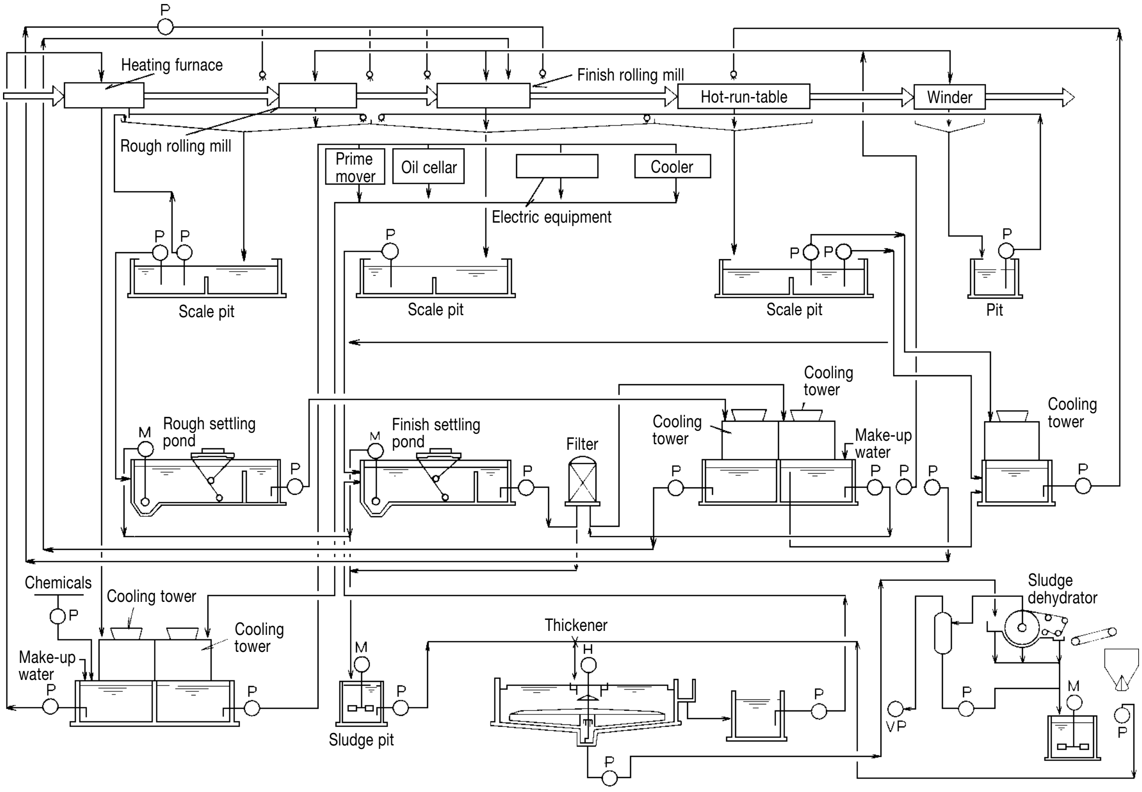


Fig. 8.10 Water flow diagram of a hot rolling mill

Table 8.3 Yield and composition of blast furnace gas

Yield (Nm^3/ton steel)	Calorific value (kcal/ Nm^3)	Composition (%)			
		CO	CO_2	H_2	N_2
1,400–1,700 (1,550)*	630–830 (737)*	20.0–23.5 (22.0)*	18.0–23.0 (21.1)*	1.6–6.0 (2.8)*	48.0–57.0 (54.1)*

* ( ) : Average value

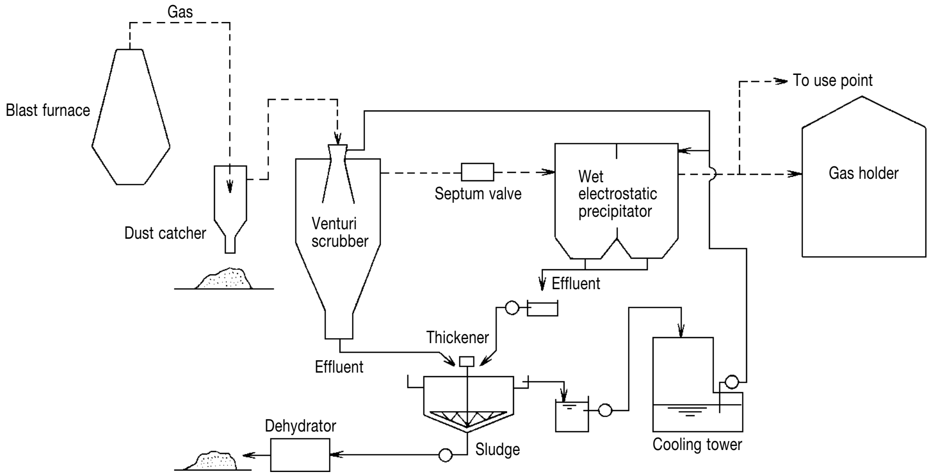


Fig. 8.11 Flow diagram of a blast furnace gas cleaning plant

ered and used as a fuel for the hot stove, coke oven, heating furnace, boiler for power plant, etc.

The BFG discharged from the furnace top contains much dust (10 to 20 g/Nm^3)* and moisture. If this gas is used without any treatment, it causes not only the reduction of thermal efficiencies of the combustion systems but also their operation troubles. Thus, the BFG is cleaned by using the gas cleaning plant shown in Figure 8.11 and dehumidified by cooling.

The gas cleaning facility usually consists of a dry-type dust separator, a wet-type venturi scrubber (VS), and an electrostatic precipitator (EP). The BFG cleaning water system employs a water recirculation system for recovering the gas cleaning water.

Using dust collectors, the dust in the BFG is reduced to less than 10 mg/Nm^3.

The return water from the VS and EP has 600 to 4,000 mg/*l* of suspended solids. The water is sent to a thickener, where suspended solids are removed by sedimentation treatment. The water treated by the thickener is recycled as the gas cleaning water. In some cases, the water is cooled in a cooling tower** and supplied to dust collectors.

Sludge removed by the thickener is dewatered with a dehydrator, and then utilized as a raw materials for iron production together with the dust removed by the dust separators.

Table 8.4 shows the compositions of dusts in BFG removed by a dry or wet-type dust collector.

In order to increase the electric power generation of top pressure recovery turbine (TRT), the conventional wet-type dust collection system has been recently replaced by the dry or semi-dry type dust collection system of which minimizes the energy loss due to the reduction of the gas temperature and pressure.

In other words, the conventional method based on the two stage VS or based on VS and the wet-type EP has been gradually replaced by the dry-type EP system, the VS-dry EP system, or the system of VS equipped with EP.

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* The allowable maximum dust content in the gas as fuel is 30 mg/Nm^3 for the heating furnace or the boiler, and 15 mg/Nm^3 for the hot stove or the coke oven. Generally, the value of below 10 mg/Nm^3 is adopted in field.

** The use of cooling tower is seldom in this system in Japan.

Table 8.4 Chemical analyses of dusts in blast furnace gas Unit (%)

Dust	T-Fe	FeO	SiO_2	Al_2O_3	CaO	MgO	TiO_2	Mn	P	S	Cu	Zn	K_2O	Na_2O	C
Wet dust	28.2	3.3	6.2	2.8	3.2	0.8	0.3	0.34	0.068	0.315	0.01	0.29	0.13	0.07	44.8
Dry dust	36.6	5.7	6.1	2.8	3.9	0.8	0.4	0.37	0.080	0.472	0.01	2.09	0.13	0.06	27.0

In the dry-type dust collection system, a drain containing hydrochloric acid is generated in the gas line immediately after the TRT, and it cuases the corrosion of the gas line. To prevent the corrosion, water including an alkali is sprayed to the gas line immediately behind the TRT, but the alkali consumption is usually high. Therefore, the dust collected by the dry-type EP, containing alkaline components, is sometimes dosed into the circulating water.

(2) Scale troubles and their countermeasures

In the blast furnace gas cleaning system, the gas cleaning water is recirculated. Since zinc and calcium compounds in the dust of BFG dissolve into the gas cleaning water and concentrated, they deposit again as scales in the circulation water line and so on. Those scales reduce the water flow in the piping and clog the water spray nozzles.

To prevent those scale problems, the quality of gas cleaning water must be adequately controlled and scale inhibitors have to be applied.

(a) Quality of gas cleaning water and scale composition

Table 8.5 shows the typical qualities of gas cleaning water after the sedimentation treatment and the compositions of scales deposited in the pipings. The quality of gas cleaning water is greatly changed by the recirculation rate of the water and the amount of alkalis using for the pH control. Recently, the gas cleaning water systems have been generally operated at a high water recirculation rate with a small amount of water blowdown because of water saving and environmental preservation. Therefore, the electrical conductivity of the water has tended to rise. The quality of the water is affected by the kinds and compositions of raw materials charged into the blast furnace, and the furnace operational conditions.

Especially, the zinc content of pellets or sinters, and the amount of limestone used as the flux affect the amount of zinc and calcium compounds dissolving into the gas cleaning water.

When an appropriate flocculation and sedimentation treatment is carried out, the suspended solid concentration of the treated water is reduced to 50 mg/*l* or below.

Scales deposited in the blast furnace gas cleaning water system contain basic zinc carbonate [$Zn_4CO_3(OH)_6 \cdot H_2O$], calcium carbonate and iron oxide, as the main components. In the system where the pH of gas cleaning water is low at 6.5 to 7.5, the main components of scales are basic zinc carbonate and iron oxides. In the case that the pH is high at 8.0 or higher, the main component becomes calcium carbonate.

Table 8.5 Qualities of blast furnace gas cleaning waters and the scale compositions

Gas cleaning system		A	B	C	D
Water quality	pH	6.9–7.2	7.5–7.6	7.6–8.0	8.0–8.5
	Conductivity (μS/cm)	4000–4500	2900–4300	2000–2500	10000–15000
	M-alkalinity (mg $CaCO_3/l$)	180–220	1000–1500	250–350	3000–5000
	Calcium hardness (mg $CaCO_3/l$)	700–800	1000–1500	200–250	100–200
	Zinc ion (mg/*l*)	80–100	30–50	3–5	5–8
	Suspended solids (mg/*l*)	25–50	20–35	10–30	20–30
Scale composition (%)	Calcium oxide (CaO)	Trace	4.2	7.4	40.0
	Iron oxide (Fe_2O_3)	20.2	3.8	4.5	1.3
	Zinc oxide (ZnO)	32.2	54.2	42.4	13.7
	Carbonic anhydride (CO_2)	4.1	—	8.8	27.6
	Ignition loss (600 ± 25°C)	18.5	24.6	15.4	9.0
Chemical component of scale		$Zn_4CO_3(OH)_6 \cdot H_2O$ Fe_2O_3	$Zn_4CO_3(OH)_6 \cdot H_2O$ ($CaCO_3$)	$Zn_4CO_3(OH)_6 \cdot H_2O$ ($CaCO_3$)	$CaCO_3$ $Zn_4CO_3(OH)_6 \cdot H_2O$

(b) Process of scale formation

In the blast furnace gas cleaning system, basic zinc carbonate and calcium carbonate deposit in the water when the water becomes a supersaturation solution with them.

The BFG contains about 20% of carbon dioxide (CO_2). The gas cleaning water absorbs the carbon dioxide gas during dust collection in scrubbers, and the pH is lowered. Accordingly, the zinc and calcium compounds in the BFG dust dissolve into the gas cleaning water. When the gas cleaning water is exposed to the atmosphere at the thickener, etc., the pH is risen by releasing the carbon dioxide gas.

The solubilities of basic zinc carbonate and calcium carbonate widely drop as pH rises as shown in Figure 8.12. For this reason, when zinc and calcium ions in the water exceed their solubility, basic zinc carbonate and calcium carbonate deposit as the scales in the pipings.

Especially in the cooling tower, much carbon dioxide gas is released and the pH of gas cleaning water is rises by 0.5 to 1.0. Therefore, much scales deposit and adhere to the tower packing and so on.

In the blast furnace gas cleaning water system, suspended iron oxides and colloidal iron compounds leaked from the thickener form the flocs by their aggregation. Then those flocs precipitate and adhere as scales to a low flow rate part of the piping. Since this type of scale weakly attaches to the solid surface, the scaling infrequently occurs when the water flow rate is not low.

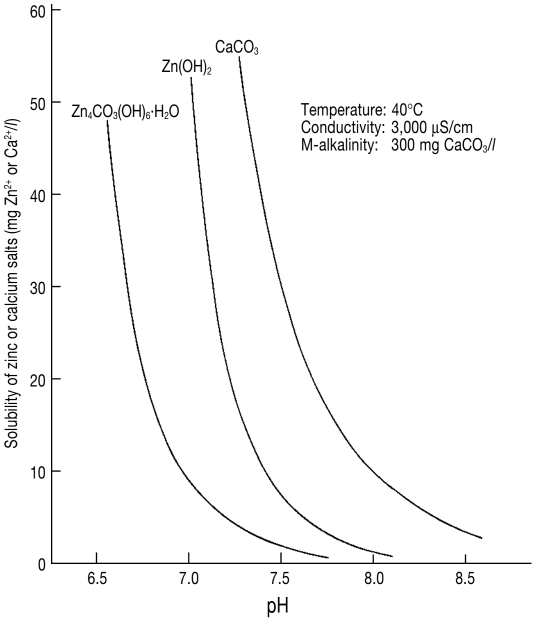


Fig. 8.12 Relationship between pH and solubilities of various scale components in a gas cleaning water

However, deposit type scales, such as calcium carbonate, deposit on the surfaces of metal and suspended solids, where act as crystal nuclei, and grow up. As the result, the deposition type scale captures the suspended solids and adheres as a hard scale to the piping wall.

Thus, the inhibition of the deposition type scales also reduces the scaling rate of sedimentation type scales as shown in Figure 8.13.

(c) Scale prevention

Generally, following two methods are utilized for the scale control:

① Removal of scale-forming components from water,

② Use of scale inhibitors.

In the blast furnace gas cleaning system, the both methods are applied in the combination. Zinc, a main component of scale, is precipitated by increasing the pH up to 8 or more, and sedimented together with suspended solids in the thickener. Then the zinc concentration in the water is reduced to 5 mg/*l* or below at the thickener outlet. Scale inhibitors are used to prevent the scaling of remaining zinc and calcium carbonate.

Generally, caustic soda is used as an alkali and added into the gas cleaning water at the inlet of the thickener. Alkaline effluents yielded in iron and steel works, such as the converter gas cleaning water, are sometimes supplied to the blast furnace gas cleaning water to control the pH.

Polyphosphates, phosphonates and low-molecular weight polyacrylates have been widely used as scale inhibitors. These inhibitors show the suffi

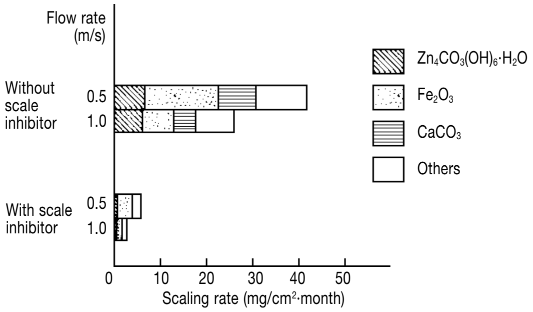


Fig. 8.13 Effect of a scale inhibitor and the influence on the scale composition

cient effects when the pH is satisfactorily controlled at 8 or higher. However, the pH reduction deteriorates the effects of inhibitors because the zinc concentration in the water increases at the thickener outlet.

Recently, acrylic acid based copolymers and terpolymers preventing zinc scales have been developed and applied for the blast furnace gas cleaning water systems. Figure 8.14 compares the scale inhibition effects of a polyacrylate and a copolymer in a water of low pH and high zinc concentration.

The use of scale inhibitors for zinc and calcium carbonate scales reduces the alkali consumption for the zinc removal in the thickener.

The injection point of scale inhibitors is generally the suction side of the circulation pump of the gas cleaning water. The inhibitors are continuously injected into the circulation water because most of them are consumed during the one cycle of water circulation by the adsorption with the suspended solids and so on.

8.5.2 Converter Gas Cleaning Water Systems

(1) Outline of system

In a converter, steel is produced by blowing pure oxygen gas and removing the carbon from molten iron. A large quantity of high temperature gas (about 1,600° C) composed of mainly carbon monoxide containing fine iron oxide dust of 300 μm or below is generated during the blowing. The amount of dust generated from converter is generally several kilograms per ton of crude steel.

The converter gas is cooled and the dust is removed for recovering the energy. Energy recovering methods are divided into combustion and non-combustion methods. In the combustion method, the flue over the converter has a boiler structure and the energy of the gas is recovered as steam. In the non-combustion method, a movable skirt is installed between the converter throat and the flue for shutting out air from the recovered gas. Venturi scrubbers are generally used as the dust collector in this method.

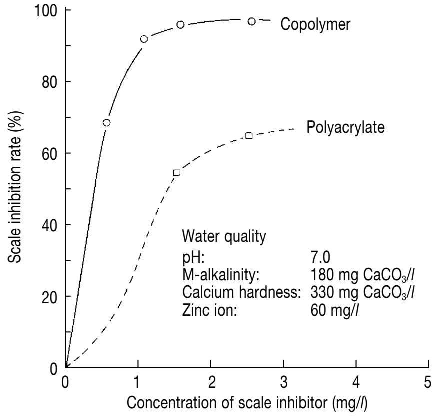


Fig. 8.14 Comparative scale inhibition effects of a polyacrylate and a copolymer on a mixed scale of zinc and calcium carbonates

The non-combustion methods, include the OG, IRSID·CAFL, BAUMCO methods and so on. In Japan, the OG method was developed and has been widely adopted.

Figure 8.7 (p.8-8) shows the flow diagram of the OG system. The converter gas is cooled from around 1,600° C to about 1,000° C in the hood and the radiation sections.

Then it passes through the primary and secondary ventury scrubbers, and is cooled to about 70° C. The dust content is reduced to less than 0.1 g/ Nm^3.

The gas cleaning water collects the dust in the gas in the primary and secondary scrubbers. The suspended solid concentration in the water is 100 to 500 mg/l in the non-blowing time, and increases 1,000 to 2,000 mg/l in the blowing time. After passing through a coarse grain separator, the water is treated by the thickener to remove the dust and to recycled.

(2) Scale troubles and their prevention

(a) Scale formation and its problems

Calcium compounds, such as quicklime and light-burned dolomite, are used as a flux, etc., in converters. The composition of those calcium compounds are shown in Tables 8.6 and 8.7. Molten steel is intensively stirred by blowing pure oxygen in the converter, then dust is formed. This dust is collected by the gas cleaning water and it suspends or dissolves into the water. Accordingly, the gas cleaning water includes a high concentration of calcium ions and the pH becomes an alkaline. As the results, scales composed of calcium

Table 8.6 Chemical compositions of a limestone and a quicklime Unit (%)

Kind of lime	CaO	SiO_2	MgO	Fe_2O_3	Al_2O_3	P	S
Limestone	54–56	0.5	1.8–5	0.5–3	0.05–0.2	< 0.01	trace
Quicklime	90–95	1–2	0.8	0.3	0.1–0.2	0.02	< 0.05

Table 8.7 Chemical composition of a light-burned dolomite Unit (%)

CaO	MgO	Ignition loss	SiO_2	Al_2O_3	Fe_2O_3	CO_2
> 65.5	> 32.0	< 1.5	< 0.5	< 0.2	< 0.2	< 1.0

carbonate mainly deposit and adhere to various parts of the system.

Table 8.8 shows the chemical analyses of scales in converter gas cleaning water systems.

The scale adhesion in the piping reduces the circulation rate of the gas cleaning water. The scaling in the scrubbers deteriorates the dust collection efficiencies and the gas ventilation in the systems.

The main components of the scales are calcium carbonate and, the particles of iron and iron oxides. As the gas cleaning water is a supersaturation solution with calcium carbonate, calcium carbonate deposits in the piping, scrubbers and so on. The suspended solids in the water are caught by the deposited calcium carbonate and form the scale.

Table 8.8 Chemical analyses of scales in converter gas cleaning water systems (wt.%)

Sample	1	2	3
Calcium oxide (CaO)	17.2	21.4	13.9
Magnesium oxide (MgO)	2.5	3.7	2.9
Iron oxide (Fe_2O_3)	38.1	42.1	45.7
Acid insoluble matter	3.1	2.5	5.2
Sulfuric anhydride (SO_3)	trace	trace	trace
Carbonic anhydride (CO_2)	17.3	17.5	18.6
Phosphoric anhydride (P_2O_5)	0.8	0.8	0.9
Ignition loss (600 ± 25°C)	8.8	7.3	17.7

(b) Scale prevention

As the main component of scale is calcium carbonate in converter gas cleaning water systems, the prevention of the crystal deposition or the reduction of the crystal growth rate is an effective scale control method.

The former method is acid injection into the water to keep the pH in the unsaturation condition with calcium carbonate. This method is scarcely applied in the present because the low pH accelerates the metallic corrosion. The latter method is the use of scale inhibitors.

The quality of converter gas cleaning water widely varies according to the difference in the operational conditions of the converter or the structure and the operational conditions of the gas cleaning system.

The water qualities are basically classified into the four categories. Table 8.9 shows the typical water analyses of those four types of water. The features of those water types are as follows:

① A-I type

This is the most common type in Japanese iron and steel works. The supersaturation degree of water with calcium carbonate is not so high. Therefore, the scaling in this type of water is easily prevented by dosing scale inhibitors with the low dosages.

② A-II type

When the A-I type of water is concentrated at a higher ratio, it changes to the A-II type. This water is characterized by the high M-alkalinity, however, the use of scale inhibitors effectively controls the scale formation.

③ B-I type

This type is observed when a large amount of calcium based flux transfers from the converter into the exhaust gas. This type of

Table 8.9 Classification of the qualities of converter gas cleaning waters

Type of water	A-I	A-II	B-I	B-II
pH (25°C)	9.0	9.1	11.5	12.4
Electrical conductivity (μS/cm)	1,815	20,700	1,075	3,420
P-alkalinity (mg $CaCO_3/l$)	16	2,450	120	690
M-alkalinity (mg $CaCO_3/l$)	296	11,550	173	770
Calcium hardness (mg $CaCO_3/l$)	14	33	92	692
Chloride ion (mg/l)	58	560	48	72
Sulfate ion (mg/l)	123	451	36	152
Total iron (mg/l)	6.4	84	3.6	8.5
Suspended solids (mg/l)	11	50 >	20	50 >

water is a high pH, high alkalinity and high calcium hardness. Accordingly, the supersaturation degree with calcium carbonate becomes very high.

The scaling tendency of this water is higher than that of A-II type. However, the use of scale inhibitors is still effective.

④ B-II type

This type has higher pH, alkalinity and calcium hardness than those of B-I type. In case of this water, the use of scale inhibitors is not sufficient for the scale inhibition. The modification of water quality to the B-I or A-I type by dosing a special agent is required. Then scale inhibitors effectively control the scale problems.

Table 8.10 shows the effect of a polyacrylate based inhibitor for a gas cleaning water of B-I type. The scale thickness is reduced around 90% by applying the inhibitor. Table 8.11 shows the effect of a combined treatment of a polyacrylate based scale inhibitor and a water quality modification against a gas cleaning water of the B-II type. The scale inhibitor scarcely shows the inhibition effect against the B-II type water. However, the combined treatment of scale inhibitors together with the chemical water quality modification remarkably reduces the scaling rate.

8.6 Supply Water, Wastewater and Sludge Treatments

In iron and steel works, many kinds of coagulants and flocculants are used for treating supply water, gas cleaning water, oily wastewater, acidic wastewater, etc., at thickeners, clarifiers and so on. Sludge dewatering agents are also applied for dewatering sludges discharged from those equipments.

Table 8.12 summarizes the typical usages and kinds of those chemicals in iron and steel works. Among those chemicals, an organic coagulant used for oily wastewater shows the unique feature. The organic coagulant is a low molecular weight cationic polymer and has the higher coagulation activity than those of inorganic coagulants because of the higher cationic electrical charge density.

The combined use of this organic coagulant and an inorganic one widely reduces the dosage of inorganic one and the sludge volume. Accordingly, its reduces the cost of chemicals and sludge treatment.

Table 8.13 shows the advantage of this combined treatment comparing to a conventional coagulant treatment for an oily wastewater discharged from a cold rolling mill.

Table 8.10 Effect of a scale inhibitor against a converter gas cleaning water of the B-I type

Scale inhibitor	Scale thickness in second dust catcher (mm)	Inhibition rate (%)	Scale composition (wt.%)
Polyacrylate 3 mg/*l*	2.5	87.2	CaO 25.0, Fe_2O_3 42.5 CO_2 17.6, I.L. 19.7
None	17.0	—	CaO 37.0, Fe_2O_3 24.2 CO_2 26.7, I.L. 23.0

Test period: 30 days

Table 8.11 Effect of the combined treatment of a scale inhibitor and a water quality modification against a converter gas cleaning water of the B-II type

Polyacrylate based inhibitor (mg/*l*)		3	3
Chemical for water quality modification (mg/*l*)		0	200
Water quality	pH	12.4	9.4
	Electrical conductivity (μS/cm)	3,420	—
	P-alkalinity (mg $CaCO_3$/*l*)	690	20
	M-alkalinity (mg $CaCO_3$/*l*)	770	210
	Ca-hardness (mg $CaCO_3$/*l*)	692	40
Scaling rate in second dust catcher (mm/week)		50–60	Below 5
Frequency of scale removal		Once/week	Once/3 months

Table 8.12 (1) Typical usages and kinds of coagulants, flocculants and sludge dewatering agents in iron and steel works

Plant	Raw water treatment plant	Raw material yard	Sintering plant	Chemical plant	Blast furnace gas cleaning water system
Water to be treated	River water, well water, etc.	Cleaning water for conveyer	Gas cleaning water	Ammonia liquor waste	Gas cleaning water
Coagulants and flocculants	Ferric chloride, PAC,* Alum, Anionic polymers	PAC, Anionic polymers	PAC, Alum, Anionic or nonionic polymers	Ferric chloride, Ferric sulfate, Anionic polymers	(PAC) Anionic polymers
Sludge to be treated	Sludge from thickener	—	—	Excess sludge, Coagulation sludge	—
Dewatering agents	Anionic polymers	—	—	Cationic polymers	—

*PAC: Polyaluminium choloride

Table 8.12 (2) Typical usages and kinds of coagulants, flocculants and sludge dewatering agents in iron and steel works

Plant	Converter gas cleaning water system	Hot rolling mill		Cold rolling mill	
		Settling pond	Sludge pit		
Water to be treated	Gas cleaning water	Direct cooling water	Back-wash water of filter	Oily wastewater	Acidic wastewater
Coagulants and flocculants	Anionic or nonionic polymers	Anionic polymers	PAC, Anionic polymers	PAC, Cationic polymers, Nonionic or anionic polymers	Anionic polymers
Sludge to be treated	—	—	—	Scum from flotator	—
Dewatering agents	—	—	—	Nonionic or anionic polymers	—

Table 8.13 Advantages of an organic coagulant treatment for an oily wastewater in a cold rolling mill

Wastewater quality	Conventional inorganic coagulant treatment	Organic coagulant treatment	Advantage of organic coagulant treatment
SS: 300 mg/l COD: 400 mg/l Oil: 400 mg/l	PAC: 2,000 mg/l $Ca(OH)_2$: 200 mg/l Anionic flocculant: 2 mg/l	Organic coagulant: 15 mg/l PAC: 1,000 mg/l $Ca(OH)_2$: 120 mg/l Anionic flocculant: 2 mg/l	1. Reduction of water treatment cost: 30% 2. Reduction of sludge treatment cost: 25% 3. Large improvement in SS and oil removal

8.7 The Other Specialty Chemicals

8.7.1 Dust Blow-away Preventives for Raw Material Yards

The iron and steel works use a large amount of raw materials, such as iron ore and coal. Those raw materials are transported by ships, etc., unloaded, transported to raw material yards by beltconveyors, and piled there.

The dusts of raw materials are scattered during their unloading, transportation and storing. The dust blowing-away causes many problems, such as the deterioration of working environment, air pollution and the loss of raw materials. Dust blow-away preventives are used to prevent these problems.

These preventives are divided into the “wetting” and “coating” types. The wetting type is used for preventing the dust blowing-away when raw materials are transporting by unloaders or beltconveyors. The preventives are sprinkled from the nozzles installed in those transportation equipments. The preventives are dissolved or dispersed with water to make the 0.3 to 0.5% solutions. Then the solution is sprayed at the rate of 5 to 10 liters against 1 ton of raw material.

The coating type forms a durable film on the surfaces of raw material piles and prevents their dust scattering by wind. This type of preventives is sprinkled at the rate of 5 to 10 L/m^2 pile surface after preparing the 3 to 5% emulsion. Water sprinkling cars or sprinklers installed in the yard are used for the chemical application.

Figure 8.15 illustrates the application methods in the yard. Photograph 8.1(p. 8-22) shows the chemical spraying in a yard by using a sprinkling car.

8.7.2 Moisture Reducing Agents for Coal Piles

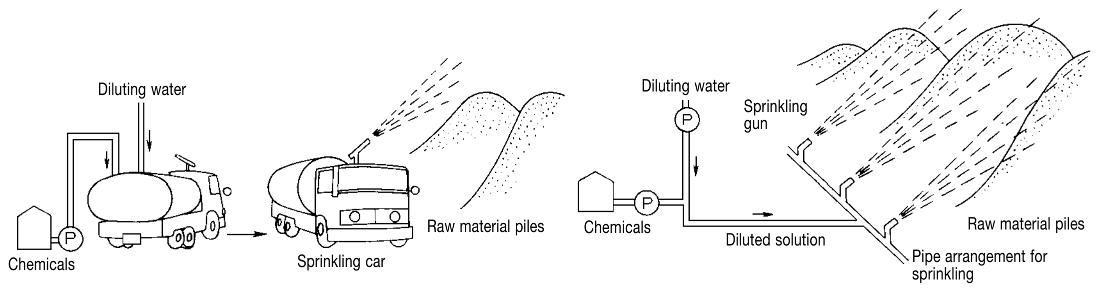
In the season of a high rainfall with 100 mm per month or over, the moisture of coal piles increases 1 to 2% comparing to that in a low rainfall season. Especially, a long and heavy rain causes the flow-out of coal because the moisture of the pile surface extremely increases. The coal flow-out results in the raw material loss and the deterioration in the quality of effluent from the yard. When the flow-out becomes a heavy, it may cause the break of the pile.

The 1% increase in the coal moisture increases the calorific value of about 1.3 x 10^4 kcal for drying of 1 ton coal. This means 2% increase in the fuel cost of coke plants.

Moisture reducing agents of the film forming type are used to prevent those problems. This type of agents is also effective to prevent dust blow-away. These moisture reducing agents are characterized by the water repellent property of film formed by them. Figure 8.16 (p. 8-22) shows the function of moisture reducing agents.

Acrylic resin based emulsions having high water repellent forces are used to prevent the rain water penetration to the piles and to reduce the coal moisture. For obtaining a sufficient moisture reducing effect, the surface of coal pile should be mechanically uniformed and stabilized. For this purpose, the surface conditioning of coal pile is carried out by pressuring the surface with roll, etc. A crane truck with a roll is generally used for the surface conditioning as shown in Photograph 8.2 (p. 8-22). The surface strength of coal pile is increased from 0.5 kg/cm^2 to 3.5 kg/cm^2 by applying the surface conditioning.

After the surface conditioning, the 5 to 10% solution of a moisture reducing agent is sprinkled on the coal piles with the dosage of 2 to 3 L/m^2. Photograph 8.3 (p. 8-22) shows the effect of the



(a) Method to sprinkle the chemical solution diluted in the tank of a sprinkling car

(b) Method to sprinkle the chemical solution diluted in the pipe

Fig. 8.15 Sprinkling methods of dust blow-away preventives

agent to prevent the break of coal piles. Figure 8.17 shows the effect of a moisture reducing agent on coal piles under various rainfalls. The chemical treatment reduces around 1% of coal moisture in the wide range of rainfall.

8.7.3 Pulverization Aids for Quicklime

The quicklime is made by calcinating limestone and its main component is calcium oxide (CaO). The quicklime is used for steel making, sintering, the production of ferroalloys and so on in iron and steel works. These processes share the 60% of quicklime consumption in Japan.

Figure 8.18 shows the uses of quicklime, etc., in iron and steel making processes. The hot metal discharged from the blast furnace is pretreated by the injecting a flux including pulverizred quicklime into the ladle before the converter to remove silicon and phosphorous. Quicklime and limestone are also added to the converter for removing phosphorous and sulfer.

The sizes of quicklime using in steel making processes are 3 to 6 mm for large one and around 100 μm for small one.

Figure 8.19 shows the flow sheet of a pulvarization process for quicklime. The aggregation of fine quicklime particles deteriorates the efficiency of pulvarizator. The addition of a pulvarization aid inhibits the aggregation of fine particles and promotes the pulvarization. It also improves the fluidity of fine particles. Accordingly, quicklime particles produced by using the pulvarization aid are easily and smoothly injected into hot metal.

Figure 8.20 shows the effect of an pulvarization aid on the pulvarization of quicklime. The use of the aid increases the ratio of fine particles with diameter of 125 μm or less.

8.7.4 Bulk Density Improving Agents for Coal

The increase in the bulk density of coal charged into coke ovens increases the strength and production of cokes. As the results, the energy consumption in the oven is reduced.

The conventional methods for improving the bulk density of coal include "the molded coal adding method"*, "the coal moisture adjusting method"** and "the oiling method"***.

The use of bulk density improving agents is more effective than those conventional methods. Generally, surfactants are used as the bulk density improving agents. This agent is uniformly

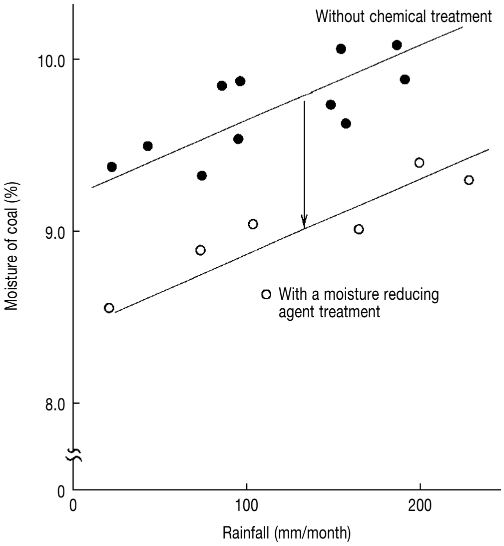


Fig. 8.17 Effect of a moisture reducing agent under various rainfalls

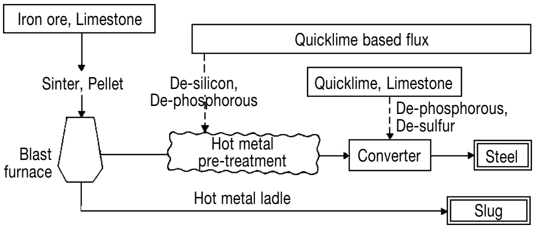


Fig. 8.18 Uses of quicklime in iron and steel making processes

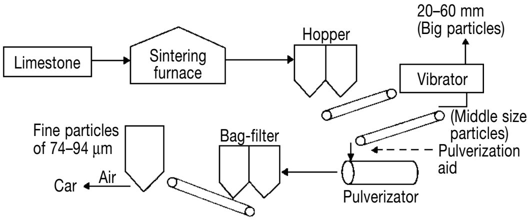


Fig. 8.19 Flow sheet of a pulverization process of quicklime

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* Molded coal made from powdered coal is mixed with powdered coal charged into a coke oven at the ratio of 10 to 30%.

** The moisture of coal is reduced to 5 to 6% by utilizing the waste heat of a coke oven. Then the coal is charged into the coke oven.

*** Heavy oil is sprayed on the coal charged into a coke oven.

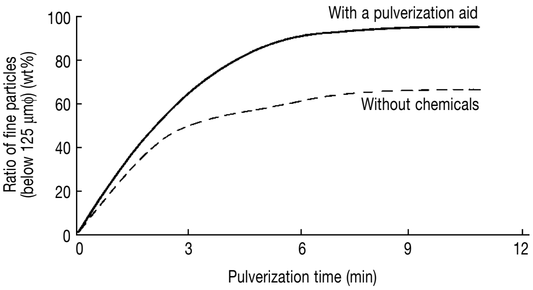

Fig. 8.20 **Effect of a pulverization aid on the pulverization of quicklime**

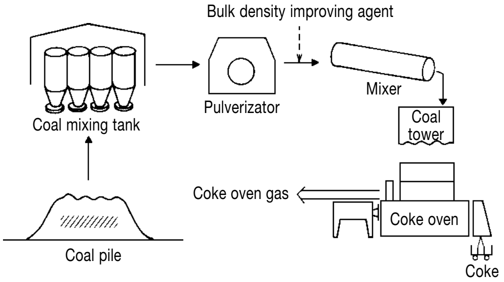

Fig. 8.21 **Flow diagram of a coke plant and the injection point of a bulk density improving agent**

mixed with powdered coal by using a mixer. The agent attached on the coal surface ensures the smooth flow of coal and minimizes the bad influence of the moisture increase which reduces the bulk density of coal. Figure 8.21 shows the flow diagram of coke plant and the injection point of a bulk density improving agent. Figure 8.22 shows the bad influence of moisture increase on the bulk density of coal and the effect of a bulk density improving agent.

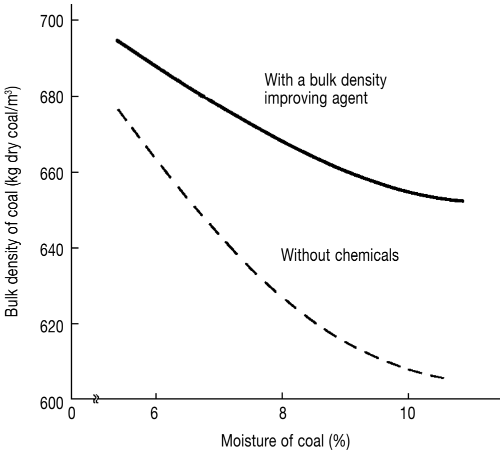

Fig. 8.22 **Effect of a bulk density improving agent**

Table 8.14 Effect of a bulk density improving agent in a coke oven (wt.%)

Dosage of agent (% vs. dry coal)	0	0.05
Bulk density of coal (kg/m^3)	730	771
Carbonization time (h)	21.6	21.3
Carbonization calory (kcal/kg)	603	574

Table 8.14 shows a typical effect of the bulk density improving agent in a field. In this case, the 80% of a powdered coal with the size of below 3 mm and the 20% of a molded coal are mixed. The moisture of the coal is 8.5%. The bulk density improving agent is sprayed to the coal on the belt conveyer with the dosage of 0.05% against dry coal. The use of the agent increases the bulk density at around 6% and reduces the fuel consumption in the coke oven at around 5%.

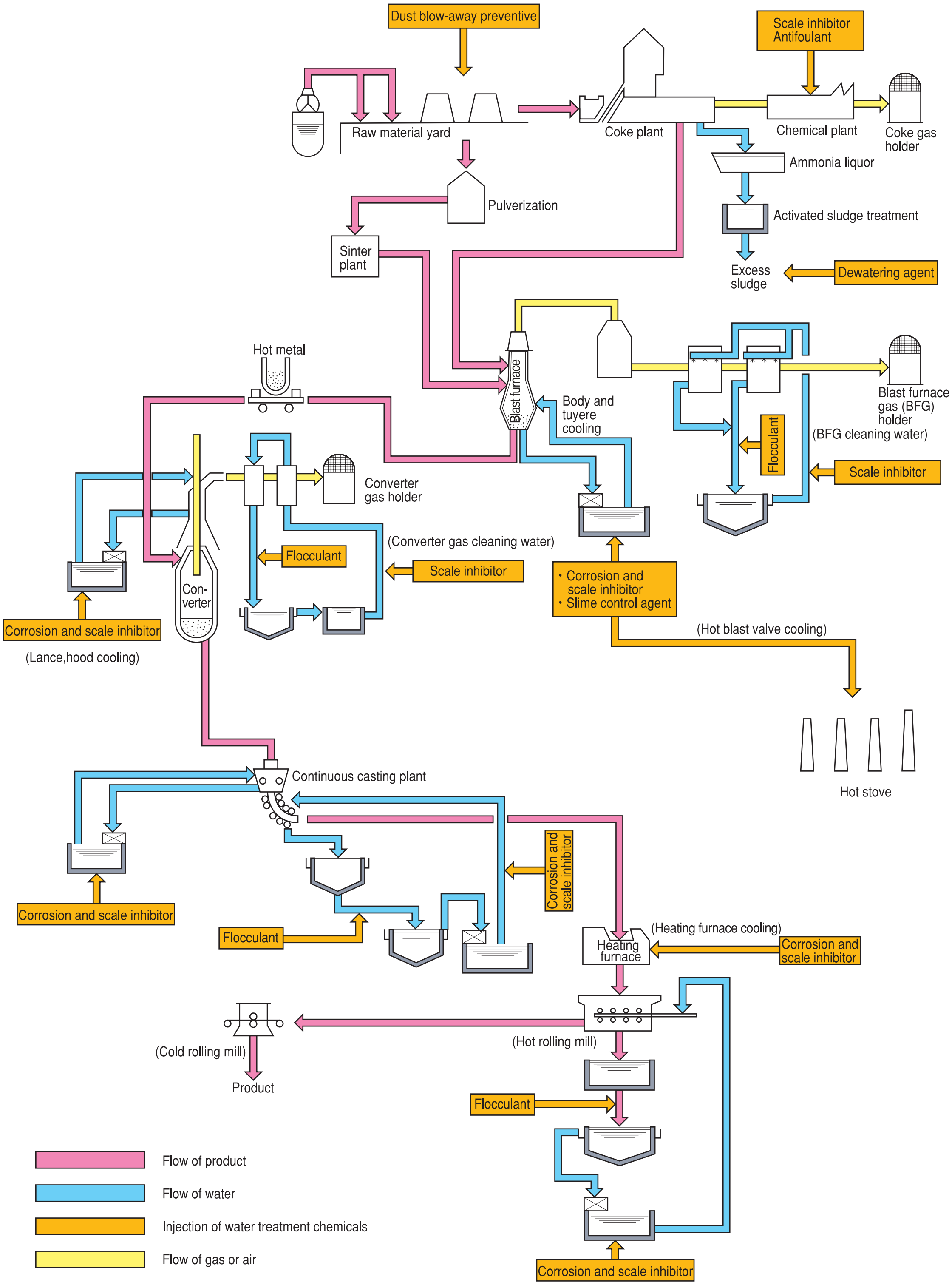

Fig. 8.2 Flow diagram of iron and steel making processes, and the use points of water treatment chemicals

9. Cleaning of Plants and Equipments

9.1 Purposes of Cleaning

The technical progresses in the design and construction of various production plants have made them large size and complicated systems. Accordingly, those plants require the advanced operational and maintenance technologies.

The operation of those plants cause the fouling of equipments, pipings, etc., with scales, corrosion products and so on. Those fouling reduce the operational efficiencies of plants and sometimes deteriorate the product qualities.

Especially, the fouling of high pressure and high temperature plants may cause the accidental troubles, such as the explosion and the fire. Those troubles may result in not only a reduction of products due to the plant shutdown, but also a loss of social trust in the enterprise.

Therefore, the scheduled shutdown maintenance of plants is generally carried out to recover the efficiencies and to prevent the trouble occurrences beforehand as well as to ensure the safe and efficient operation of plants after the restart-up. The cleaning of plants and equipments is an important measure for the maintenance.

Formerly, the cleaning of plants was generally carried out after detecting the problems, such as a reduction of the output. In the present, the cleaning is periodically carried out as a preventive measure. The purposes of cleaning are summarized as follows:

① Keeping of a designed thermal efficiency,
② Keeping of a designed flow rate,
③ Keeping of the performance of materials, such as strength,
④ Minimization of the damage of materials, such as corrosion and fatigue,
⑤ Minimization of a radiation exposure to workers in a nuclear power plant.

The details of the purposes are described below for main plants to be cleaned.

9.1.1 Boilers

Boilers are used as a power source and as a steam source in many processes. A main problem in the boiler operation is the scaling on the heating surfaces. The scaling reduces the thermal efficiency and causes the damages, such as the embrittlement and bursting of the heating tubes under the scale, by overheating.

Consequently, the cleaning is carried out to remove deposits and scales for recovering the thermal efficiency and for minimizing the damages of metals.

The occurrence of troubles like the bursting of heating tubes may require a large cost due to the reduced production, the repair of boiler and so on. The scheduled cleaning of boiler gives a large merit to ensure the safe and efficient operation until the next scheduled cleaning.

9.1.2 Nuclear Power Plants

As the operation of a nuclear power plant gradually increases the radiation of the auxiliary equipments, pipings, etc., the radiation exposure to the workers is also increased. Moreover, the workers are exposed to more radiation during the shutdown maintenance than that in the normal operation.

The cleaning, usually called decontamination, of nuclear power plants is carried out to reduce the radiation during the normal operation and the shutdown maintenance.

The reduction of radiation by the decontamination of the auxiliary equipments, etc., will reduce the radiation exposure to workers during the shutdown maintenance. As the result, the number of workers for the repair and the inspection can be reduced.

This is essential to realize the safe and efficient operation of nuclear power plants.

9.1.3 Industrial Manufacturing Plants

Petroleum refining and chemical plants have the various cooling and heating units, such as furnaces and heat exchangers. In those equipments, foulings are formed at the both sides of water and process fluids. The foulings cause the many problems, such as the reduction of production and thermal efficiencies, the shortening of their service lives and the deterioration of product qualities.

The cleaning is carried out to prevent those problems. In case of a large size manufacturing plant, since various equipments are comprehensively connected as one system, the operation stoppage of one equipment leads to the stoppage of whole system. In this case, it brings heavy losses.

The cleaning of those equipments during the scheduled shutdown maintenance is essential to ensure the safe and efficient operation of the plant until the next shutdown maintenance.

9.2 Cleaning Objects and Their Scale Problems

9.2.1 Boilers

In case of low or medium pressure boilers, the main components of the scale are hardness components, silica and metallic oxides.

In case of high pressure boilers, scale forming components, such as hardness and silica, scarcely enter to the boilers with the feedwater. However, the deposition of iron oxide on the heating tube surfaces is inevitable because the heating tubes are gradually attacked by the high temperature and high pressure water, and the boiler water is contaminated with corrosion products from the preheater and economizer.

Corrosion resistance materials, such as aluminum brass, cupronickels and monel metals, are used for the preheater and condenser tubes. Those metals are gradually attacked by the feedwater and condensate. As the result, the corrosion products of those metals enter into the boiler water and form the metallic oxide scales.

The scale thickness gradually increases during the boiler operation and may cause following problems.

(1) Damage of tube materials caused by the increased temperature

The thermal conductivities of scales are extremely small comparing with those of metals as shown in Table 9.1[1]. The conductivity of scale becomes smaller under a higher pressure with the higher boiler water temperature, as shown in Figure 9.1[2].

The deposition of a scale on the heating tube surface of boiler increases the tube wall temperature as shown in Figure 9.2. This increase of metal temperature causes the change in the crystal structure of the metal. The temperature beginning the metallic structure change is depending on the kinds of metals. Table 9.2[3] shows the temperatures at which the pearlite structures of various steels begin their spheroidizations during 10,000 hours of the use. Photographs 9.1 and 9.2 show

Table 9.1 Thermal conductivities of metals and boiler scales

Materials	Thermal conductivity (kcal/m•h•°C)
Carbon steels	40–60
Stainless steel (SUS304)	14
Copper	320–360
Scale of supercritical pressure boilers	1.2–1.5*1
Scale of subcritical pressure boilers	1.5–2.0*1
	2.0–2.5*2
Silica scale	0.2–0.4
Carbonate scale	0.4–0.6
Sulfate scale	0.6–1.0

*1 Boilers with feedwater preheater made of carbon steel tubes

*2 Boilers with feedwater preheater made of copper tubes

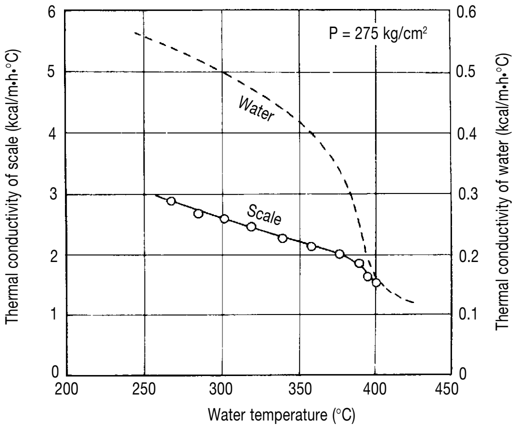

Fig. 9.1 **Changes in the thermal conductivities of water and a scale with the temperature increase under a high pressure**

Table 9.2 Temperatures changing the crystal structures of various steels

Kind of steel (JIS)	Composition (%)	Temperature* (°C)
STB 410	C below 0.18	500–520
STBA 12	Mo 0.45–0.65	520–540
STBA 22	Cr 0.80–1.25, Mo 0.45–0.65	550–580
STBA 23	Cr 1.00–1.50, Mo 0.45–0.65	550–580
STBA 24	Cr 1.90–2.60, Mo 0.87–1.13	550–590

* Temperature at which the pearlite structure begins the spheroidization during 10,000 hours of the use.

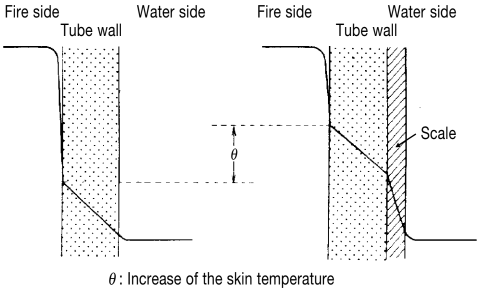

Fig. 9.2 Increase in the skin temperature of boiler tube caused by scale formation

the normal pearlite structure and a spheroidized pearlite structure of a carbon steel. The spheroidization of pearlite structure reduces the creep rupture strength of the carbon steel to cause the embrittlement and bursting of boiler tubes.

(2) Reduction of thermal efficiency

A scale formation increases the skin temperature of a boiler tube because of a small thermal conductivity of the scale. When the heat is supplied to the boiler at a constant rate, as the increase in the skin temperature rises the temperature of exhaust gas, the heat discharged with the gas is increased. That is, the scaling reduces the thermal efficiencies of boilers.

When the heat supply is increased to keep a constant steam generation from the boiler, the scaling increases the fuel consumption.

(3) Sludge accumulation in boilers

An increase in the scale thickness may cause the exfoliation from tube surfaces. The exfoliated scales gradually accumulate as the sludges on the bottoms of the drums and headers. Those sludges disturb the normal water flow in the boiler and sometimes cause their overheating.

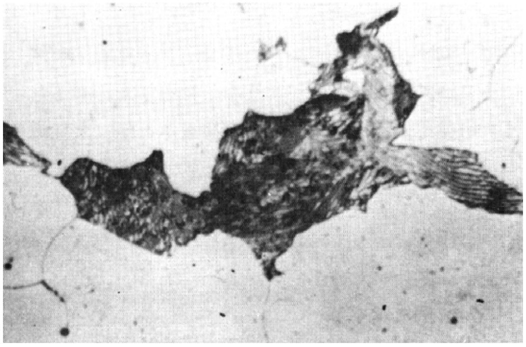

Photo 9.1 Normal pearlite structure of a carbon steel

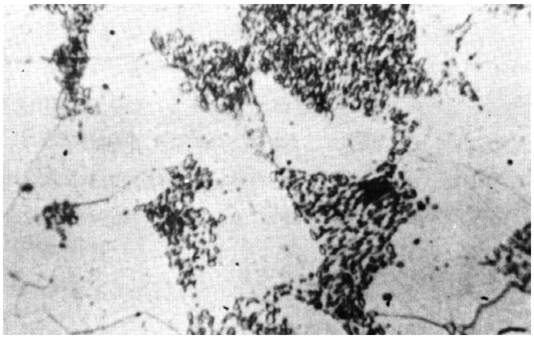

Photo 9.2 Spheroidized pearlite structure of a carbon steel due to a high temperature

(4) Acceleration of corrosion

The formation of ununiform scale or sludge accumulation may cause the under deposit corrosion, a kind of local corrosion, and shortens the service lives of boilers.

9.2.2 Nuclear Power Plants

In nuclear power plants, the most serious scale problems are the increase of radiation and the corrosion of equipments caused by the accumula tion of CRUD*. Those may jeopardize the safe operation of nuclear power plants.

9.2.3 Industrial Manufacturing Plants

In the industrial manufacturing plants, such as chemical plants, scaling (fouling) occurs at the both sides of process fluids and cooling water.

The problems caused by scaling are widely different at the process side and the water side as described below.

(1) Problems at the process side

(a) Deterioration of product qualities

Raw materials and their impurities may form scale or fouling by changing their qualities or by their excess concentration on the heating surfaces. The contamination of products with fouling matters deteriorates the product qualities.

(b) Reduction of production and thermal efficiency

The deposition of scale on the heat transfer surfaces of heat exchangers, etc., reduces their thermal efficiencies. A heavy scale formation may decrease the flow of process fluids or clog the heat exchanger tubes, etc., and reduce the production.

(c) Corrosion of equipments

In the process side, suitable corrosion resistance materials are generally used according to the kinds of the fluids and the operational conditions. However, the deposition of ununiform scale, sludge accumulation and so on may cause the local corrosion of equipments and pipings. The reduction in the flow rate of fluids changes the operational conditions of the system and sometimes causes the corrosion problems.

(d) Problems caused by overheating

In case of high temperature units like heating furnaces, the scaling at the fire side may cause the damage of heating tubes, such as bursting by their overheating.

(2) Problems at the water side

(a) Reduction of thermal efficiency

In cooling water systems, hard soluble salts, such as calcium carbonate, in the make-up water are concentrated in the cooling water and deposit as scale on the heat exchanger tube surfaces. The scaling reduces the thermal efficiencies of heat exchangers because of the small thermal conductivity.

(b) Corrosion of equipments

The formation of ununiform scale, sludge accumulation and so on accelerates the local corrosion of heat exchangers, pipings, etc. The formation of corrosion products also causes the under deposit corrosion and reduces the thermal efficiencies of heat exchangers because of the small thermal conductivity.

9.3 Cleaning Objects and Their Cleaning Methods

To effectively clean an aimed system, a suitable cleaning method has to be selected according to the composition of the scale, the structure of the system and so on.

Table 9.3 shows the typical analyses of scales sampled from various plants. Table 9.4 summarizes the typical cleaning methods and systems to be cleaned by those methods. The cleaning methods are classified into chemical and mechanical cleanings.

In this section, suitable cleaning methods for various plants are briefly described.

9.3.1 Boilers

Boilers are generally cleaned by chemical methods. In case of small-size boilers, tube cleaners or high pressure water jet cleanings are sometimes applied to remove their scales.

9.3.2 Nuclear Power Plants

The decontamination methods of nuclear power plants are divided into chemical and mechanical methods. A proper cleaning method is selected by taking the structure of a cleaning object and the properties of deposits (CRUD) into consideration.

The chemical methods are classified into dilute and concentrated chemical decontaminations.

The former uses dilute chemical solutions with the concentration of about 0.1% and the radioactive substances in the wastewater are removed by using ion exchange resins. Accordingly, this method yields only solid radioactive waste. This method is suitable for the decontamination of whole system. However, the decontamination effect is lower than that of the latter method.

The latter uses high concentration chemical

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* CRUD originates from the word, <u>C</u>halk <u>R</u>iver <u>U</u>nidentified <u>D</u>eposits. It means suspended solids formed in the primary cooling water systems of nuclear reactors, such as sludges in the water pipings and oxide films on the fuel rods.

Table 9.3 Analyses of typical scales sampled from various equipments

Sampling point of scale	Water cooled heat exchanger	Heating tubes of boilers (boiler pressure, kgf/cm^2)				Tube of naphtha cracking plant
		(18)	(60)	(180)	(255)	
CaO	19.7	7.9	2.8	0.1	trace	0.1
MgO	trace	5.4	0.7	trace	trace	0.1
Fe_2O_3	53.8	60.5	72.3	61.2	99.3	28.5
CuO	trace	0.4	23.0	19.3	trace	trace
ZnO	—	0.8	1.1	3.6	trace	trace
NiO	—	trace	1.2	16.7	trace	trace
Al_2O_3	—	4.8	trace	1.0	trace	—
P_2O_5	0.3	7.5	1.7	0.3	trace	—
SO_3	trace	—	trace	—	—	8.7
CO_2	1.7	—	—	—	—	—
Acid insoluble residue	2.0	10.5	1.0	2.1	1.0	0.6
Ignition loss	12.2	—	—	—	—	76.8

(w/w %)

Table 9.4 Cleaning methods and their cleaning objects

Cleaning method		Cleaning objects
Chemical cleaning		Boilers, heat exchangers, tanks, towers, pipings, nuclear power plants, etc.
Mechanical cleaning	High pressure water jet cleaning	Same as above
	Pig cleaning	Pipings
	Wet blast cleaning	Tanks, towers, nuclear power plants, etc.
	Tube cleaner	Low pressure boilers, pipings, etc.

solutions and shows the better decontamination effect. However, it yields a large amount of wastewater including radioactive substances and requires a large size wastewater treatment facility. This method is generally applied for the equipment or its parts.

In the chemical decontamination, acids, alkalis, surface-active agents, organic solvents and so on are used.

A high pressure water jet cleaning is applied for the mechanical decontamination. This method is suitable for removing a larger amount of scale or for a system with a larger water capacity, comparing with the chemical decontamination.

9.3.3 Industrial Manufacturing Plants

Various cleaning methods are applied for the industrial manufacturing plants according to the structures of objects, the composition of scales and so on.

9.4 Time for Cleaning

The cleanings of various plants are carried out not only to remove the scales after the trouble occurrence but also to prevent the scale problems beforehand.

In case that the cleaning is applied for a preventive measure, a time for cleaning has to be determined by taking various factors into consideration. Since the important factors may vary depending on the types of cleaning objects, the purposes of cleaning and so on, the typical determination methods of cleaning time are discussed below for each object.

9.4.1 Boilers

Boilers are generally divided into high, medium and low pressure boilers according to their operational pressures. As the structures of boilers and the compositions of scales vary depending on the pressure, the determination methods of cleaning time are discussed for each pressure boiler.

(1) High pressure boiler

In case of high pressure boilers with the pressure of above 75 kgf/cm^2, the components of the scales are mainly iron oxides and are followed by the copper, nickel oxides, zinc oxides, etc. The deposition amounts of magnetite and copper on the heating tubes of a boiler are widely influenced on the heat load as shown in Figure 9.3[4]. The influence of the heat load is not so clear on the deposition of nickel and zinc oxides.

N.N. Mankina[5] reported that the relationship between the heat load and the deposition rate of ferric oxide (Fe_2O_3) was expressed by the equation (9.1).

$$A = KC_{Fe}Q^2 \quad \text{.......... (9.1)}$$

where,

A = deposition rate of ferric oxide (mg Fe_2O_3/cm^2•h)

K = constant

C_{Fe} = iron concentration in boiler water (mg Fe/*l*)

Q = heat flux (kcal/m^2•h)

The K value was reported at 8.3 … 10^{-14} for the field test data or at 5.7 … 10^{-14} for the laboratory test data. Figure 9.4[5] shows the relationship among the deposition rate of iron oxide, the iron concentration in boiler water and the heat flux in the case of the K value of 5.7 … 10^{-14}.

Figure 9.5[6] shows the increases in the skin temperature of boiler tube by the scale depositions with various thermal conductivities and the thicknesses. The thickness of scale with the amount of 1 mg/cm^2 is in the range of 2.1 to 3.4 µm[7].

Therefore, the scaling rate is estimated from the iron concentration in a boiler water and the heat flux of a boiler tube. Then an increase in the skin temperature is calculated from the scale thickness and the thermal conductivity. The allowable tube wall temperatures for various steels are calculated from the temperatures causing the changes of their metallic structures or influencing on their creep rupture strengths as shown in Table 9.5[4].

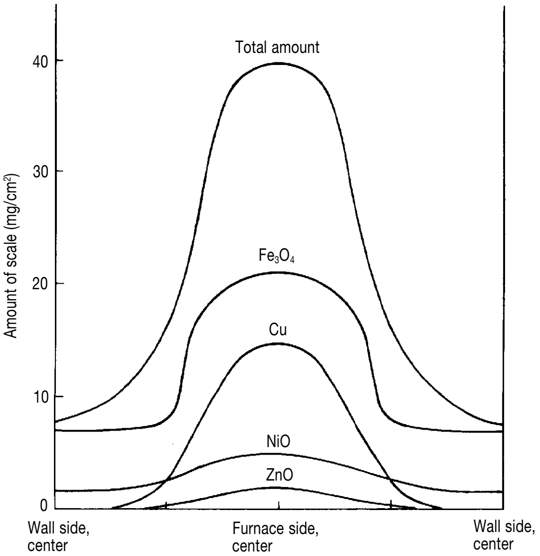

Fig. 9.3 **Influence of the heat load of a boiler tube on the deposition rates of various scale components**

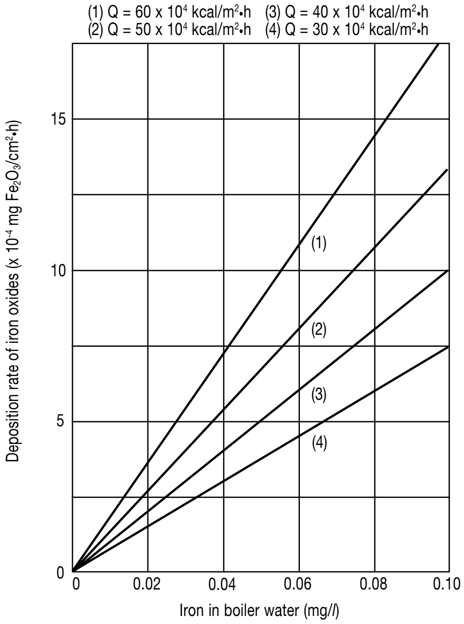

Fig. 9.4 **Relationship among the deposition rate of iron oxide, iron concentration in boiler water and heat flux**

By using those methods, the time for boiler cleaning is determined from the increase in the wall temperature of the heating tube.

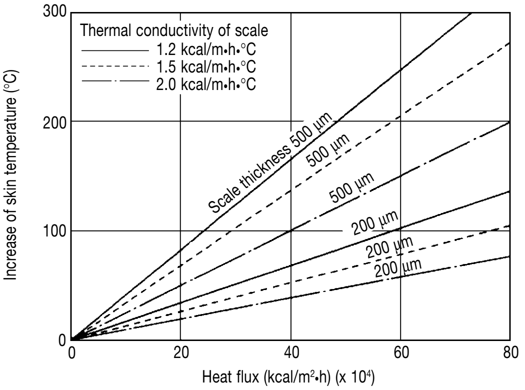

Fig. 9.5 Increases in the skin temperature of boiler tube by scale depositions with various thermal conductivities and thicknesses

Generally, the allowable temperature increase of boiler tube is set at 50°C. The above calculations give the time or the frequency of boiler cleaning, however, those calculations are rather complicated. Therefore, Tables 9.6[8] and 9.7[9] are proposed to easily determine the time or the interval of boiler cleaning. In case of gas-burning boilers, the cleaning interval is almost same to that of oil-burning boilers shown in Table 9.7. The interval of cleaning for coal-burning boilers may be extended 1 to 2 years longer than that of oil-burning boilers.

Generally, the cleaning interval of a boiler is determined by using those estimation methods to safely operate it until the next scheduled shutdown maintenance. However, an extremely long time operation of a boiler may bring a disadvantage to increase the ratio of extremely hard soluble substances, such as nickel ferrate and zinc aluminate with the spinal structures, in the scale. Those scales are very difficult to be removed by conventional chemical cleaning methods. Among spinal type metal oxides, zinc aluminate ($ZnAl_2O_4$) has the extremely low solubility.

The shortening of the cleaning interval is effective to minimize the formation of zinc aluminate.

Table 9.5 Permissible tube wall temperatures for various steels

Kind of steel (JIS)	Permissible temperature (°C)	
	Average wall temperature	Fire side skin temperature
STB 410	450	490
STBA 12	500	540
STBA 20	520	560
STBA 22	550	580
STBA 23	550	580
STBA 24	555	590

Table 9.6 Critical scale thickness or amount requiring a boiler cleaning

Fuel	Necessity of cleaning	Boiler pressure (kgf/cm²)			
		80	120	180	Above 246
Coal	Indispensable	—	0.30–0.45 mm (90–135 mg/cm²)	0.25–0.35 mm (75–105 mg/cm²)	—
	Better to clean	—	0.25–0.30 mm (75–90 mg/cm²)	0.20–0.25 mm (60–75 mg/cm²)	—
Mixture of coal and heavy oil	Indispensable	0.30–0.40 mm (90–120 mg/cm²)	0.25–0.35 mm (75–105 mg/cm²)	0.20–0.30 mm (60–90 mg/cm²)	—
	Better to clean	0.25–0.30 mm (75–90 mg/cm²)	0.20–0.25 mm (60– 75 mg/cm²)	0.15–0.20 mm (45–60 mg/cm²)	—
Heavy oil	Indispensable	0.25–0.35 mm (75–105 mg/cm²)	0.20–0.30 mm (60–90 mg/cm²)	0.15–0.20 mm (45–75 mg/cm²)	0.08–0.12 mm (24–36 mg/cm²)
	Better to clean	0.20–0.25 mm (60–75 mg/cm²)	0.15–0.20 mm (45–60 mg/cm²)	0.10–0.15 mm (30–45 mg/cm²)	0.06–0.08 mm (18–24 mg/cm²)

Table 9.7 Standard chemical cleaning intervals for oil-burning boilers

Type	Pressure (kgf/cm^2)	Chemical cleaning intervals (year)
Water-tube boiler	80–100	5–7
	120	3–5
	180	2–3
Once-through boiler	120	2–5
	180	1–3
	Above 240	1–3

(2) Medium pressure boilers

Generally, a demineralized water is used as the feedwater for most medium pressure boilers with the pressure of 20 to 75 kgf/cm^2. A softened water is fed to some boilers.

The main component of the scale is iron oxides. Calcium phosphates are sometimes included in the scale but silicate scales are scarcely found. Some boiler scales in waste-heat boilers include organic substances of above 10%, in petroleum refining, petrochemical, pulp and paper plants, etc.

Since the structures of boilers, the compositions of scales and so on are widely d .ifferent in case of medium pressure boilers, the estimation of the scaling rate and the determination of the suitable cleaning frequency are very difficult.

Considering the heat flux of boiler tubes, the cleaning of medium pressure boilers is usually carried out when the scale amount on the inner tube surface reaches around 60 mg/cm^2 or more[10] at the fire side. The average cleaning frequency is once per few years.

(3) Low pressure boilers

The main scale components of low pressure boilers with the pressure of below 20 kgf/cm^2 are calcium carbonate, calcium phosphates, calcium silicate, silica and so on. Figure 9.6 shows the increase in the fuel consumption by the scale adhesion.

In case of cylindrical boilers, the scale thickness is measured by using an electromagnetic film thickness meter, etc., during their operation stoppages to determine the time for the cleaning.

In case of water-tube boilers, the scale thickness measurement is impossible. Therefore, the following criteria are used for determining the cleaning intervals:

(a) Boilers operating for three years should be cleaned, however, the cleaning of a boiler is not required when the scaling, corrosion and the other problems are not observed at the internal inspection.

(b) Boilers observing the following problems have to be cleaned regardless of the operation periods:

① Thick scale adhesion on the heating tube surfaces,

② Reduction in the steam or the hot water generation accompanied by the increase in the fuel consumption,

③ Boiler water contamination with organic substances, oils and fats,

④ Increase in the total iron of boiler water.

(4) Tube walls in boiler furnaces

Tube walls in boiler furnaces are gradually covered with scales containing vanadium, sulfur, sodium, etc., originated from fuels. The scaling reduces the thermal efficiencies of boilers and causes a high temperature corrosion, vanadium attack, of superheaters, reheaters and so on. The

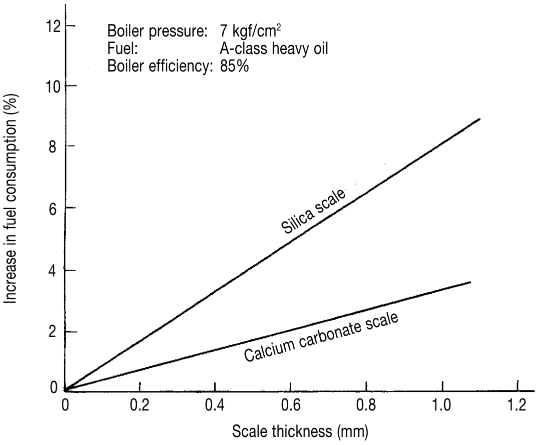

Fig. 9.6 Increase in the fuel consumption of a boiler by the incerease in the scale thickness

scaling rate varies depending on the kinds of fuels, the types of burners, the operational conditions of boilers, etc.

A high pressure water jet cleaning is generally applied to remove the scale.

9.4.2 Nuclear Power Plants

The radiation exposure of workers per unit time has been increased as the operation period of a nuclear power plant has been prolonged.

One reason of this increase in the radiation exposure is an accumulation of the radiation in the primary cooling water system. The second reason is an increase in the maintenance works with the prolonged operation time.

Those increases in the radiation exposure are minimized by improving the water treatment methods, the construction materials and the reliability of the facilities, equipment, apparatus, etc. However, the periodic decontamination is essentially required to reduce the radiation in the system.

The system decontamination is carried out to reduce the radiation in the whole reactor and auxiliary equipment. The decontamination interval is generally two to five years.

9.4.3 Industrial Manufacturing Plants

In the petrochemical plants, etc., the water cooled heat exchangers are gradually fouled with scales, corrosion products and so on. As those fouling materials reduce the thermal efficiencies and sometimes accelerate the corrosion, the fouling materials have to be periodically removed.

Formerly, heat exchangers were usually cleaned at once a year. However, the progresses in the cooling water treatment technology have extended the cleaning interval up to once two years to five years in the present.

The high pressure water jet cleaning is generally applied for the heat exchangers during the scheduled turnaround period of the plant.

9.5 Chemical Cleaning

9.5.1 Chemicals for Cleaning

(1) Main cleaning chemicals

Various kinds of chemicals are used as main cleaning chemicals as shown in Table 9.8.
Since those chemicals have various advantages and disadvantages, a suitable chemical and a cleaning method have to be selected according to the composition of the scale, the kinds of the materials and so on in an aimed plant.

The properties of the cleaning chemicals are described below.

(a) Inorganic acids

(i) Hydrochloric acid

Hydrochloric acid is widely used for chemical cleaning because it has a strong dissolving power for various scales except silica scale, and it is economic. In addition, its salts formed by reacting with scales have high solubilities and their redeposition scarcely occurs in the neutralization process after the acid cleaning. The surface conditions of metals after cleaning are better.

However, hydrochloric acid may cause the stress corrosion cracking or pitting corrosion of austenitic stainless steels, by chloride ions. A sufficient attention should be paid for the hydrochloric acid cleaning of an object using the stainless steels.

Another disadvantage of hydrochloric acid is the generation of corrosive hydrogenchloride gas to the environment.

Hydrochloric acid is used together with various cleaning aids, such as corrosion inhibitors and sequestering agents for cupric ions.

(ii) Sulfuric acid

Sulfuric acid is a non-volatile acid and applicable in a wide temperature range. The solubilities of sulfates are less than those of chlorides. However,

Table 9.8 Kinds of main cleaning agents

Inorganic acids	Hydrochloric acid, sulfuric acid, sulfamic acid, phosphoric acid, nitric acid, hydrofluoric acid
Organic acids	Citric acid, glycolic acid, formic acid, malic acid, oxalic acid, gluconic acid
Chelating agents	EDTA
Alkalis	Ammonia, sodium hydroxide, sodium carbonate, sodium phosphate

utilizing this property, a sulfuric acid based cleaning solution is regenerated and recycled by removing the dissolved metallic ions with a precipitation method, etc.

Since the solubility of calcium sulfate is a low, sulfuric acid is scarcely used for removing calcium based scales. The handling of sulfuric acid is required for sufficient cares because the concentrated one is highly reactive and generates a large amount of heat by the dilution with water.

Because of those features, sulfuric acid is generally applied for the pickling of iron and steel products in iron and steel works. The mixing of sulfuric acid with citric acid improves the disadvantages of sulfuric acid and the mixed acid has been used for boiler cleaning since 1960's.

(iii) Sulfamic acid

Sulfamic acid is a powder and easy to handle. Sulfamic acid shows the strong dissolving power for carbonates, hydroxides and calcium salts, but not so good for iron oxides. Therefore, sulfamic acid is mainly applied as a cleaning agent for cooling water systems or chilled and hot water systems of air-conditioning systems, where the main components of scales are calcium carbonate and iron hydroxides.

Sulfamic acid decomposes and yields sulfuric acid at the temperature of 60° C or more as shown in Figure 9.7. Therefore, sulfamic acid is not suitable for the cleaning of calcium scale at a high temperature.

As sulfamic acid and its salts show a strong toxicity to the plants of rice family, the discharge of the cleaning solution requires sufficient cares.

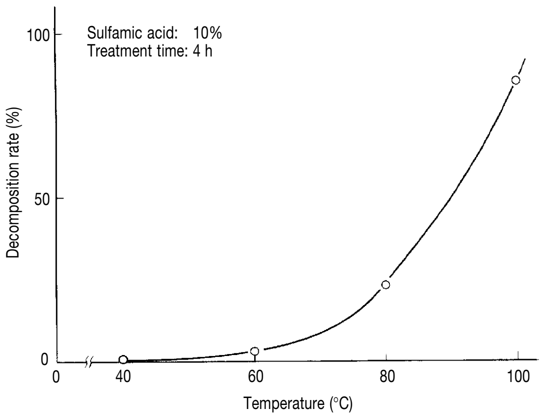

Fig. 9.7 Relationship between temperature and the decomposition rate of sulfamic acid to sulfuric acid

(iv) Phosphoric acid

Though phosphoric acid is a strong acid, its corrosivity to metals is relatively low. Especially, it prevents iron and steel products from the corrosion by forming an iron phosphate protective film on their surfaces.

Phosphoric acid is frequently used for the cleaning of parts and the precleaning of metals before the painting. It is scarcely applied for the cleaning of large-size plants because of the high price and the low solubilities of its metallic salts.

(v) Nitric acid

Nitric acid has a high chemical reactivity and the solubilities of nitrates are high. It shows the strong oxidizing power and passivates stainless steels, aluminum and its alloys, etc. However, nitric acid shows a strong corrosivity to iron and steels.

Nitric acid is generally used for the cleaning of stainless steel made plants and scarcely applied for iron and steel made equipment.

(vi) Hydrofluoric acid

Hydrofluoric acid has a strong chemical reactivity and dissolves silica scales. The solubilities of fluorides are high except the alkali earth metal salts.

The handling of hydrofluoric acid is very difficult because of the high corrosivity and high toxicity. The use of hydrofluoric acid as a main cleaning agent is seldom in Japan.

(b) Organic acids and chelating agents

In case that the structure of cleaning object is difficult to completely discharge the cleaning solution or the sensitive materials to the stress corrosion cracking are used, inorganic acids are scarcely used for the chemical cleaning.

In those cases, such as high pressure once-through boilers, organic acids and chelating agents are used for their cleanings.

(i) Citric acid

Citric acid shows a better dissolving power for various scales and the solubilities of its salts are higher comparing with the other organic acids. Especially, the solubility of iron citrate is relatively high and scarcely yields the ferric hydroxide precipitation even in an alkaline solution.

Utilizing this property of citric acid, it is widely used for the cleaning of high pressure and large-scale boilers. In that case, ammonia and/or the other organic acids are used together with citric acid to perfectly prevent the ferric hydroxide or ferric citrate precipitation in the system.

As the dissolving power of citric acid for scales is lower than those of inorganic acids, the citric acid based cleaning is generally carried out at a high temperature of 80 to 100°C to improve its cleaning effect.

As the solubility of calcium citrate is not so high, citric acid is scarcely used for the cleaning of calcium based scales.

Citric acid is a powder and not toxic, so that, it is often used as the cleaning chemicals of household goods.

(ii) Glycolic acid (hydroxyacetic acid) and formic acid

Glycolic acid and formic acid have the equal or better dissolving powers for iron oxides than that of citric acid, but lower than inorganic acid. Those acids are used at a high temperature of 80 to 100°C.

As the iron salts of those acids are deposited in an alkaline solution, those acids are generally used together with the other organic acids. L.G. McLaughlin[11)] reported a chemical cleaning method using glycolic and formic acid in 1963. KURITA carried out a power plant boiler cleaning using citric and glycolic acids in 1967.

(iii) Malic acid

The dissolving power of malic acid for iron oxides is somewhat lower than that of citric acid, but the solubilities of the iron salts are sufficiently high even in an alkaline solution.

KURITA has used malic acid as a main cleaning chemical since 1970.

(iv) Oxalic acid

Oxalic acid has an extremely strong dissolving power to iron oxides comparing with the other organic acids. Oxalic acid is able to use at a relatively low temperature of about 60°C. However, the solubilities of calcium oxalate and ferrous oxalate are low, and they may deposit in the cleaning solution. Therefore, a sufficient care should be taken to prevent their deposition problems.

Oxalic acid has been used together with citric acid for the decontamination of equipments using for nuclear power plants since 1960. This method is called "citric decontamination[12)]".

(v) Gluconic acid

Gluconic acid is a weak acid and sequesters iron, copper, calcium, magnesium ions, etc. Gluconic acid is able to dissolve iron rust and is frequently used as a precleaning agent for metal plating or painting.

(vi) EDTA

Since EDTA forms the stable complex salts with various metal ions in a wide pH range, it is used as a cleaning agent applicable for a wide pH range. EDTA is used at a high temperature of up to 150°C because the decomposition temperature is around 155°C.

M. Blake, et al.[13)], reported a chemical cleaning method using EDTA or EDTA sodium salt in 1962. The use of EDTA ammonium salt[14)] as a cleaning agent was patented in 1964 in U. S. A. In 1960's, KURITA also realized a chemical cleaning method using EDTA.

(c) Alkalis

(i) Ammonia

As ammonia forms water soluble complex ions with copper ions and shows a strong dissolving power for copper based scales, it is used as a cleaning chemical for scales containing a large amount of copper salts.

The use of ammonia at a high temperature of above 60°C is difficult because it is volatile and generates the irritative fume.

(ii) Sodium hydroxide

Sodium hydroxide is used to dissolve silica scales and to remove foulings including oils and fats.

(iii) Sodium carbonate

Sodium carbonate changes acid-insoluble calcium sulfate scale to acid-soluble calcium carbonate. Sodium carbonate is used together with sodium hydroxide for "hot alkaline cleaning" to prevent the formation of insoluble metallic soaps in the cleaning solution.

Sodium carbonate is also used as a pH buffering agent to stabilize the pH and the effect of cleaning solution.

(2) Cleaning aids

The main cleaning chemicals have the advantages and the disadvantages. Various cleaning aids are generally used together with main cleaning agents to intensify their advantages or to supplement their disadvantages. The selection of not only suitable main cleaning agents but also appropriate cleaning aids is very important for obtaining a sufficient cleaning effect.

The kinds, features, functions, etc., of cleaning aids are discussed below.

(a) Acid corrosion inhibitors

The acid corrosion inhibitors are chemicals which prevent or minimize metallic corrosion caused by acids using for chemical cleaning.

(i) Functional mechanism of inhibitors

Various organic substances with the relatively high molecular weights, such as aliphatic amines, are generally used as corrosion inhibitors for acid cleaning. A typical corrosion inhibitor has two kinds of functional groups; one is a polar group to adsorb on a metallic surface and another one is a hydrophobic hydrocarbon group.

This type of inhibitor is called the adsorption type inhibitor and forms the protective film on a metallic surface as shown in Figure 9.8. This film repels a cleaning solution from the metallic surface after removing the scale and prevents the corrosion.

(ii) Selection of inhibitors

Since no all-round corrosion inhibitor is present, an appropriate one has to be selected according to the cleaning conditions. Important factors influencing on the inhibitor performances are discussed below for the hydrochloric acid chemical cleaning mainly.

① Dosage of inhibitor ;
The effect of a corrosion inhibitor generally increases up to a some critical point as the dosage increases. Over this critical point, an improvement in the effect is scarcely obtained. Therefore, an insufficient or an excess dosing of inhibitor should be avoided.

② Acid concentration ;
Generally, the hydrochloric acid solution of 5 to 10% is used for the acid cleaning. Most corrosion inhibitors show the stable effects in this acid concentration level.
However, the formulation of a corrosion inhibitor with a high concentration hydrochloric acid is sometimes prepared and the solution is diluted at a site before cleaning. In that case, a stable inhibitor in the high concentration acid must be used.

③ Cleaning temperature ;
Acid cleanings are generally carried out at a higher temperature than ambient one. As each inhibitor has a critical applicable temperature, a suitable one has to be selected considering the cleaning temperature.

④ Cleaning duration ;
The duration of hydrochloric acid cleaning is generally 4 to 8 hours. However, a longer duration is sometimes employed for some kinds of scales. In that case, a stable inhibitor for a long time cleaning should be selected.

⑤ Oxidizing ions ;
Oxidizing ions, such as ferric ion and cupric ion, accelerate the acid corrosion of iron as shown below in the section (b). This corrosion by oxidizing ions is difficult to prevent by using acid corrosion inhibitors.

⑥ Flow velocity ;
The higher flow velocity generally gives the better cleaning effect. However, the flow velocity also influences on the effects of inhibitors. A suitable inhibitor must be selected according to the planned flow velocity of cleaning.

⑦ Generated gasses by scale dissolving ;
Scales including sulfides, sulfites, etc., generate hydrogen sulfide, sulfur dioxide and so on during the acid cleaning. Since those gasses deteriorate the performance of some inhibitors, the gas generation has to be taken into the consideration for the inhibitor selection.

(b) Reducing agents

Various metals in scales dissolve into acid cleaning solutions as their ions. Among them, oxidizing ions, such as ferric and cupric ions, accelerate the iron corrosion as follows:

$$2Fe^{3+} + Fe \rightarrow 3Fe^{2+} \quad \cdots\cdots (9.2)$$

$$Cu^{2+} + Fe \rightarrow Cu + Fe^{2+} \quad \cdots\cdots (9.3)$$

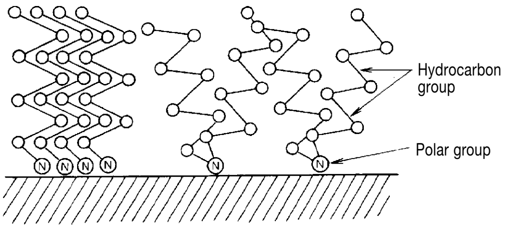

Fig. 9.8 A schematic model of protective film formation by an adsorption type inhibitor

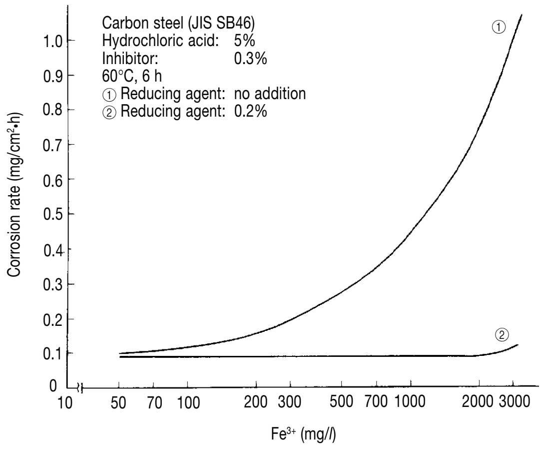

Fig. 9.9 Acceleration of carbon steel corrosion by ferric ion and the effect of a reducing agent

Reducing agents are used to minimize this corrosion by reducing those ions. Figure 9.9 shows the acceleration of corrosion with ferric ion and the inhibition effect of a reducing agent. The increase in the ferric ion concentration accelerates the carbon steel corrosion and the use of the reducing agent eliminates the bad influence of ferric ion.

(c) Copper dissolving agents

Copper and copper alloys are often used as the condenser and preheater tubes in boiler systems. Copper ion is generated by the corrosion of those metals and deposits as the metallic copper on carbon steel surfaces. This copper scale is scarcely dissolved by a conventional acid cleaning. In that case, copper dissolving agents are used to promote the copper dissolving. Figure 9.10 shows the effect of a copper dissolving agent.

In case of a high copper content scale, an ammonia cleaning is usually applied. Even in case of ammonia cleaning, copper dissolving agents are generally used to promote the copper dissolving.

(d) Silica dissolving agents

Silica scarcely dissolves into any acids except hydrofluoric acid. Therefore, when hydrochloric acid is used for dissolving a scale containing silica, silica dissolving agents are used together with the acid. Figure 9.11 shows the effect of a silica dissolving agent.

(e) Degreasing and wetting agents

Oils and fats are hardly wetted with acid or alkaline cleaning solutions. Surface-active agents are used to wet, and to emulsify the oils and fats in the cleaning solution.

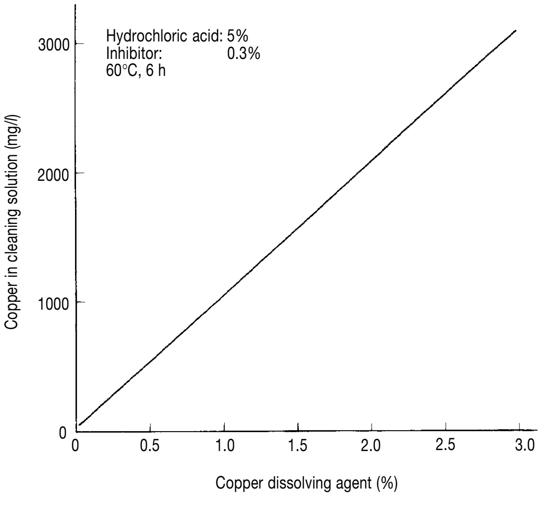

Fig. 9.10 Effect of a copper dissolving agent on a metallic copper scale

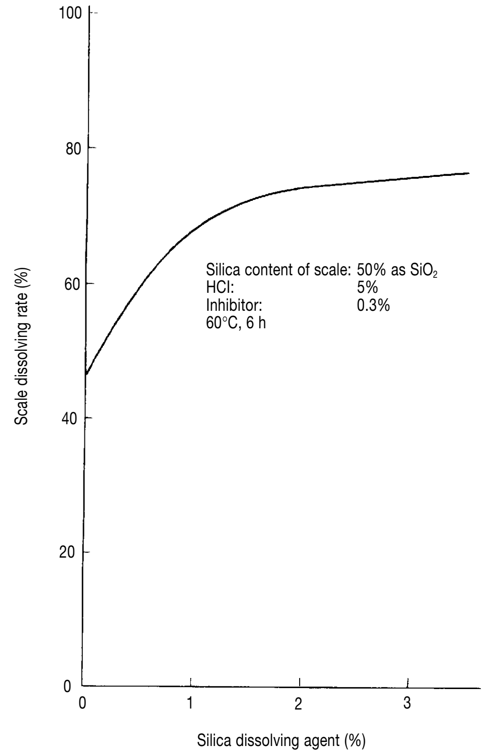

Fig. 9.11 Effect of a silica dissolving agent on a scale containing silica

Wetting agents are also used to promote the penetration of cleaning solutions into a dense and hard scale.

(3) Chemicals using for neutralizing and rust-preventive processes

In the chemical cleaning processes, not only scale removal but also rust-preventive measures until the system restart-up are required. Therefore, neutralizing and rust-preventive treatments are carried out after the acid cleaning. After the acid cleaning, the surfaces of metals become very active and easily rust, especially in the case of carbon steels. The neutralizing and rust-preventive treatments are employed to stabilize the active metallic surface and to prevent the rusting.

The following chemicals are used for those treatments.

(a) Sequestering agents for neutralization

In the water rinsing and neutralizing processes after acid cleaning, the solution pH increases and the iron ions deposit as iron hydroxides on the cleaned metallic surfaces. Sequestering agents effective for iron ions in neutral to alkaline solutions are used to prevent this deposition.

Sequestering agents using for this process should have the following features:

① Excellent sequestering power for iron ions in neutral to alkaline solution to prevent the iron hydroxide deposition,
② Excellent dissolving power for iron hydroxides,
③ Low corrosivity on various metals, especially carbon steel, with the applicable dosage.

(b) Neutralizing agents

The pH is controlled in the range of 9 to 10 in a neutralizing process. Ammonia, sodium hydroxide and sodium carbonate are used as neutralizing agents. Ammonia is the best neutralizing agent because it has an excellent neutralizing power and minimizes the increase of the dissolved solid concentration in the neutralizing process comparing with the other neutralizing agents.

(c) Corrosion inhibitors (rust-preventives)

(i) Sodium phosphates

Phosphates form the iron phosphate rich protective film on carbon steel surface. As the stability of iron phosphate is not sufficient, another inhibitor treatment is required to obtain a stable corrosion inhibition after the phosphate treatment.

(ii) Nitrites

Nitrites form the very stable protective film on carbon steel surface during a short time at the temperature of above 60° C. The main component of the protective film is γ-ferric oxide[15]. This film is very thin but very stable in a dry condition after the cleaning.

(iii) Hydrazine

Hydrazine forms magnetite (Fe_3O_4) film on carbon steel surface and sufficiently inhibits the corrosion after the acid cleaning. However, as hydrazine is a very toxic, sufficient cares are required for the handling.

9.5.2 Cleaning Conditions

Various factors influence on the effect of chemical cleaning and the metallic corrosion at the same time. Therefore, appropriate cleaning conditions have to be selected to obtain the sufficient effect and to prevent the corrosion.

(1) Cleaning temperature

Most chemical cleaning agents dissolve various scales with higher rates at higher temperature. However, the increase of temperature brings the following disadvantages:

① Increase of metallic corrosion rate;
Generally, metallic corrosion rates increase as the temperature increases. Even if a corrosion inhibitor is used, the inhibitor has the maximum allowable temperature for the corrosion inhibition.
② Decomposition of chemicals;
Some chemicals are decomposed and their performances are deteriorated at a higher temperature. Moreover, some decomposition products sometimes form the precipitate with metallic ions in a cleaning solution.
③ Volatilization of chemicals;
Some organic substances volatilize at a relatively low temperature. Among inorganic substances, ammonia and hydrochloric acid volatilize at an elevated temperature.

Taking those advantages and disadvantages of temperature increase, the features of chemicals, etc., into consideration, an appropriate cleaning temperature should be determined.

(2) Concentrations of cleaning chemicals and aids

The required concentration of a cleaning chemical is generally determined by the amount of a scale and the chemical equivalence to the scale composition. However, as the progressing of cleaning consumes the cleaning chemicals and cleaning aids, the dosages of chemicals have to be increased at certain amount higher than the theoretically required ones.

(3) Flow velocity

Under a stagnant condition, the concentration of a cleaning agent is reduced on a metallic surface because it is consumed by the scale dissolving. As the result, the scale removal effect is deteriorated.

The flow of cleaning solution supplies the fresh chemicals to the metallic surface and maintains a constant scale dissolving rate. The higher flow velocity also accelerates the mechanical removal of the scale.

On the other hand, the higher flow velocity accelerates the metallic corrosion.

Considering those factors, an appropriate flow velocity of a cleaning solution is determined.

9.5.3 Cleaning Methods

(1) Circulation cleaning

In the circulation cleaning, the cleaning solution is circulated through the system by using existing or temporary pumps. This method is most frequently applied because the chemical concentration and the solution temperature are easily controlled in the appropriate ranges to maximize the cleaning effect.

(2) Surging cleaning

The surging cleaning is an intermediate method between the circulation and the immersion cleanings.

In this method, a cleaning solution is supplied and filled in the cleaning object. After a specified time, the solution is discharged from the bottom of the object and is supplied again. The change of the supply and discharge points of the cleaning solution improves the cleaning effect.

This method is applied for the objects where the circulation of cleaning solution is difficult.

(3) Immersion cleaning

The immersion cleaning is carried out by filling the cleaning solution into the cleaning object and by keeping it at a stagnant condition for a specified time.

(4) Spray cleaning

A cleaning solution is sprayed on the surface of objects.

This method is applied for water tanks, etc., which have the large surface areas. Various spray nozzles are used according to the structures of objects.

(5) Daub cleaning

The daub cleaning is applied when a specified part of object is cleaned. The mixture of a cleaning agent and an adhesive is used for this cleaning method. This mixture is daubed on the surface of object and it is wiped with a duster and so on after a specified time passing.

9.5.4 Cleaning Processes and Their Procedures

A chemical cleaning consists of various cleaning processes. It requires the selection of suitable chemicals, and the safe and efficient process operations.

Table 9.9 shows the typical cleaning processes and the specifications of the cleaning.

(1) Flushing

(a) Purpose

The flushing is carried out to discharge the foreign matters and accumulated sludge from a cleaning object.

(b) Specifications

Demineralized water is used for the flushing. The hydrazine of around 50 mg/l is sometimes added into the flushing water to minimize the corrosion.

(c) End point of flushing

The flushing should be finished when no foreign matter is found in the discharge water, and no turbidity difference between the supply and discharged waters are observed.

(d) Cautions

When a temporary piping is installed for the cleaning, the foreign matters in the piping have to be perfectly removed to prevent the cleaning object from the contamination with them.

(2) Degreasing

(a) Purpose

Oils and fats disturb the contact of cleaning solution with scales, and cause foaming problems. The oils and fats include cutting oils, lubricating oils, etc., used for the fabrication or the construction of new plants.

The degreasing is carried out to remove those oils and fats for preventing the above problems before acid cleaning.

(b) Specifications

A typical specification for the degreasing is shown in Table 9.9. Alkalis form water-soluble fatty acids and glycerols by saponificating the oils and fats. The surface-active agents emulsify and disperse the oils and fats.

In case that the perfect removal of oils and fats is required, like a piping for oxygen transportation, organic solvents are used for the degreasing.

(c) End point of degreasing

When no increase of oils and fats in the degreasing solution is determined by the analysis, the degreasing is finished.

(3) Swelling

(a) Purpose

The swelling is carried out to convert hard-soluble scales, such as silicates and calcium sulfates, to easy-soluble salts like sodium silicate and calcium carbonate. It is also applied to soften and swell dense and hard scales, heavy oils, etc., for promoting their removal.

(b) Specification

A typical specification of swelling is shown in Table 9.9.

Table 9.9 Typical cleaning processes and the specifications

Process	Chemicals and dosages (%)		Temperature (°C)	Duration (h)	Purpose
Degreasing	NaOH	0.1–0.3	60–80	6–8	Removal of oils and fats
	Na_2CO_3	0.1–0.3			
	Surface-active agent	0.05–0.2			
Swelling (Wetting)	Na_2CO_3	1–5	Above 80	10–24	Removal of silica and organic substances
	NaOH	1–5			
	Swelling agent	0.1–0.3			
Hot alkaline cleaning	NaOH	0.1–0.3	Working pressure x (1/5–1/3) (Maximum 20 kgf/cm^2)	2–3 days	Removal of oils and fats, Drying of heat insulating materials
	Na_3PO_4	0.1–0.3			
	Na_2CO_3	0.03–0.1			
	(Surface-active agent)	(0.05–0.2)			
Ammonia cleaning	NH_3	1–3	40–60	4–6	Removal of copper
	Copper dissolving agent	0.3–1			
Hydrochloric acid cleaning	HCl	5–10	50–65	4–8	Removal of iron oxides or hardness components
	Corrosion inhibitor	0.3–0.5			
	Reducing agent	0.2–0.5			
	Copper dissolving agent	0.5–3			
Organic acid cleaning	Organic acid	2–7	80–90	4–8	Removal of iron oxides
	Corrosion inhibitor	0.3–0.5			
	Reducing agent	0.1–0.3			
	Copper dissolving agent	0.5–2			
Chelate cleaning	EDTA salts	2–10	120–150	4–8	Removal of iron oxides or hardness components
	Corrosion inhibitor	0.1–0.5			
	Reducing agent	0.1–0.3			
Neutralizing and rust preventing	Sequestering agent for neutralization	0.1	50–100	2–4	Temporary rust preventing after acid cleaning
	NH_3(pH = 9 - 10)				
	Corrosion inhibitor	0.05–0.5			
Copper removing and rust preventing	Sequestering agent for neutralization	0.1	50–70	2–4	Removal of a small amount of copper and passivation
	NH_3 (pH = 9 - 10)				
	Corrosion inhibitor	0.2			
	Copper removing agent	0.3–0.5			

(c) End point of swelling

The specification of swelling is determined from the laboratory test results using a scale sample before the field application. The swelling treatment is generally finished according to the planned treatment period.

No analytical method to determine the end point is present.

(d) Cautions

① Because of the high temperature treatment, the cavitation of pumps and any leakages from the pipings should be avoided.

② The alkaline corrosion of the object should be prevented by gradually increasing the swelling agent concentration.

(4) Hot alkaline cleaning

(a) Purpose

The hot alkaline cleaning is carried out to remove oils, fats and silica from newly installed boilers. It is also carried out for drying the heat insulating materials of boilers and for measuring the elongation of boiler tubes.

(b) Specification

A typical specification of the hot alkaline cleaning is shown in Table 9.9. The temperature increasing or decreasing rate of the cleaning solution should be controlled within 50°C per hour. After increasing the temperature and the pressure up to the specified levels, they are kept for 3 to 4 hours. Then after reducing the temperature and pressure, the cleaning solution is discharged from the boiler up to the permissible lower water level and the fresh cleaning solution is fed again into the boiler.

This operation is usually repeated twice or three times.

(c) End point of the treatment

When no oil, fat and silica are detected in the cleaning solution, the hot alkaline cleaning is finished.

(d) Cautions

The boiler pressure shall be always checked and kept in an permissible range during the hot alkaline cleaning. Especially, the boiling of the cleaning solution in the economizer must be avoided.

(5) Ammonia cleaning

(a) Purpose

The ammonia cleaning is carried out to remove scales containing a large amount of copper, which are generally formed in medium or high pressure boilers with copper or copper alloy made preheaters, condensers and so on.

(b) Specification

A typical specification of the ammonia cleaning is shown in Table 9.9.

(c) End point of the cleaning

When no increase of copper concentration in the cleaning solution is observed, the ammonia cleaning is finished.

(d) Cautions

① Since the ammonia cleaning attacks equipments made of copper or copper alloys, those equipments must be isolated from the system to be cleaned.

② As oxidizing type copper dissolving agents may attack carbon steel, an excess dosing of the agent must be avoided.

(6) Acid or chelat cleaning

(a) Purpose

The main purposes of the acid or chelate cleaning are as follows:

① Removal of mill scale which forms during the fabrication or construction of new plants,

② Removal of scales, such as iron oxides and calcium carbonate, formed during the plant operation.

(b) Specification

Typical acid or chelate cleaning methods are described below:

(i) Hydrochloric acid cleaning

A typical specification of the hydrochloric acid cleaning is shown in Table 9.9.

(ii) Organic acid cleaning

A typical specification of the organic acid cleaning is shown in Table 9.9.

Citric acid mono-ammonium salt, the mixture of citric acid and glycolic acid or the mixture of glycolic acid and formic acid is generally used for the organic acid cleaning.

(iii) Chelate cleaning

A typical specification of the chelate cleaning is shown in Table 9.9.

(iv) Degreasing and acid cleaning

In case of new plants, surface-active agents are sometimes added into the acid cleaning solution to remove scales, oils and fats at the same time. Surface-active agents using for this treatment have to be stable in a wide pH range of a strong acidic to alkaline.

(v) Ammonia-citric acid single-stage cleaning

This cleaning is a single-stage cleaning method that an ammonia cleaning and a citric acid cleaning are carried out at the same time by using one solution.

This method is applied for scales containing copper. At first, the ammonia solution of 0.2 to 0.3% is used to dissolve copper in the scale. After dissolving copper, the solution is treated by an ammonium-type cation-exchange resin to remove copper. Citric acid is added into the copper-free regenerated ammonia solution and the solution is used for removing scales such as iron oxides.

(c) End point of cleaning

The concentrations of main substances composing the scale in the cleaning solution, such as iron, are periodically analyzed during the cleaning. When no increase in their concentrations is observed, the cleaning is finished. Figure 9.12 shows an example of cleaning solution analysis. The scale removal condition of test coupons installed in a bypass line is also effective to determine the end point.

(d) Cautions

① When the iron concentration in a cleaning solution exceeds 20,000 mg/l, the cleaning solution must be renewed because the high concentration of iron deteriorates the effect of a corrosion inhibitor.

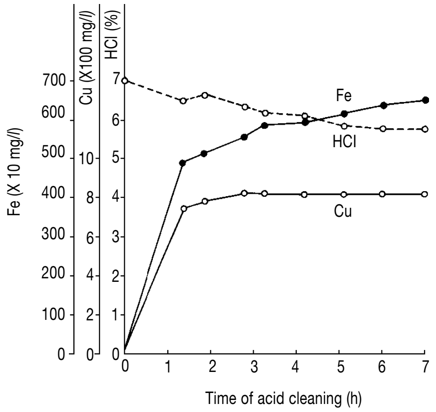

Fig. 9.12 An example of acid cleaning solution analysis

② The use of open flame is strictly prohibited at the site of acid cleaning because hydrogen gas yields during acid cleaning.

③ When the generation of toxic gasses is anticipated, the suitable gas treatment systems must be used for the safety operation.
The following cases may yield toxic gasses:
- Process side cleaning of petroleum refining and petrochemical plants; H_2S generation,
- Cleaning of black liquor evaporators in pulp and paper mills; H_2S generation,
- Cleaning of exhaust gas desulfurization plants; SO_2 generation,
- Cleaning of carbonate scales; CO_2 generation,
- Cleaning of scales containing nitrogen oxides; NOX generation.

④ Use nitrogen gas to discharge the cleaning solution or the rinsing water from the system to prevent the corrosion of the cleaned surface by contacting with air.

(7) Water rinsing

(a) Purpose

The water rinsing is carried out to discharge cleaning solutions and sludge from the system after each cleaning process.

(b) End point of the rinsing

In the cases of degreasing, swelling, hot alkaline cleaning and ammonia cleaning, the rinsing is finished when the pH of the rising water becomes below 9. The rinsing after acid cleanings is finished when the pH rises above 5.

(c) Cautions

① The increase of rinsing water temperature up to around 60° C is desirable because it shortens a time required for the temperature increase at the next treatment process.

② In case that a perfect discharge of the cleaning solution is difficult because of its system structure, such as once-through boilers, the cleaning solution should be discharged by feeding the rinsing water gradually.

③ In case that the sludge accumulation of a large amount is anticipated, it is better to discharge the sludge by a water flushing before the water rinsing.

(8) Sealing and backwashing of superheaters

(a) Purpose

This treatment is carried out to prevent the contamination of superheaters with cleaning solutions.

(b) Specification

During the chemical cleaning, superheaters must be filled with demineralized water including a volatile corrosion inhibitor, such as the 50 to 100 mg/*l* of hydrazine.

After finishing the acid cleaning and neutralizing-and-rust preventing treatment, the superheater is backwashed with the demineralized water including the inhibitor from the water outlet to the inlet (boiler side) to prevent the contamination.

(c) End point of the backwashing

The backwashing is finished when the chloride ion concentration of the water becomes lower than 0.1 mg/*l*

(9) Neutralizing and rust preventing treatments

(a) Purpose

The neutralizing and rust preventing treatments are carried out to stabilize the metallic surfaces of a system after the cleaning and to prevent the corrosion until the system restart-up. Especially, the rust prevention of carbon steel requires sufficient cares because the surface becomes very active after the acid cleaning.

(b) Specification

A typical specification of neutralizing and rust preventing treatments is shown in Table 9.9. More detail informations are described below:

(i) Pretreatment for neutralization

The acid cleaning solution is discharged from the system and the system is rinsed with demineralized water. After discharging the rinsing water, demineralized water is fed into the system and circulated for 1 to 2 cycles at the temperature of 50 to 60°C to remove the remaining metallic ions, metallic oxides, etc.

Those treatments have to be carried out under the nitrogen gas sealing condition to prevent the corrosion.

(ii) Neutralization

Ammonia is added into the above circulating water to increase the pH up to 9 to 10.

(iii) Rust prevention

After controlling the pH at 9 to 10, the water temperature is increased up to a specified temperature, generally 80 to 100°C. A corrosion inhibitor is added into the water and circulate it for 2 to 4 hours.

(c) End point of treatment

After controlling the water pH and temperature, the rust prevention treatment is finished in the specified period of time.

(d) Cautions

① Since the increase in the iron concentration during the pretreatment deteriorates the rust prevention effect, the concentration should be kept as low as possible.

② The higher temperature gives the better rust prevention and shortens the time for drying the system after the rust preventing treatment.

(10) Copper removing and rust preventing treatments

After finishing an acid cleaning, the removal of copper, the neutralization and the rust prevention are carried out at the same time by using a diluted ammonia solution including corrosion inhibitors, etc.

A typical specification of this treatment is shown in Table 9.9. This treatment is applied for boilers whose scales contain a small amount of copper.

9.5.5 Planning and Operation of Cleaning

The condition of a system must be investigated and the cleaning plan should be determined for effectively carrying out the system cleaning.

Figure 9.13 shows a typical procedure of boiler chemical cleaning from the investigation to the final reporting of the cleaning results. The procedures of system investigation and the planning of the cleaning are described below.

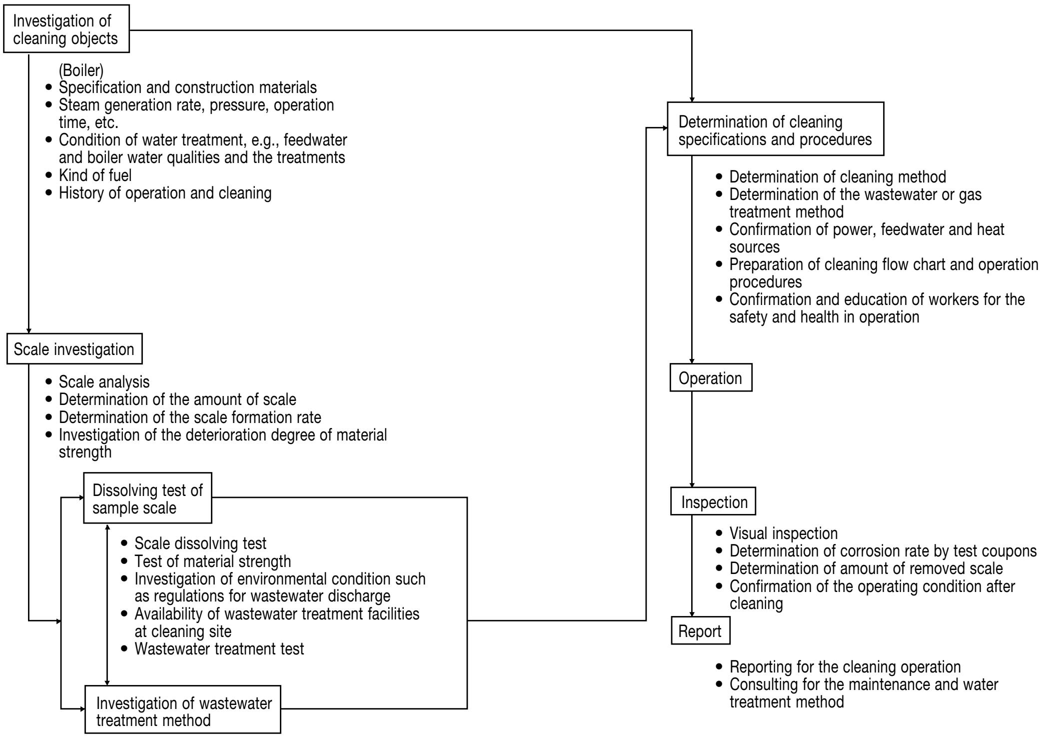

Fig. 9.13 Typical procedures for the chemical cleaning of a boiler

(1) Investigation of scales

(a) Sampling of scale

To determine an exact adhesion conditions of scales, the scales are generally sampled at the following portions of the cleaning object.

① The portion with the highest heat load;
In case of a boiler, this portion is generally the surrounding of the top burner. In this part, the amount of scale becomes the largest and the composition is usually complicated.,

② Section where water or process fluid is stagnant,

③ Section where scales and sludges easily accumulate because of the structure,

④ Section experiencing the scale problems in the past.

In the above sections, scales and sludges easily adhere and accumulate. Moreover, their removal by chemical cleaning is usually difficult. Therefore, a cleaning method effective for those sections easily removes scales and sludges in the other portions.

It is desirable to get tube samples with scales by cutting tubes. When the tube cutting is difficult, the sampling of scales should be carried out from several portions of the objects, where represent the typical system conditions.

(b) Measurement of scale amount

The measurement of scale amount is required to estimate the total amount of the scale in the system and to determine the required dosage and the amount of cleaning chemicals. The cleaning time is also estimated from the total amount of the scale.

In case of a tube sample, the scale amount is obtained from the weight difference before and after the acid cleaning. Generally, a hydrochloric acid solution with a corrosion inhibitor is used for the scale removal.

In case of a scale sampling from the object, the whole scale is perfectly removed from a specified surface area and the weight is measured.

The total scale amount is calculated from the amount of the above scale sample and the total surface area of the object.

(c) Measurement of scale thickness

The measurement of the scale thickness is required to determine the adhesion condition of the scale and the chemical cleaning method. The scale thickness is also utilized to determine the time of cleaning.

The sample tube with scale is cut to make a piece of 1 to 3 cm. This piece is mounted into a resin and polished to observe the cross section by a metallurgical microscope. The cross section is photographed and the scale thickness is measured from the photograph.

The metallic structure is also determined by the microscopic observation.

Photograph 9.3 shows the microscopic observation of a boiler tube with scale.

When the sampling of tubes is impossible, an exact scale thickness measurement is difficult.

(d) Scale analysis

The scale analysis is essential to determine the cleaning specification.

After dissolving the scale sample by using an acid solution, the metallic ion concentrations, etc., are analyzed. The scale analytical methods are described in the section 11.2.3.

Generally, chemical analyses are carried out to determine the scale compositions. A X-ray deffractometer uses to determine the substances composed of the scale. A X-ray microanalyzer is also used to make clear the element distribution in the scale.

Photograph 9.4 shows the element distributions in a boiler scale.

(e) Scale dissolving test

The scale dissolving test is carried out to determine an appropriate cleaning specification, such as the kinds and dosages of chemicals, the temperature and the time.

Before the scale dissolving test, a rough cleaning specification is determined by referring to the amount, thickness and composition of the scale. Then changing the chemical dosages, temperature, time and so on, the scale dissolving tests are carried out by using the scale samples to determine the best cleaning specifications.

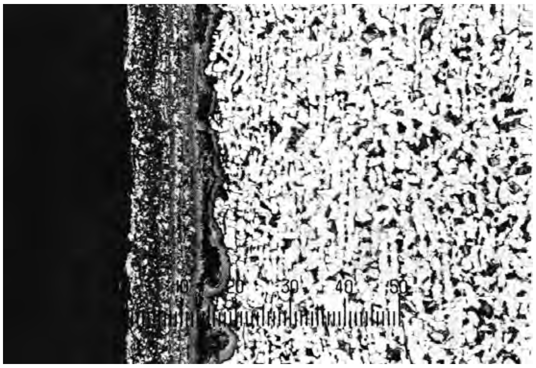

Photo 9.3 **Measurement of scale thickness on a boiler tube by the microscopic observation**

In case of a scale dissolving test for a tube sample, the cleaning effect is judged by the visual inspection. The measurement of surface electrical resistance of tube or the microscopic observation of the surface is also carried out to determine the effect.

In case of a scale sample without tube, the effect is judged from the scale dissolving rate.

(2) Cleaning of medium or high pressure boilers

(a) Investigation of boiler conditions

The following operational conditions and structure of a boiler system have to be investigated for determining the cleaning specification.

① Outline of boiler; type, pressure, evaporation rate, service time, etc.,
② The parts to be cleaned and the holding water volumes,
③ Layout and flow-diagram of the boiler system including the auxiliary equipments and pipings,
④ Perfect water filling is possible or not,
⑤ Water circulation is possible or not.

(b) Investigation at site

The cleaning of medium or high pressure boilers is carried out at the site. Following items have to be investigated at the site beforehand.

(i) Water for use

Generally, demineralized water is used for the cleaning of medium or high pressure boilers. Though the required amount of water varies depending on the cleaning specification, it is generally 5 to 8 times of the holding water volume of the part to be cleaned. In addition, a considerable amount of water is required for sealing the portions not to be cleaned and for backwashing them after the cleaning.

Since a large amount of demineralized water is required for the cleaning, the water should be prepared and stored in demineralized water tanks, temporary tanks, etc., before the cleaning.

(ii) Heat source

The existing burner of the boiler or steam is used to heat the cleaning solution.

When the burner is used, the temperature control of the cleaning solution is difficult because the tube wall temperature becomes higher than that of the cleaning solution. Therefore, a sufficient care must be paid for the temperature control. This heating method is generally applied for a chelate cleaning because the temperature control range is a wide and the permissible maximum temperature is a high at 150°C.

The cleaning solution heating by using steam is generally applied for the medium or high pressure boiler cleaning. In that case, as the steam is directly injected into the cleaning solution, the tube wall temperature never exceeds the solution one. The temperature control is easier than the burner heating. The time for increasing the temperature becomes longer than that of the burner heating.

The required amount of steam should be confirmed from the temperature, the amount of cleaning solution, etc. If the steam supply at the site is difficult, the installation of temporary boilers is required.

(iii) Electric power

Chemical cleaning requires electricity to operate the injection and circulation pumps of the cleaning solution. The welding of temporary pipings, the lighting and so on also require the electricity. A sufficient electric power should be obtained at the site.

Since the power failure during the cleaning remarkably deteriorates the cleaning effect, the separation of power source for the cleaning from the other ones is desirable.

(iv) Installation space of cleaning equipments

The installation of tanks, pumps, temporary pipings and so on is required for the cleaning at the site. Their installation at the one space near the cleaning object is desirable.

(c) Preparation of cleaning instruction

The cleaning specification is determined from the above investigations and testings, the agreements with the customer, etc. Then the cleaning instruction is prepared. The instruction should include the following items:

① Purpose of cleaning,
② Outline of boiler,
③ Part to be cleaned and the amount of cleaning solution,
④ Types and numbers of equipments, and materials for the cleaning,
⑤ Battery limits and specifications,
⑥ Kinds, amounts and dosages of chemicals,
⑦ Cleaning conditions, such as temperature, time and circulation rate,
⑧ Determination methods of the end points for each cleaning process,
⑨ Methods for the injection, circulation and discharge of cleaning solutions,
⑩ Flow-diagram of cleaning ;
Figure 9.14 shows an example of the flow-diagram,
⑪ Progress sheet of cleaning processes ;
The required time for each process is written down in the order of treatments.,

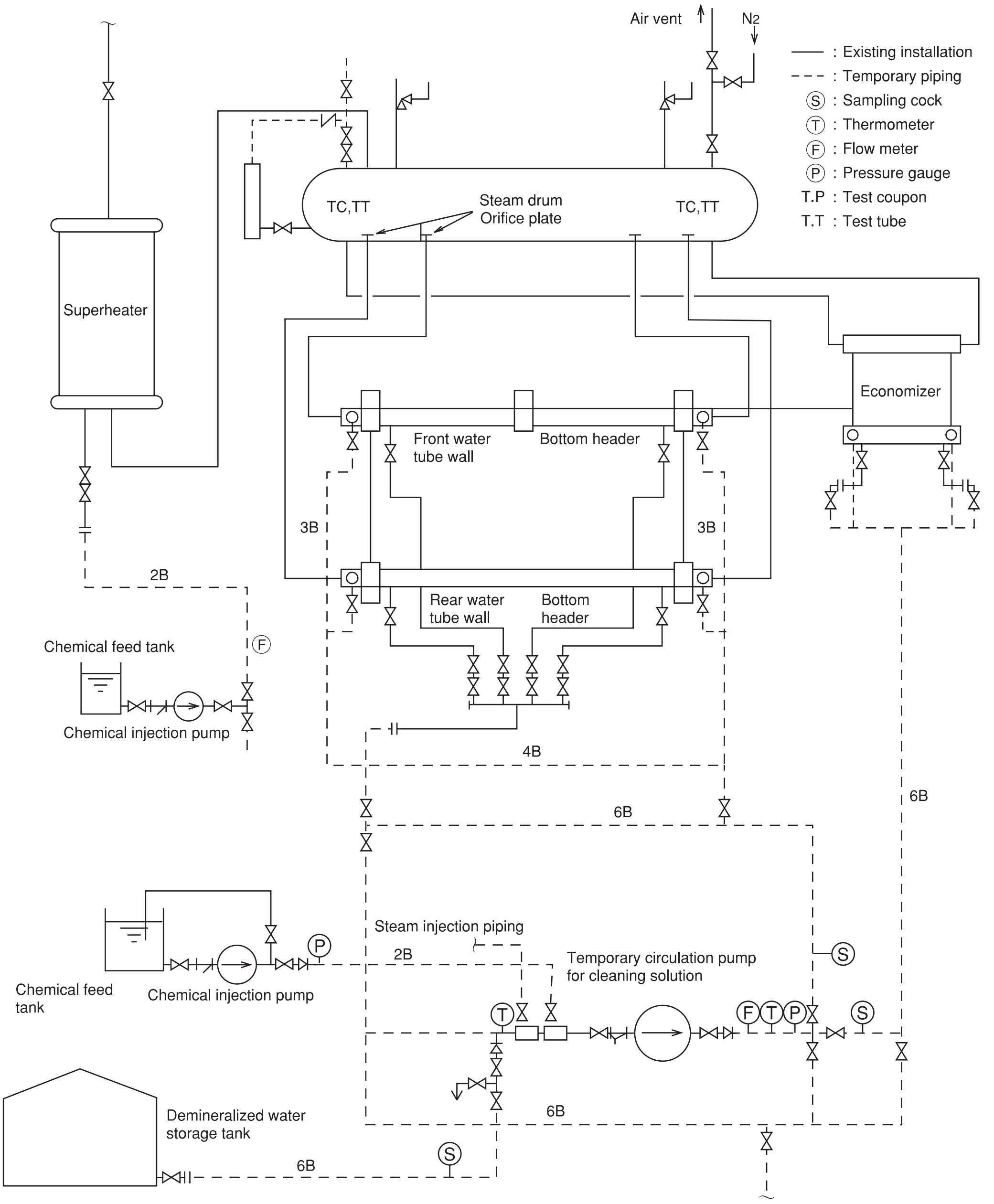

Fig. 9.14 Flow-diagram of a boiler cleaning

⑫ Inspection points and methods,
⑬ Restoration methods,
⑭ Treatment methods of cleaning wastewaters,
⑮ Required utilities and their amounts for each cleaning process,
⑯ Organization chart of the project team including the customer's staffs,
⑰ Operation manuals for each cleaning process.

(d) Cautions for each cleaning process

(i) Installation of equipments and materials for the cleaning

① Installation of pumps ;
The pumps must be installed at the levels to keep out the rain on grounds with the sufficient strengths for the pump weights. The

electric motors and the switchboards must be grounded.

② Valves ;
The valves are mounted in places where are easy to operate them. Then it is confirmed that they are closed. Especially, at the connection point of a cleaning solution piping with a demineralized water supply line or with a part of not to be cleaned, two valves or a check valve must be installed to prevent the contamination with the cleaning solution and the solution leakage.

③ Pipings ;
Clean pipes should be used for the pipings. The absence of foreign matters has to be confirmed before connecting the pipes. Any connecting points and welded parts must be inspected to prevent the cleaning solution leakage.

(ii) Water flushing and hydraulic test

After the installation of the temporary pipings for the chemical cleaning, the water flushing is carried out to discharge the foreign matters from the pipings. Then the cleaning solution line is filled with demineralized water and the hydraulic test is performed to confirm no water leakage.

(iii) Preheating

After finishing the hydraulic test, the preheating of the boiler filled with demineralized water is carried out. The purposes of the preheating are to heat the boiler up to a specified temperature, and to confirm the operational conditions of the equipment and the circulation condition of water. During the preheating, the temperature increasing rates are investigated at several parts of the boiler. If the temperature increasing rates at those parts are considerably varied, countermeasures, such as the modification of pipings and heating method, should be applied to minimize the difference.

(iv) Chemical cleaning

Since various chemicals are used for chemical cleaning, one mistake on the operation may cause troubles and accidents. Therefore, a perfect supervising must be required for the whole cleaning processes and all members working for the cleaning.

The important cautions in chemical cleaning processes are as follows:

① Check a cleaning solution leakage during cleaning. Even if no leakage was observed in the hydraulic test, a chemical cleaning solution sometimes leaks.

② Measure the temperature, pressure and flow rate of the cleaning solution, and analyze the chemical and dissolved ion concentrations at a specified interval.

③ Purge generated gasses during the cleaning.

④ Finish the cleaning when the increase of dissolved ion concentrations and the decrease of the cleaning chemical concentration are terminated.

⑤ Use nitrogen gas to discharge the cleaning solution.

(v) Water rinsing

Use nitrogen gas to discharge the rinsing water.

(vi) Neutralization and rust prevention

Carry out the neutralization and rust prevention treatment at the highest possible temperature to maximize the corrosion inhibition effect.

(vii) Inspection

After the cleaning, the inspection of the boiler is carried out. The water and steam drums, and headers are opened and inspected. If the removed sludges are accumulated there, they are removed to clean up there.

(3) Cleaning of low pressure boilers

The preparation and planning for the cleaning of low pressure boilers are essentially same to those of medium or high pressure boiler cleaning. However, as the scale compositions are often different from those of medium or high pressure boilers, a suitable cleaning method has to be selected according to the composition. The typical scale compositions and the appropriate cleaning methods are described below.

(a) Grease of new boilers

Degreasing agents are generally alkaline chemicals including surface active agents and the dosages are 0.3 to 1.0%. The degreasing is carried out by circulating the cleaning solution at 60 to 100°C for 6 to 8 hours.

(b) Silica scale

A boiler scale containing a large amount of silica is very hard. This kind of scale should be processed by a swelling treatment to be swelled and softened. The swelling agents are alkalis and their dosages are 2 to 10%. The swelling is carried out at 80°C or more for 10 to 24 hours.

After the swelling treatment, an acid cleaning or a high pressure water jet cleaning is carried out to remove the scale.

(c) Hardness scale

Hardness scales are removed by inorganic acid cleanings or alkaline-chelate cleanings.

In case of the acid cleaning, the acid solution of around 5% is circulated at an ambient temperature until a CO_2 gas generation is terminated. Then the acid concentration and the solution temperature are increased up to 10 to 20% and 50 to 60°C respectively. The cleaning time is generally 4 to 6 hours.

The alkaline-chelate cleaning is applied for boilers of which the perfect discharge of cleaning solution is difficult because of their structures. The cleaning solution is heated by using the boiler burner and pressurized up to 2 to 5 kgf/cm^2. The cleaning time is 3 to 4 hours.

(d) Iron oxide scale

For the iron oxide scales, inorganic acid cleanings, organic acid cleanings or neutral-chelate cleanings are applied.

The inorganic acid cleanings are carried out with the dosages of 10 to 20% at the temperature of 50 to 60°C for 4 to 8 hours.

The dosage, temperature and time of organic acid cleanings are 10 to 15%, 80 to 90°C and 4 to 8 hours respectively.

The neutral-chelate cleaning agents are used with the dosages of 10 to 20%. The cleaning temperature and time are 120 to 150°C and 4 to 8 hours.

(4) Cleaning of nuclear power plants

The cleanings of nuclear power plants are divided into two categories. The former is the cleaning to remove the foreign matters, such as rust preventing agents, entered into the system during the plant construction. The latter is the decontamination to remove the CRUD after the plant operation.

(a) Cleaning during the construction

The cleanlinesses of pipes and equipments using for the nuclear power plants are strictly controlled during their manufacture, fabrication, packing and transportation. The construction of the power plant is also carried out to keep the cleanliness. However, the cleaning of each part is carried out and finally the total system is also cleaned after finishing the construction to confirm the cleanliness.

Those cleanings are required to minimize the CRUD accumulation after the plant start-up.

(b) Decontamination after the start-up

During the plant operation, the CRUD is gradually accumulated in the piping and the equipment of the primary cooling water system, and increases the radiation exposure of workers and inspectors. The decontamination is carried out to minimize the radiation exposure.

The decontamination methods are classified into chemical, electrochemical and mechanical methods. Table 9.10 shows the various decontamination methods and their applicable objects.

The following items must be taken into consideration for the planning of decontamination:

① Factors relating to the decontamination effect;
  - Characteristics of CRUD,
  - Decontamination index,
  - Man-rem saving,

② Properties of construction materials, such as the strength,
③ Prevention of recontamination,
④ Minimization of waste volume.

(5) Cleaning of industrial manufacturing plants

In case of industrial manufacturing plants, the cleaning objects include various equipments, such as reactors, heat exchangers, pipings and tanks. Therefore, the structures, materials and so on of the object must be confirmed to determine a suitable cleaning method.

To determine the cleaning method, the sampling and analysis of scales, the dissolving test using scales and so on have to be carried out, like to boilers.

Typical cleaning methods for various equipments are described below.

(a) Pipings and heat exchangers of cooling water systems

The compositions of scales formed in cooling water systems vary depending on the kind of make-up water, the operational conditions of system, the kinds of water treatment chemicals and so on. Generally, fresh water is used as the make-up water and the scales are composed of calcium carbonate, silicates, iron oxides, etc.

Hydrochloric acid or sulfamic acid of 5 to 15% is used for the cleaning of the heat exchangers and pipings. The cleaning temperature and period are 50 to 60°C and 4 to 6 hours. In the case of heat exchangers made of stainless steels, organic acid based solutions are used.

After the cleaning, a sufficient neutralization and a rust preventing treatments have to be applied to keep the clean surface conditions of equipments.

In case of heat exchanger shell sides, the perfect discharge of the cleaning solution and removed sludge from them is very difficult. Therefore, the remaining acid and sludge sometimes cause the secondary corrosion problems after cleaning. A sufficient care is required for discharging the cleaning solution and sludge from

Table 9.10 Decontamination methods and the applicable objects

Decontamination method		Applicable objects
Chemical decontamination	Dilute chemical method	All objects
	Concentrated chemical method	All objects
Electrochemical decontamination	Electropolishing	Mechanical parts Tanks and containers Large diameter pipes (short length) Waste
Mechanical decontamination	High pressure water jet	Insides of tanks and vessels Lose contaminants Insides of large diameter pipes
	Wet blast	Tools Wastes
	Brushing	Insides of pools and tanks
	Sucking	Bottom plates of pools Suppression chambers
	Ultrasonic	Mechanical and precision parts Insides of pools

them.

(b) Blast furnace stave coolers

As demineralized water is generally used for cooling stave coolers, the main component of the scale is iron oxides.

Since the cleaning of stave coolers is carried out by utilizing the heat of blast furnace during the stoppage of the hot stove operation, the cleaning solution temperature rises up to 120 to 130°C. Because of this high cleaning temperature, organic acid or neutral chelating agent based cleaning solutions are used for this system. The concentration of the cleaning solution is 10 to 20%. The cleaning period is usually 6 to 8 hours.

(c) Water jackets of reactors and polymerization vessels

Since fresh water is usually used for cooling water jackets, the main components of the scale are calcium compounds and iron oxides. For the carbon steel jackets, hydrochloric acid of 5 to 15% is used. In case of stainless steel jackets, nitric acid and so on are used.

The cleaning temperature and period are 50 to 60°C and 6 to 8 hours.

(d) Pulp and paper making plants

(i) Digesters

The main components of scales adhering to digesters are calcium compounds. They are easily dissolved by inorganic acid based cleaning solutions. The cleaning is carried out by using hydrochloric acid of 5 to 10% at 50 to 60°C for 4 to 6 hours.

(ii) Black liquor evaporators

The main scale components of black liquor evaporators are organic substances and calcium compounds.

At first, a swelling treatment is carried out by using a swelling agent of around 3% at 70 to 80°C for about 10 hours to wet and dissolve the organic substances. Then the hydrochloric acid of 10 to 15% is used at 50 to 60°C for 6 to 8 hours to remove calcium compounds.

(e) Fins of air-fin coolers

The fins of air-fin coolers are made of aluminum and the surfaces are fouled by dusts and organic substances in the air. The cleaning of fins is carried out by spraying a neutral or alkaline cleaning agent of 10 to 15% at 50 to 60°C for 6 to 8 hours. As removed scales often accumulate between the fins, a water jet cleaning is carried out to remove the sludge after the chemical cleaning.

During the cleaning, the other equipments surrounding the air-fin coolers have to be protected from the contamination with the cleaning solution, etc.

(f) Filter cloths of filter presses for exhaust gas desulfurization plants

Scales composed of calcium compounds and carbon adhere to the filter cloths of filter presses for the exhaust gas desulfurization plants of a lime-gypsum method. Those scales are removed by dipping the cloths into an alkaline cleaning solution of around 1% at an ambient temperature for 15 to 20 hours.

(g) Polymerization vessels of polypropylene

In the inside of polypropylene polymerization vessels, a small amount of the polymer, the catalyst and the other organic substances are adhered.

For stainless steel vessels, a high pressure water jet cleaning is applied to remove the scale. For glass lined vessels, an inorganic alkaline cleaning agent of 3 to 5% is used at 60 to 80°C for 8 to 10 hours.

(h) Hydraulic machinery

As hydraulic machinery is precision machines, a small amount of foreign matters in the hydraulic oils may cause the operational troubles such as the wearing of parts and the miss-working of valves. To prevent those troubles, the foreign matters in the pipings, etc., of newly installed hydraulic machinery have to be discharged from systems by careful and sufficient flushings.

In case of a conventional method, the hydraulic machinery is temporarily assembled in the site and dismantled again to transport them from the site to the manufacturer's factory for carrying out the perfect flushing. Therefore, the flushing requires much man powers and a long working term.

A new flushing method developed by KURITA realizes the flushing of them at site soon after the assembling. This flushing method remarkably reduces the flushing period and its cost.

(i) Flow meters for tap water

The adhesion of iron oxides, etc., to the flow meters for tap water causes the mis-working. Cleaning agents composed of food additives are used for the cleaning at 40 to 50°C during a short time.

(j) Evaporators for distilling plants for ships

Scales composed of calcium compounds adhere to the evaporators and reduce the water production. Organic acids of 10 to 15% are used for the cleaning at 80 to 100°C for 5 to 6 hours. The heat source is the waste heat of the marine boilers or engines.

9.5.6 Treatments of Waste Cleaning Solutions[16)]

The waste chemical cleaning solutions include large amounts of heavy metals originate from scales and remaining cleaning agents. Generally, the wastewater is deeply colored and includes a high COD. The pH and salt concentrations of the wastewater vary in wide ranges. The qualities of wastewater are widely different depending on the cleaning processes. The wastewater is usually discharged at a short time at the final stage of each cleaning process. Table 9.11 shows typical qualities of wastewater from various cleaning processes.

The treated wastewater qualities have to satisfy the local regulations. The pH is easily controlled by a neutralization using acids or alkalis. The treatment methods of heavy metals, COD and sludges are described below.

(1) Removal of heavy metals

The solubilities of metallic ions reduce in some pH ranges because of the formation of the hard-

Table 9.11 Typical qualities of wastewaters from various cleaning processes

Kind of wastewater	pH	Turbidity (degree)	Color (degree)	Iron (mg Fe/*l*)	Copper (mg Cu/*l*)	COD_{Mn} (mg/*l*)	SS (mg/*l*)
Ammonia cleaning	10.9	—	—	4.6	290	80	11
The first rinsing	10.6	9	Below 10	Trace	4.8	60	5.5
Hydrochloric acid cleaning	Below 1	2	Below 10	7,400	680	14,000	45
The first rinsing	1.2	10	Below 10	320	10	470	7.2
The second rinsing	4.8	12	50	20	Trace	5	Below 5
Organic acid cleaning	3.7	53	560	4,200	3.5	12,800	8.3
The first rinsing	4.4	15	Below 10	160	Trace	240	Below 5
Chelate cleaning	9.5	—	—	3,430	64	28,600	18
Neutralization and rust prevention	10.1	70	620	45	Trace	250	Below 5

soluble hydroxides, as shown in Figure 9.15. Therefore, metallic ions in the wastewater are precipitated as the hydroxides by controlling the water pH.

Most wastewater includes a high concentration of iron ions and they are removed as iron hydroxide precipitate from the water by controlling the pH in the range of 10 to 12. In case of a wastewater containing a high concentration of amphoteric metal ions, such as aluminum and zinc ions, an appropriate pH range for the hydroxide precipitation is a narrow as shown in the Figure 9.15. Therefore, a sufficient care must be required for the pH adjustment.

Copper ions in ammonia cleaning wastewater form the complex salts with ammonia and are difficult to separate by only pH adjustment. Those copper ions are separated from the water by using ion exchange resins or by precipitating the hard-soluble salt with a special agent.

The former almost perfectly removes copper ions but the treatment cost becomes higher than that of the latter.

(2) Removal of COD

Table 9.12 shows the COD_{Mn} and BOD values of 0.1% solutions of various chemical cleaning agents.

The COD is treated by oxidizing decomposition, biological decomposition or hardsoluble salt precipitation methods. In case of chemical cleaning wastewater, the oxidizing decomposition method is generally applied because the water quality and the water discharge are not constant, and the treatment should be completed in a short period of time.

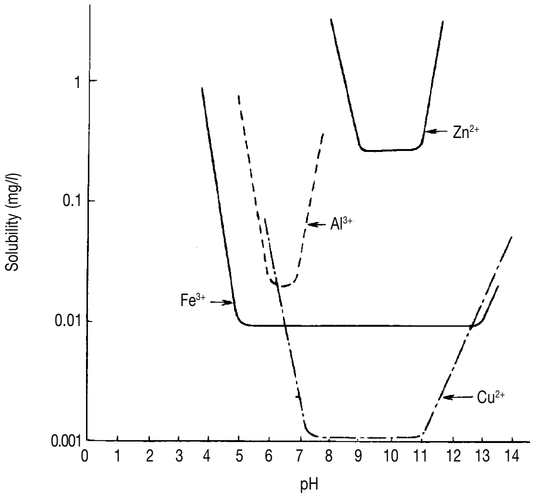

Fig. 9.15 Relationship between pH and the solubilities of metallic ions

Figures 9.16 and 9.17 show the flow diagrams of the oxidizing decomposition methods for hydrochloric acid cleaning and organic acid cleaning wastewater. In both cases, the COD are reduced to 10 mg O/*l* or less, and the heavy metal concentrations are sufficiently reduced to discharge into public water areas.

(3) Sludge treatment

Sludges formed by neutralization and sedimentation treatments are dehydrated to reduce the moisture content below 85% by using centrifugal dehydrators, vacuum dehydrators and so on. The dewatered cakes are transported and finally treated according to the local regulations.

9.6 Mechanical Cleaning

Mechanical cleanings are applied for the following two kinds of scales:

① Scales difficult to remove by chemical cleaning,

② Scales that the chemical cleaning cost becomes higher than that of the mechanical cleaning.

9.6.1 Mechanical Cleaning Methods

(1) High pressure water jet cleaning

The high pressure water jet cleaning was developed in the United States in 1950. This cleaning method is employed in almost all refineries, petrochemical plants, atomic power plants and so on.

The water jet cleaning is the method to remove the scales and sludges by the impulse of high pressure water jet spouting from a small-size nozzle.

The equipment and parts necessary for the water jet cleaning are high pressure pumps, pump driving units, pressure control units, feedwater pipings, high pressure water hoses, nozzles and various attachments. Diesel engines or electric motors are used as the pump driving units. Generally, mobile water jet cleaning systems are used in fields. In the present, the available maximum water pressure is 700 kg/cm^2 and the maximum capacity is 10 m^3/h in Japan.

Photograph 9.5 (p. 9-38) shows a mobile high pressure water jet cleaning system.

In case of not so high pressure, below 150 kg/cm^2, a small and light weight (100 kg) water jet cleaning apparatus is available. Photograph 9.6

Table 9.12 $\mathrm{COD_{Mn}}$ and BOD of the 0.1% solutions of various chemical cleaning agents

Cleaning chemicals	$\mathrm{COD_{Mn}}$ (mg O/l)	BOD (mg O/l)
Citric acid	520	550
Glycolic acid	640	430
Formic acid	60	200
EDTA	450	0
Corrosion inhibitor	50	10
Reducing agent	170	65
Copper ion sequestering agent	500	60
Wetting agent	120	140
Rust preventing agent	115	0
Hydrazine	125	55

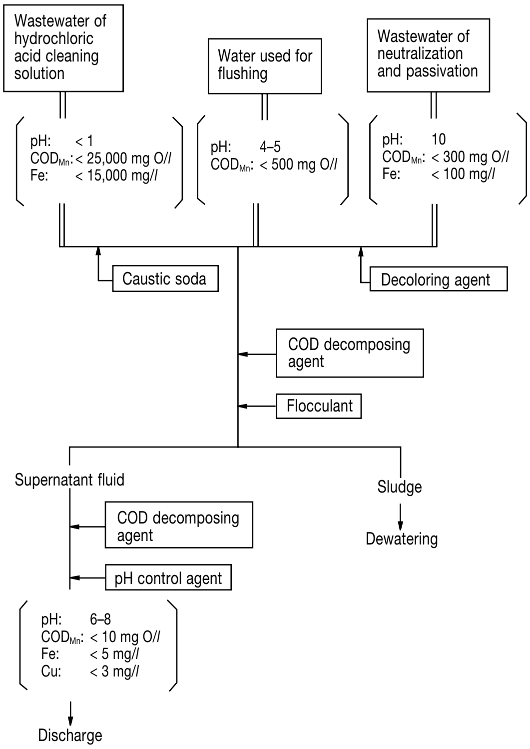

Fig. 9.16 Flow diagram of a wastewater treatment for a hydrochloric acid cleaning

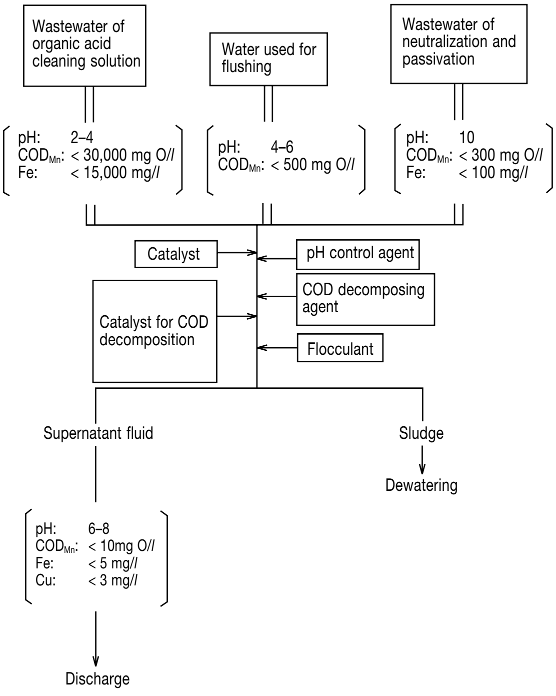

Fig. 9.17 Flow diagram of a wastewater treatment for an organic acid cleaning

(p. 9-38) shows a small-size water jet cleaning apparatus. The capacity of this apparatus is 1 m^3/h.

As the contact with a high pressure water jet is very dangerous and may wound workers, sufficient cares are required for the safe cleaning works. Various automatic operation control units for the water jet cleaning have been developed and applied for the safe and efficient operation. Photograph 9.7 (p. 9-39) shows an automatic high pressure water jet cleaning system for the tube bandles of heat exchangers.

A wet sand jet cleaning is used as a kind of water jet cleaning. In this cleaning method, minute sand particles are mixed with a high pressure water to increase the cleaning effect. Photograph 9.8 shows a small-size wet sand jet cleaning appa

Photo 9.8 Wet sand jet cleaning apparatus and its nozzles

ratus and its nozzles.

(2) Pig cleaning

Pig cleaning removes scales, deposits and sludges by moving pigs with the pressure of water or air, through the insides of tubes or pipings. The pigs are made of expanded polyurethanes with the excellent elasticity, pressure resistance, compressibility and abrasion resistance. They have cylindrical or shell shapes. The pigs were developed in the United States in 1960's.

The equipment and parts required for the pig cleaning are pigs, launchers and catchers which discharge and receive the pigs, and driving units for pigs, such as compressors and pumps.

Photograph 9.9 (p. 9-39) shows the pigs. A pig having suitable hardness, shape, etc., has to be selected according to the purpose of cleaning, the feature of scales and so on. The diameters of pigs are 2 to 36 inches. Pigs with superprecision specifications are used for the pipings of atomic power plants.

Pigs are available for the complicated pipings of various manufacturing plants and so on because they have sufficient flexibilities and elasticities. However, the use of pigs is difficult in case of pipings with special structures. Table 9.13 shows the applicable structures of pipings and joints for the pig cleaning.

A typical procedure of pig cleaning is as follows:

① The launcher and catcher are installed at the both ends of a piping to be cleaned.
② The driving unit of pig, pressure gauges, etc., are installed.
③ A pig is loaded to the launcher.
④ The valve of the driving unit is gradually opened to send the pig into the piping.
⑤ The movement of pig is confirmed by checking pressure gauges.
⑥ The valve of driving unit is closed when the pig reaches the catcher, and the pig is taken out from the catcher.
⑦ The operation of ③ to ⑥ is repeated until the piping becomes clean.

The driving pressure of pig is 4 to 5 kg/cm^2 for pipings with the diameter of 4 inches or more. The pressure of around 10 kg/cm^2 is sometimes required for the pipings with the diameter of below 4 inches.

The required times of pig transportation to clean the piping are generally 3 to 4 times for new pipings and 3 to 10 times for existing pipings. At first, a pig with the same diameter to the piping is used. Then the pig size is increased little by little for

Table 9.13 Applicable structures of pipings and joints for the pig cleaning

Objects		Applicable structure, etc.
Piping	Diameter	2 to 36 inches
	Connection method	Welding or flange connection
Joints	Elbow	Short or long elbows of 90°C and 180°C
	Valve	Sluice or ball valves
	Tee	Normal tee; one side must be blinded Reverse tee; applicable when the piping is filled with water
Materials		Resistant for the back pressure

repeating the pig driving.

(3) Wet blast cleaning

The wet blast cleaning is the method to remove scales or deposits by striking them with the mixture of water and abrasives using highly compressed air. Water using this method minimizes the dust scattering and the erosion of metals with abrasives.

Figure 9.18 shows the outline of a wet blast cleaning equipment. Photograph 9.10 (p. 9-40) shows a typical wet blast cleaning equipment.

The fine particles of alumina, various steels, glass, etc., are used as the abrasives. The abrasive of a suitable material and particle size should be selected according to the scale composition and the structure of the object to be cleaned.

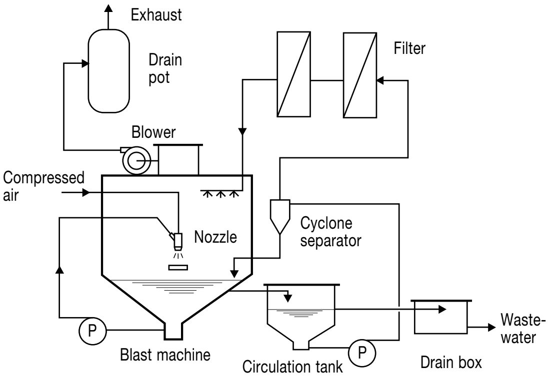

Fig. 9.18 Outline of a wet blast cleaning equipment

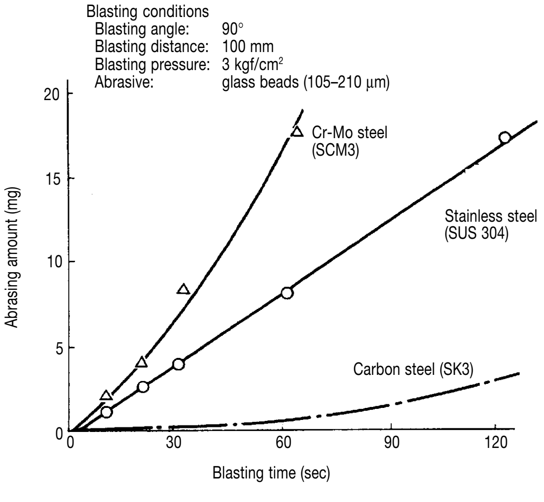

Fig. 9.19 Relationship between the abrasing amounts of metals and the blasting time

The effect of wet blast cleaning is influenced by the diameter and hardness of abrasives, the angle and distance of abrasing, etc. The abrasing rates of base metals are changed by the metallic compositions. Figure 9.19 shows the abrasing amounts of three kinds of steels by a wet blast cleaning with glass beads.

(4) Ultrasonic cleaning

The ultrasonic cleaning is the method of removing scales by a vibration or cavitation impact yielded with ultrasonic waves applied through a liquid medium such as water. When water is used as the medium, the sound pressure of above 1 atmospheric pressure forms air bubbles in water, and the bubbles disappear when the pressure becomes 0 atmospheric pressure. When the bubbles disappear, the energy stored in the bubbles is released and the impact pressure reaches over 1,000 atmospheric pressure. This impact removes a scale from the surface of object.

The equipment and parts using for the ultrasonic cleaning are a tank filled with the medium and an ultrasonic generator.

The ultrasonic cleaning is especially suitable for cleaning objects with the complicated structures and minute gaps. The ultrasonic cleaning is applied to clean the parts of machines, etc., with not so large sizes, because the distance where the ultrasonic wave is effectively transmitted is not so long.

(5) Electrolytic polishing

The electrolytic polishing is a kind of metal surface finishing methods, which was developed by Jacquet in 1930's in France. An object is immersed into an electrolytic solution and connected with an external direct current source as an anode to face a cathode. The application of electric current electrochemically dissolves the scale, etc., on the anode surface and polishes the anode (object). Therefore, the cleaning objects polished by this method have to be metals. In the present, this method is applied for almost all kinds of metals including stainless steels. The cleaning effect is influenced by the applied electrical potential and current density, the compositions of electrolytic solutions, etc.

Recently, the electrolytic polishing has been applied for the decontamination of parts and equipments composed of nuclear power plants because it is able to remove radioactive substances diffus ing into the base metals and to obtain the excellent decontamination effect.

However, as the electrolytic solutions contain a high concentration of sulfuric acid, phosphoric acid, etc., the sufficient treatment for the waste solutions is inevitable.

(6) Suction cleaning

The suction cleaning is a cleaning method to suck sludges, precipitates on the bottoms, side walls and so on of tanks, containers, etc., by using a suction port with a hose connecting to a suction pump.

The equipment and parts required for the suction cleaning are suction pumps, hoses, suction ports, etc. The cleaning efficiency is influenced by the pump capacity, the shape and size of suction port, etc. The both of manual type and a self-propelled type cleaning systems are available.

This method is suitable for cleaning objects with the wide and smooth surfaces.

(7) Brush cleaning

This is a cleaning method to remove scales and sludge by using wire brushes, rotating brushes and so on. Metallic or nylon wires are generally used as the brush materials.

In case of the decontamination for pools or tanks of nuclear power plants, self-propelled and remote control brush cleaning systems are used.

9.6.2 Examples of Mechanical Cleaning

(1) Boiler furnace

Clinkers composed of ashes accumulate on the outer heating tube surfaces of boilers, superheaters, etc. These clinkers cause various troubles, such as the thermal efficiency drop of boilers and the acceleration of tube corrosion.

A high pressure water jet cleaning is applied for removing the clinkers. Figure 9.20 shows a typical procedure of the boiler furnace cleaning.

(a) Preparation of cleaning

Before the high pressure water jet cleaning, following preparation works have to be carried out:

① Determination of clinker composition,
② Preparation of equipment, chemicals, etc., using for the cleaning,
③ Setting-up of scaffoldings, etc.,
④ Removal of clinkers from the portions not to be cleaned,
⑤ Protection of portions not to be cleaned.

Among those preparation works, the most important one is the protection of portions not to be cleaned. Since a large amount of water is used in the furnace for the cleaning, the portions not to be cleaned must be protected from the water. As the water is contaminated with sulfuric acid, etc., yielding from the clinker during cleaning, the water becomes acidic and corrosive.

Acid-resistant and waterproof sheets, and sealing compounds are used for the protection. The portions to be protected are different depending on the boiler structure. Figure 9.21 shows an example of the protected portions of a boiler. Generally, the following portions of boilers must be protected from the cleaning water:

① Furnace bottom,
② Burners,
③ Economizer,
④ Reheater,
⑤ Superheater.

(b) Water spray cleaning

Water is sprayed on the surfaces of cleaning objects at a rate of 10 to 15 m^3/h during around 20 hours to wet and swell the clinkers. During this process, the water leakage at the protection portions must be inspected and countermeasures have to be applied if the leakage is found. The test runs of the water feeding and discharging systems for the water jet cleaning should be carried out during this process.

A corrosion inhibitor is added into the spray water to prevent the corrosion of cleaning objects, caused by sulfuric acid and so on dissolved into the spray water from clinkers.

During the water spraying, the water amounts in each water receivers should be checked and the sludge should be discharged at an appropriate time. The pH and suspended solid concentration of the drainage are periodically analyzed. This process is finished when the pH becomes higher than 4.

(c) Water jet cleaning

Since most adhered matters on the internal wall surfaces of boiler furnaces are water soluble, the 50 to 70% of them are removed by the water spray cleaning. The remaining substances are hard and tightly adhere on the tubes. Moreover, the clinkers which adhere at spaces between the tubes are hardly removed by the water spraying.

Those remaining substances are removed by the high pressure water jet of 200 to 350 kg/cm^2. The water amount is 7 to 10 m^3/h and the cleaning period is 25 to 30 hours. To increase the cleaning efficiency, various types of nozzles, such as straight, lance and T-shape nozzles, are used according to the structures of the cleaning portions. A corro-

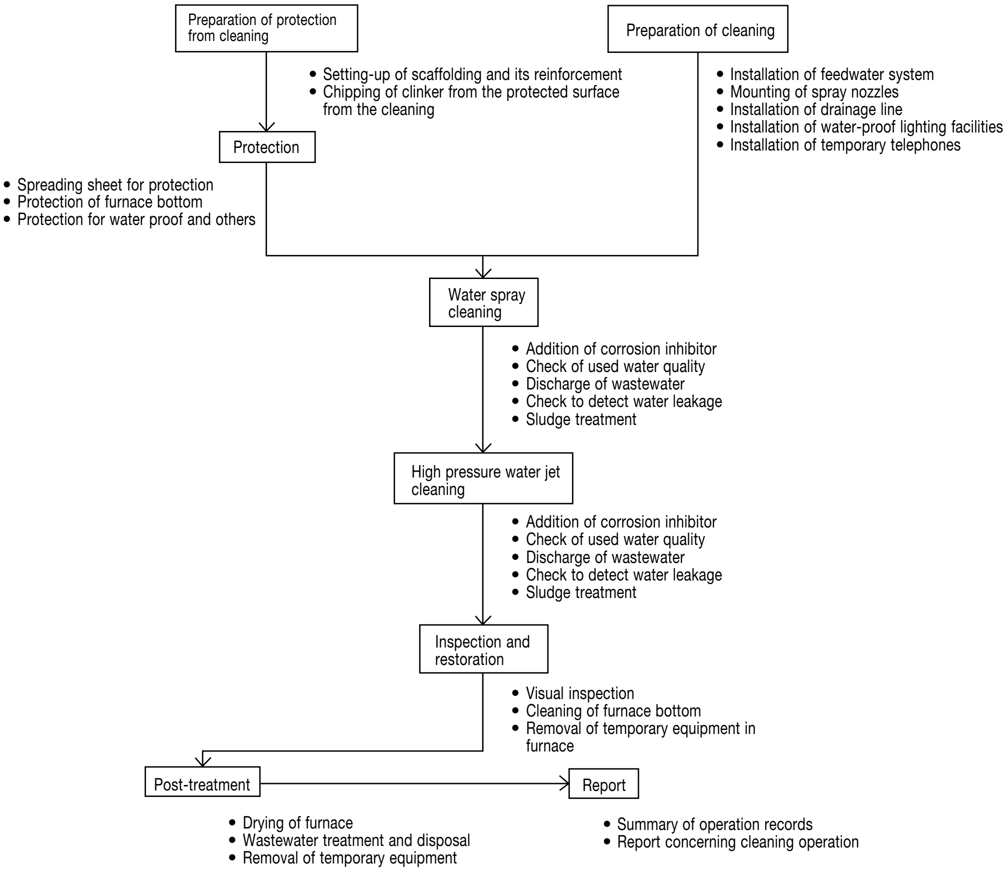

Fig. 9.20 A typical procedure for the high pressure water jet cleaning of a boiler furnace

sion inhibitor is added into the cleaning water.

At the final stage of the cleaning, an alkali and a rust preventing agent are added into the cleaning water for the neutralization and passivation.

Finally, the pH of tube surfaces and the water leakage at each part of the object are inspected.

(2) Heat exchangers

When the water jet cleaning is applied for heat exchangers, the area surrounding the heat exchanger is covered with waterproof sheets to prevent the fouling with the cleaning water and removed scales.

(a) Cleaning of heat exchanger tube inside

The water jet cleaning is carried out by using a flexible nozzle at the pressure of 200 to 350 kg/cm^2. The remaining removed scale in the tube is discharged by water flushing. Finally, the tube inside is flushed by a pressurized air to discharge the remaining water.

(b) Cleaning of tube sheets and channel covers

The water jet cleaning is carried out by using a straight nozzle at the pressure of 200 to 350 kg/cm^2 to remove scales, broken packings and so on from the tube sheets and channel covers.

(3) Steam condensers

Steam condensers installed in power plants, etc., are cooled by using cooling water passing through the tube insides. The tube insides are fouled with scales and biological fouling. Then the thermal efficiency of the condenser is reduced.

To minimize this fouling, a sponge ball cleaning is often applied for the steam condenser, however, the fouling is gradually accumulated in the tube insides. Therefore, the water jet cleaning is periodically applied for the condenser to perfectly remove the fouling.

The water jet cleaning is carried out by using a special nozzle connecting with a flexible hose at the pressure of 200 to 300 kg/cm^2. The nozzle is automatically driven in the inside of tube by using

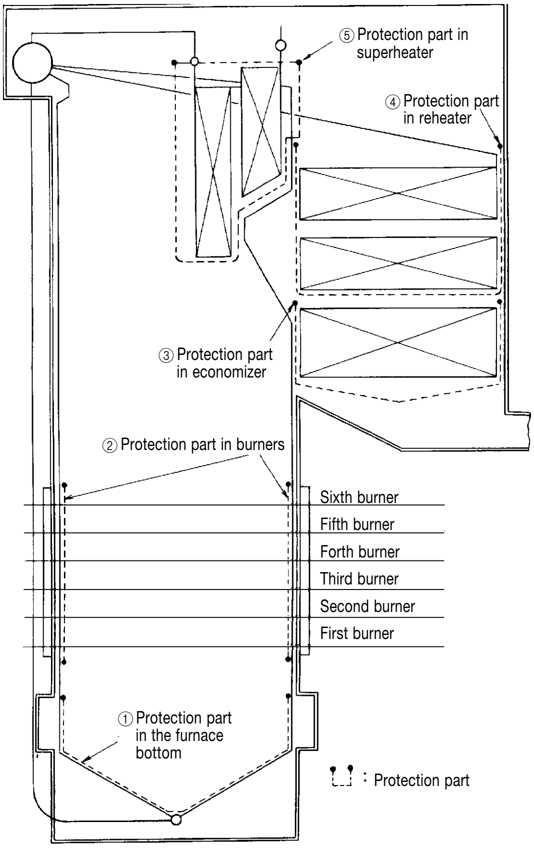

Fig. 9.21 Protection parts in a boiler from the high pressure water jet cleaning

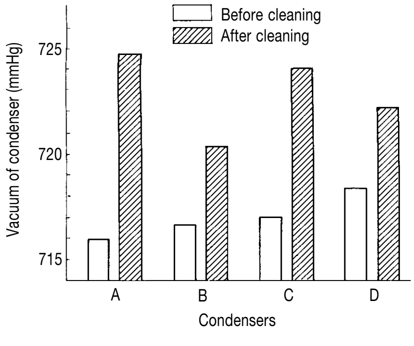

Fig. 9.22 Recoveries in the vacuums of steam condensers after their high pressure water jet cleanings

a nozzle sending and returning apparatus.

The water jet cleaning almost perfectly removes scales and scarcely damages tube materials. The abrasion rates of various metals by water jet cleaning are very small as shown in Table 3.40 (p. 3-64). Figure 9.22 shows the recoveries in the vacuums of condensers by applying the water jet cleaning.

(4) Cleaning of welded seam

The welded seam of reactor, etc., should be cleaned to inspect the welding condition. Generally, a wet sand jet cleaning is applied for the welded seam cleaning. The silica sands with the size of No.4 to 5 are used as the abrasives. The water pressure of 200 to 300 kg/cm^2 is applied to polish the surface in the width of 150 to 200 mm including the welded seam at the center line.

The other parts except polishing area have to be protected from the wet sand jet. The abrasives are recovered and reused.

9.6.3 Wastewater Treatments for Mechanical Cleaning

The application of mechanical cleaning yields various wastewaters including oils, fats, carbon, heavy metals, alkalis, acids, etc. Those wastewaters must be treated to satisfy the local regulations.

In this section, the treatment methods of high pressure water jet cleaning wastewater are described because the water jet cleaning is most widely applied among mechanical cleaning methods.

(1) Wastewater of boiler furnace cleaning

The wastewater of boiler furnace cleaning with a high pressure water jet is acidic, and includes heavy metal ions and suspended solids composed of metal oxides mainly. Table 9.14 shows the typical wastewater qualities.

The typical flow diagram of the wastewater treatment is shown in Figure 9.23. The wastewater pH is controlled to precipitate the heavy metal ions as their hydroxides. The sludge and SS are separated from the water and concentrated by a centrifugal separator. The water from the separator is filtered with a precoat filter. The pH of the filtrate is adjusted and it is discharged according to the local regulations. The concentrated sludge should be appropriately treated to satisfy the regulations.

The LAVAL SEPARATOR® shown in Photograph 9.11 (p. 9-40) is also available for separating and concentrating the sludges and SS from the wastewater. The separation effect is excellent as compared with a cyclone separator, etc. The treatment capacity is 1 to 2,500 m^3/h.

Table 9.14 Wastewater qualities of a boiler furnace cleaning with a high pressure water jet

Portion to be cleaned	pH	COD_{Mn} (mg O/l)	Iron ion (mg/l)	Nickel ion (mg/l)	Vanadium ion (mg/l)	Sulfate ion (mg/l)	SS (mg/l)
Superheater	3.4	20	52	236	34	2,400	13,640
Reheater	2.7	70	1,600	1,110	6,750	46,500	14,340
Economizer	2.5	395	6,000	3,240	42,200	27,500	3,940

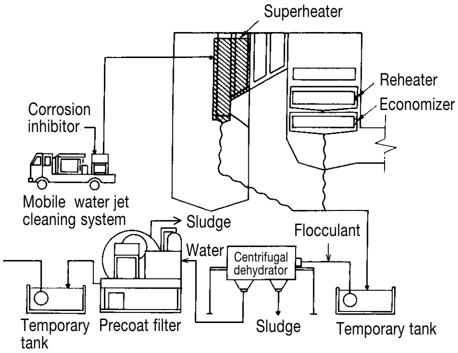

Fig. 9.23 A typical flow diagram for the wastewater treatment of a boiler furnace cleaning with a high pressure water jet

(2) Wastewater of the process fluid side cleaning of heat exchangers

The adhered matters on the process side of the heat exchangers contain oils, organic substances and inorganic substances such as iron oxides. Those matters are sticky and will make the surrounding area dirty if they are scattered. Therefore, the cleaning objects are transported to an exclusive cleaning place and cleaned by a high pressure water jet. The cleaning water is collected to the wastewater pit in the cleaning place. The wastewater is treated and recycled.

A typical flow diagram of the wastewater treatment is shown in Figure 9.24. The oils in the wastewater are removed by using an oil filter or adsorption mats. The suspended solids are separated by a precoat vacuum dehydrator. The treated water is recycled as the cleaning water to reduce the water consumption. The water recycling minimizes the water consumption for the water jet cleaning up to around 1/20 of that in case of no water recycling.

However, the water recycling increases the chloride ion concentration of cleaning water more than ten times of the raw water. The pH of recycled water reduces and becomes acidic. Therefore, the tube materials attacked by chloride ion, such as stainless steels, must be cleaned at the early stage of heat exchanger cleaning or without water recycling. The pH reduction is recovered by an alkali injection and the precipitates of metal hydroxides formed by the neutralization are removed by the precoat filter.

9.7 Safety Measures for Cleaning

9.7.1 Chemical Cleaning

Various chemicals are used for chemical cleanings. Various construction works, such as the installation of equipment, the welding of pip

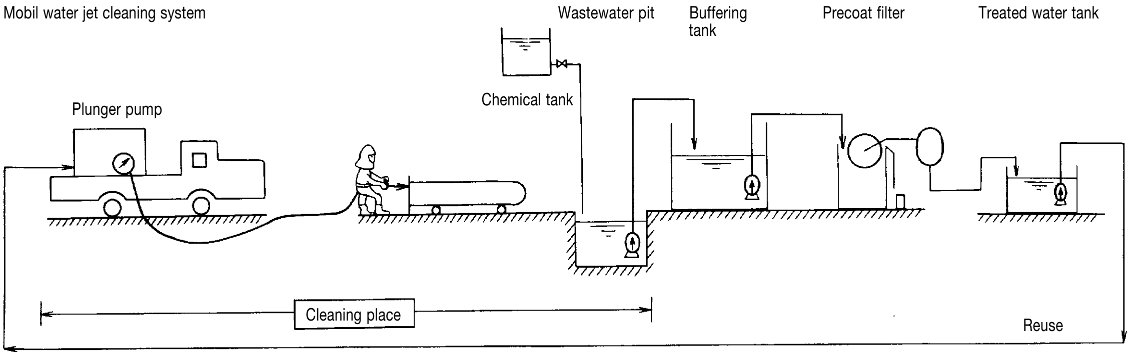

Fig. 9.24 A typical flow diagram for the wastewater treatment of the process side cleaning of heat exchanger by a high pressure water jet

ing and the building of scaffolding, are carried out at the site. These works require experts and skilled operators. Moreover, licenses are required for carrying out some specified works.

Therefore, sufficient safety measures have to be practiced in each process of chemical cleaning. The important measures are summarized below.

(1) Fire prevention

① Welding and cutting of pipe, etc., must be done after confirming no inflammable around the work site.
② Acids, alkalis, oxidizing agents and reducing agents using for the cleaning must be separately stored to avoid their contact.
③ The use of fire is strictly prohibited at the surrounding of cleaning objects because hydrogen gas generates during acid cleaning.

(2) Measures for dangerous gas generation

Some chemicals using for chemical cleaning, such as hydrochloric acid and ammonia, yield the irritative gasses. Those chemicals are stored in closed tanks and their gasses should be treated by using adsorbents.

During acid cleaning, dangerous gasses, such as hydrogen and hydrogen sulfide gasses, are generated by the reactions between acids and scales. Those gasses must be ventilated and treated with adsorbents.

(3) Prevention of electric shock and leakage

① The construction works for electric source and wiring must be carried out by licensed workers.
② The electric apparatus should be grounded.
③ Waterproof wiring must be used. The wiring keeps from the contract and friction with the other equipment and materials.

(4) Preparation of scaffolding and passage

① Proper scaffoldings must be installed and life lines have to be used for any works at over a man's height.
② Passages for cleaning works must be appropriately prepared. Stairs should be installed for any paths at crossing over the piping. Ditches and manholes are covered or enclosed with fences.

(5) Lighting

Appropriate lighting apparatus should be installed in the working places to be able to continue the cleaning even in a night time.

(6) Protective articles

Protective articles, such as goggles, mask, gloves and protective clothings, must be worn in chemical handling.

(7) Cautions for works at the inside of boiler

Prior to enter the insides of boiler furnace, steam drum, etc., the oxygen concentration and temperature must be measured. Instruments, tools, etc., bringing into the inside have to be protected from their loss in the inside.

(8) Meeting before works

A meeting should be held to inform the schedule and the items of cleaning works to the all workers before the operation. Before starting the operation, the all workers should patrol the working places to find and improve any dangerous points.

9.7.2 Mechanical Cleaning

(1) High pressure water jet cleaning

Since the water jet cleaning uses a high pressure water of 200 to 350 kg/cm^2 and it is sometimes carried out at dangerous places, such as a high place and a dark place isolated from the outside, safety countermeasures must be applied thoroughly.

The countermeasures should be applied for the both of cleaning apparatus and operations.

(a) Cleaning apparatus and protective articles

① Cleaning apparatus must be periodically inspected and appropriately maintained.
② Appropriate measuring instruments and safety articles must be used. Especially, the use of nozzle guns with safety valves is inevitable.
③ The condition of high pressure hoses must be always checked to avoid the use of abrased one.
④ Protective articles, such as goggles, masks, gloves and clothings, must be periodically checked and appropriately maintained.

(b) Cleaning operations

① The cleaning must be carried out by using appropriate and well maintained cleaning apparatus.
② The workers must be well trained and wear adequate protective articles.
③ The cleaning has to be carried out under watching by supervisors.
④ Workers operating the high pressure water nozzles must be alternated during a limited

time. A long time working must be avoided.

⑤ The start-up and stoppage of the high pressure pump has to be informed all workers by a signal, radio contact, etc.

⑥ A meeting before the operation should be held to carry out the cleaning safely.

⑦ Measures preventing the scattering of high pressure water must be applied.

⑧ In case of the cleaning work at a high place, an appropriate scaffold is constructed and the high pressure hose must be fixed to the scaffold. The workers have to wear life lines.

⑨ In case of the cleaning work at a dark place, adequate lighting apparatus should be installed.

⑩ In case of the cleaning at a closed place, a sufficient ventilation must be carried out to prevent oxygen deficiency and to discharge dangerous gasses.

(2) Boiler furnace cleaning with the water jet

① As dust containing toxic vanadium pentoxide is formed by the cleaning works, the workers must wear respirators and goggles.

② Temporary telephones should be installed between the inside and outside of the furnace to inform the operational conditions at the both sides.

③ The water jet cleaning must be carried out under watching by supervisors.

④ The worker operating the high pressure water nozzle has to be alternated within two hours.

⑤ In the furnace inside, appropriate waterproof lighting apparatus and scaffold are installed.

⑥ Worker has to wear a helmet with a flashlight and a life line.

⑦ A detachable nozzle of a gun-type with a safety valve should be used.

⑧ In the furnace inside, a sufficient ventilation is carried out and the oxygen concentration must be measured before entering the furnace.

⑨ A preoperation meeting should be held to carry out the cleaning safely.

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10. Miscellaneous Specialty Chemicals

10.1 Additives for Drinking Distilled Water

10.1.1 Drinking Water for Marine Vessels

The securing of drinking water is one of important things on marine vessels.

In case of loading tap water on a marine vessel, a long time navigation deteriorates the water quality by bacterial growth and so on. For drinking a water without bacteria, the water must be sterilized by using sodium hypochlorite, etc. In this case, the chlorine concentration at the use point should be maintained at 0.1 to 0.2 mg Cl_2/l.

Recently, most marine vessels have been equipped with distilling plants for supplying the drinking water. The installation of distilling plant minimizes the water tank capacity and always supplies a fresh water. However, the drinking of distilled water is not good for human health because it contains no mineral required for the health.

10.1.2 Influence of Drinking Distilled Water on Health

Dr. Masao Kuga, the Maritime Labor Scientific Research Institute, and KURITA WATER INDUSTRIES LTD., jointly carried out the clinical demonstration of crews on ocean vessels and the laboratory tests of rats for determining the influence of drinking distilled water on the health. The test results are summarized below.

(1) Clinical demonstration results

The Cornel Medical Index (CMI) test results and so on are shown in Tables 10.1 to 10.3 and Figure 10.1.

The crews drinking distilled water had various unpleasant feelings and had been attacked by diarrhea, etc., as shown in Tables 10.1 and 10.2.

The blood tests showed that the leukocyte number had increased as the amount of drinking distilled water had increased as shown in Table 10.3 and Figure 10.1.

(2) Results of animal experiments

Rats of 120 were divided into three groups: the first, drinking a distilled water, the second, drinking a mineral added distilled water and the third, drinking a tap water. They had been bred during 6 or 12 months. Then they were submitted to various tests.

The test results are reviewed below.

(a) Pathologic-histlogical tests

The deposits of protein were detected in the kidneys of rats drinking the distilled water. This sug

Table 10.1 Summary of questionnaire to crews who drank distilled water

Items	Complaints	Kind of vessel
Feeling after drinking	Not palatable No taste Not good feeling for the stomach	Fishing Commercial
Whole body symptoms feeling harmful	A languid feeling during distilled water drinking, and recovering by drinking tap water on land	Fishing
Developed symptoms	Diarrhea Nausea Rigor	Commercial
Others	Sticky and slippery feeling on skin, or causing the skin roughness by taking distilled water bath	Fishing Commercial

Table 10.2 Results of the CMI test for drinking distilled water

Kind of organ	Symptoms	Rate of crews getting symptoms (%)	
		Fishing vessels	Commercial vessels
Circulatory organs	Palpitation	24	25
	Short breath	28	30
	Dizziness	13	10
	Faint	8	9
Digestive organs	Furred tongue	11	10
	Meteorism	30	20
	Stomach disorder	9	10
	Diarrhea	31	21
	Constipation	11	11
Skin	Difficult recovery from injury	10	3
	Skin oversensitiveness	20	20
	Urtication	10	10

Table 10.3 Distilled water drinking conditions of crews receiving blood tests

Vessel name	Number of crews	Place of blood-collecting	Water temperature at the noon (°C)	Drinking condition of distilled water
A	17	On the Indian Ocean	24	Fully drinking
A'	19	On the Indian Ocean	27	Fully drinking
A"	17	On the Indian Ocean	26	Fully drinking
B	23	Off Hawaii Island	19	Partially drinking
B'	21	Off Hawaii Island	26	Partially drinking
C	19	In a port	23	Not drinking

Duration of voyage:
A, A', A"; 7 months
B, B'; 4 months

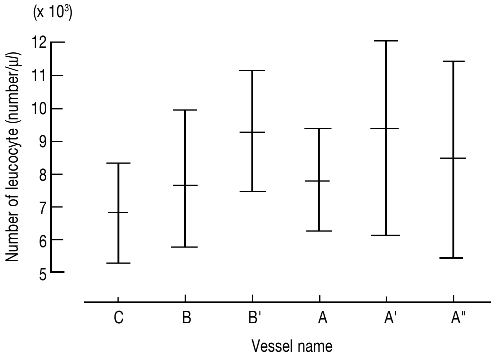


Fig. 10.1 Drinking conditions of distilled water and the number of leucocytes in blood

gests a lowering of the kidney function. The atrophy and blood congestion of their livers were observed as shown in Photographs 10.1 to 10.4 (p. 10-33).

(b) The other test results

The other test results are shown in Figure 10.2 (a) to (e).

The rats drinking the mineral added distilled water became the heaviest weight and ones drinking the distilled water became the lightest.

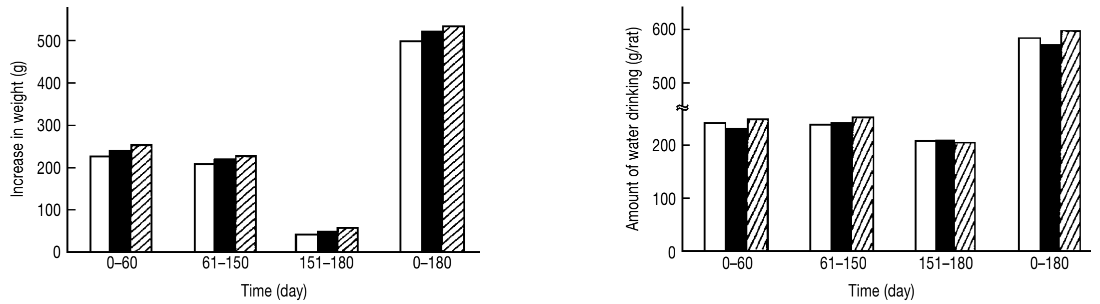
The amounts of water drinking were the largest for the rats drinking the mineral added water and the smallest for ones drinking the tap water.

In case of rats drinking the distilled water, the ratios of the heart, kidney and liver weight against the whole body weight became smaller than those of rats drinking the tap water.

In the blood tests of the rats drinking the distilled water, the numbers of leukocytes and hematocrit increased, but the specific gravity, the number of erythrocites and the amounts of hemoglobin decreased comparing with ones drinking the tap water or the mineral added distilled water.

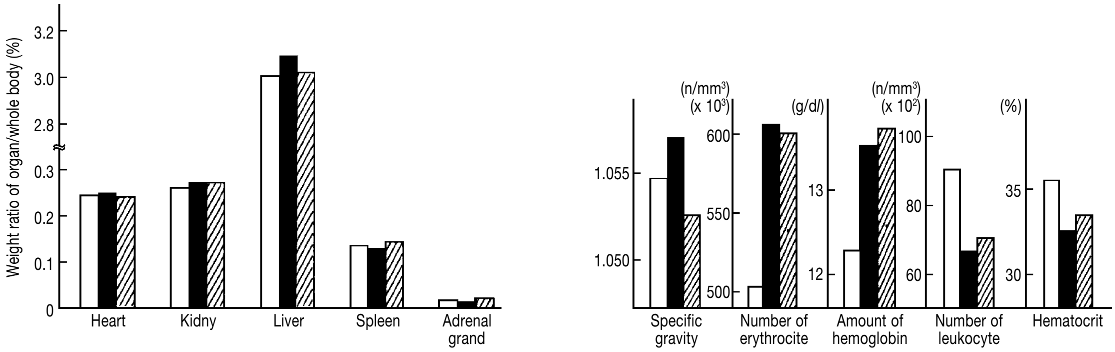
In the serum test of the rats drinking the distilled water, the total protein and urea concentrations increased, but the amylase and potassium concentrations decreased as compared with ones drinking the tap water.

Those test results suggest that the drinking distilled water for a long time may be not good for the health of living bodies comparing with drink-



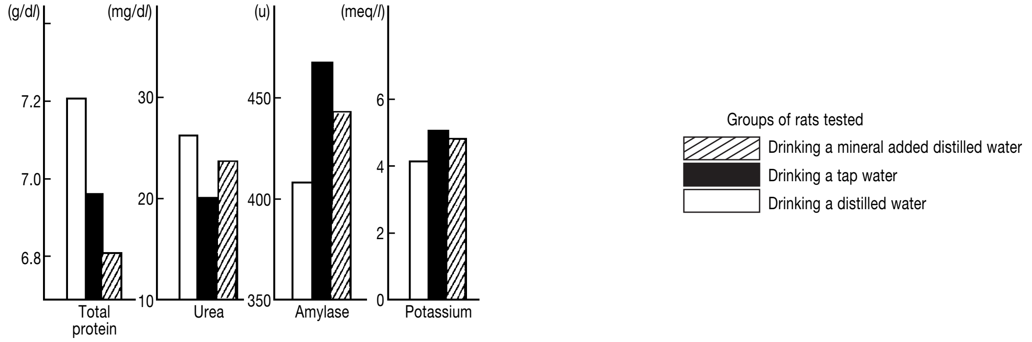
a) Influence of drinking water qualities on the weight increases of rats

b) Amounts of water drinking



c) Influence of drinking water qualities on the internal organs

d) Influence of drinking water qualities on the blood qualities



e) Influence of drinking water qualities on the serum

Fig. 10.2 Influence of drinking water qualities on the growth and health of rats

ing a tap water containing various minerals. Test results also show that the addition of minerals into the distilled water apparently minimizes the bad influences of drinking the distilled water.

10.1.3 A Mineral Additive (KUGAOKEANOS®) for Distilled Water

The KUGAOKEANOS is an additive for adding various minerals, such as sodium, calcium and magnesium compounds, to distilled water for drinking. This chemical is composed of food additives approved by the Japanese laws. The dosage is 100 mg/*l* as the product. The KUGAOKEANOS is dissolved with distilled water to make the 2 to 3% solution and dosed into drinking water tanks.

The addition of this chemical provides a safe and healthy drinking water as shown in the section 10.1.2.

10.2 Chemicals for Ultra-Pure Water Production Systems

10.2.1 Ultra-Pure Water Production Systems

The semiconductor manufacturing industry has promoted the development of various relating technologies. Ultra-pure water production technologies have been also remarkably innovated as semiconductor production technologies have been progressed.

Various types of the ultra-pure water production systems are used in the field. Figures 10.3 and 10.4 show the typical flow diagrams of the systems and the use points of the chemicals.

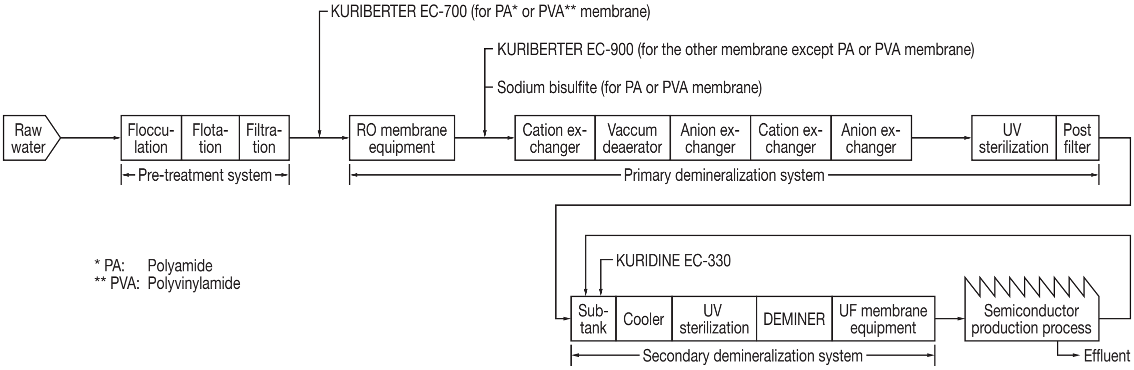
The ultra-pure water production system is generally composed of a pre-treatment system, a primary demineralization system and a secondary demineralization system. Some systems have wastewater recovery systems.

10.2.2 Problems in Primary Demineralization Systems and Countermeasures

(1) Deterioration of ion exchange resins and countermeasures

In the pre-treatment system of an ultra-pure water production system, the raw water is sterilized by using a chlorine compound to prevent the biofouling problems in the down flow systems. However, the residual chlorine oxidizes and deteriorates the ion exchange resins using in the primary demineralization system. Therefore, the residual chlorine must be removed or reduced to chloride ion before the primary demineralization system.

Sodium sulfite or sodium hydrogen sulfite is usually used for reducing the residual chlorine. KURITA provides the KURIBERTER EC-900 as the special reducing agent for the residual chlorine. The KURIBERTER EC-900 shows the excellent reducing effect and has the following



* PA: Polyamide
** PVA: Polyvinylamide

Fig. 10.3 A typical flow diagram of ultra-pure water production system (1)

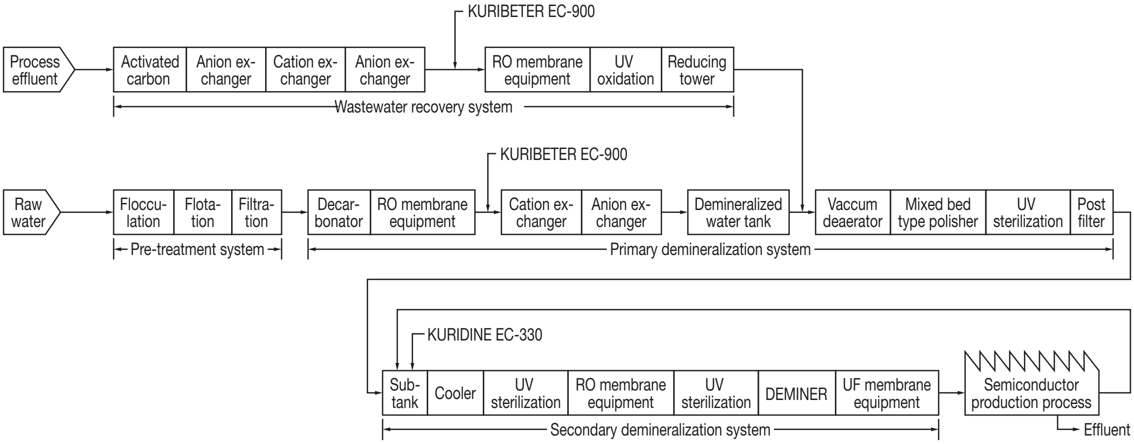


Fig. 10.4 A typical flow diagram of ultra-pure water production system (2)

advantages comparing with sodium hydrogen sulfite:

① Showing a biocidal and algalcidal effect even after chlorine reduction,
② Lower ion exchange load on the ion exchange resins than that of sodium hydrogen sulfite,
③ Excellent product stability under a low temperature season.

Table 10.4 shows the algalcidal effect of KURIBERTER EC-900. The KURIBERTER EC-900 is also available for the wastewater recovery systems as a biofouling control agent.

(2) Deterioration of reverse osmosis (RO) membranes and countermeasures

The operation pressure of RO membrane equipment in the primary demineralization system has tended to become lower for reducing the electric power consumption. Polyamide or polyvinylamide membranes suitable for the low pressure operation have the weaker resistance against chlorine than those of conventional cellulose acetate membranes.

To prevent the deterioration of those membranes by residual chlorine, the residual chlorine must be reduced or removed. Then a non-oxidizing biocide is added before the RO membrane equipment for preventing the biofouling.

For protecting the RO membranes from the chlorine attack, KURITA provides an unique chemical, KURIBERTER EC-700. This chemical combines with the chlorine and lowers the oxidizing power against the RO membranes, but still keeps the sufficient biocidal effect. Therefore, the KURIBERTER EC-700 prevents both of the deterioration of the membrane by chlorine and the biofouling.

Table 10.5 shows the comparative effects of KURIBERTER EC-700 and sodium hydrogen sulfite on the deterioration of an RO membrane system. The use of KURIBERTER EC-700 keeps the almost same desalination rate to the sodium hydrogen sulfite treatment and sufficiently reduces the bacterial number.

When the KURIBERTER EC-700 is used before the RO membrane equipment, the combined chlorine is still present. Therefore, the chlorine compound must be reduced by using the other chemicals before the next ion exchange resin equipment.

Table 10.4 Algalcidal effect of KURIBERTER EC-900

Dosage (mg/*l*)	Time after chemical dosing (week)		
	1	2	3
0	+	++	+++
1.3–1.8	-	-	-
2.6–3.9	-	-	-
5.2–7.8	-	-	-

(Kind of algae: chlorella)

-: Negative growth
+: Positive growth
++: Excellent growth
+++: Extreme growth

10.2.3 Biofouling of Secondary Demineralization Systems and Countermeasures

In the secondary demineralization system, the water is sterilized by using ultraviolet rays and finally demineralized with a non-regeneration type ion exchange resin equipment, called the DEMINER. Then, the final removal of bacteria and micro-particles is carried out by using an ultra-filtration (UF) and/or RO membranes.

Since, no daily chemical treatment is carried out in this system, the long term operation microbiologically contaminates the system and deteriorates the treated water quality. A periodical chemical cleaning of the system is applied for solving this problem. Chemicals using for the system cleaning must include extremely low impurities and give no bad influence on the RO membranes and ion

Table 10.5 Comparative prevension effects of KURIBERTER EC-700 and sodium hydrogen sulfite on the deterioration of a RO membrane system by chlorine

Chemical	Desalination rate (%)		Bacteria account of the product water after 800 to 1,000 hours operation (n/m*l*)
	After 24 h	After 1,000 h	
None*	99.0	98.1	Less than 0.1
KURIBERTER EC-700 40 mg/*l*	99.1	99.0	Less than 0.2
$NaHSO_3$**	99.0	99.1	10–20

* Residual chlorine is present.
** With a sufficient dosage to reduce chlorine perfectly

exchange resins.

KURIDINE EC-330 provided by KURITA, satisfies the above requirements for the cleaning chemicals. However, as the waste cleaning solution has a high COD value, the COD must be reduced before the water discharge.

Enzyme formulations, such as KURIBERTER EC-950, are used for reducing the COD. The KURIBERTER EC-950 of a low concentration rapidly reduces the COD.

10.3 Corrosion Inhibitors for Spot-Welding Machine Cooling Water Systems

10.3.1 Outline of Spot-Welding Machines

Spot-welding machines are widely used for welding steel sheets for car manufacturing and so on.

Figure 10.5 shows a typical portable spot-welding machine. This machine is composed of a welding gun, transformer (thyristor converter), timer and cables connecting the gun with the transformer.

Steel sheets are placed between the electrodes of the gun and welded by applying an electric charge. Since a heat generates at the gun and cables when the electric charge is applied, a circulating cooling water system is employed to cool them.

10.3.2 Troubles Caused by the Cooling Water and Countermeasures

After indirectly cooling the welding gun, the cooling water directly cools the cables. The cable consists of few thousands stranded copper wires. The copper wires are damaged by the repetition of the bending or twisting movement during the welding operation, and by the kick with the electric current application.

The flow of cooling water accelerates the damage of the copper wires by the corrosion and the fouling deposition on the wire surface. Especially, the fouling of wire accelerates the wire destruction by the under deposit pitting corrosion, and shortens the service lives of the cables.

Copper corrosion inhibitors and dispersants are used to minimize the wire destructions and to extend the service lives of cables.

Table 10.6 shows the effect of a chemical, KURISPOT M, composed of a corrosion inhibitor and a dispersant, on the wire destruction of a portable spot-welding machine. The use of the inhibitor extends the service life of the copper wire at around two times of that under no chemical treatment.

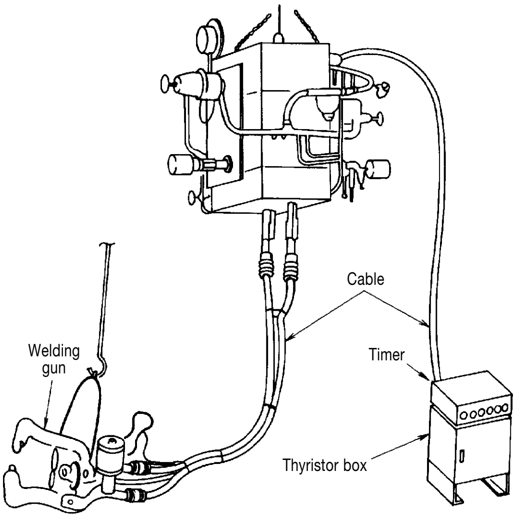


Fig. 10.5 A portable spot-welding machine

Table 10.6 Effect of a chemical treatment on the copper wire destruction of a portable spot-welding machine

Run No.	Inhibitor (mg/)	Number of spot welding until the wire destruction
1	None	26,958
2		29,766
3		25,251
Average		27,325
4	50 (KURISPOT M)	50,352
5		72,575
6		55,305
Average		59,411

Test conditions;

Number of spot welding per cycle:	25
Time for one cycle (sec):	70

Photograph 10.5 shows the comparative microstructures of broken copper wires with and without the chemical treatment. In case of no chemical treatment, no stretching of the microstructure is observed. It suggests that the wire destruction had been developed by the corrosion fatigue during a short time. In case of the chemical treatment, the stretching of the structure in the longitudinal direction is observed. This suggests the wire destruction had been gradually developed by mainly mechanical forces during a long time.

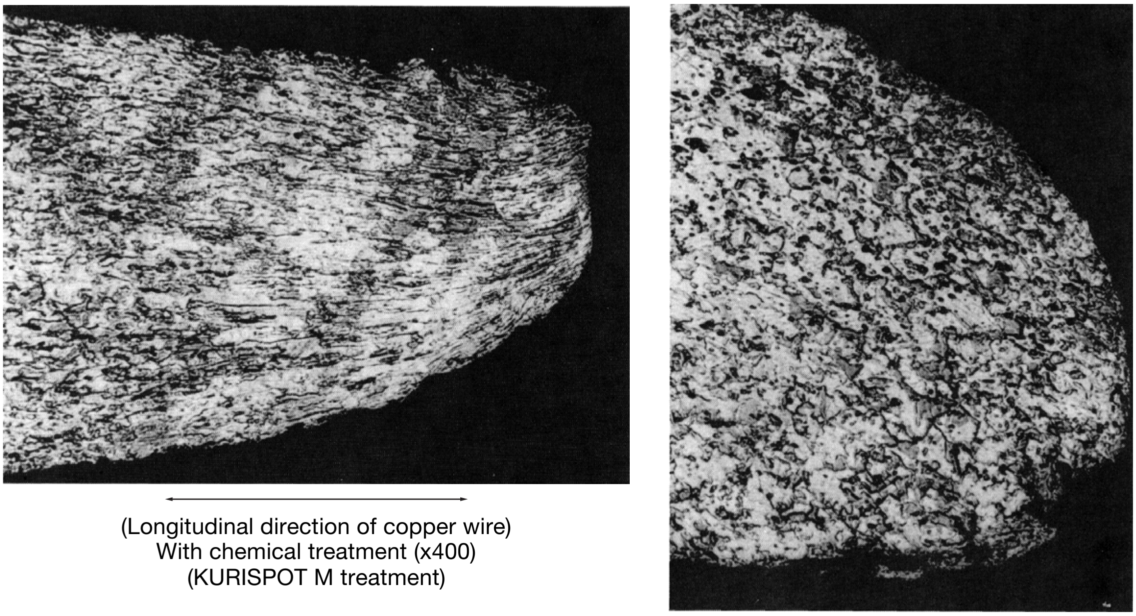
The above difference in the mechanisms of wire destruction is proved by the difference in the tensile strengths of wires treated with and without the chemical as shown in Table 10.7. The tensile strength of wires treated with the chemical is around 1.3 times of that of untreated wires.

Figure 10.6 shows the chemical treatment effect in a large scale spot-welding machine cooling water system. This system cools around one thousand spot-welding machines and the circulation rate is 400 m^3/h. The use of the chemical, KURISPOT M, reduces the number of the cable replacement from 123 per month of without chemical treatment to 75 per month.

10.4 Scale Inhibitors for Flue Gas Desulfurization Plants

In Japan, flue gas desulfurization plants have been installed for large-scale boilers using heavy oils to control the air pollution.

When a caustic soda solution is used as the absorbent for SO_X, calcium sulfate and sulfite scales deposit in the spray nozzles and the absorbent circulation pipe lines, and cause their clogging. Formerly, those plants were stopped their operations once three to six months to remove the scales. In the present, the use of scale inhibitors becomes popular and realizes one year continuous opera



(Longitudinal direction of copper wire)
With chemical treatment (x400)
(KURISPOT M treatment)

(Longitudinal direction of copperwire)
Without chemical treatment (x400)

Photo 10.5 Comparative microstructures of broken copper wires with and without a chemical treatment

Table 10.7 Comparison of tensile strengths of copper wires treated with and without a chemical at the non-corrosive parts

Run No.	Inhibitor (mg/*l*)	Wire diameter (mm)	Max. load (gf)	Tensile strength (kgf/cm^2)
1	None	0.26	1,150	21.7
2		0.26	850	16.0
3		0.26	1,070	20.2
Average		0.26	1,023	19.3
4	50 (KURISPOT M)	0.26	1,340	25.3
5		0.26	1,310	24.7
6		0.26	1,280	24.2
Average		0.26	1,310	24.7

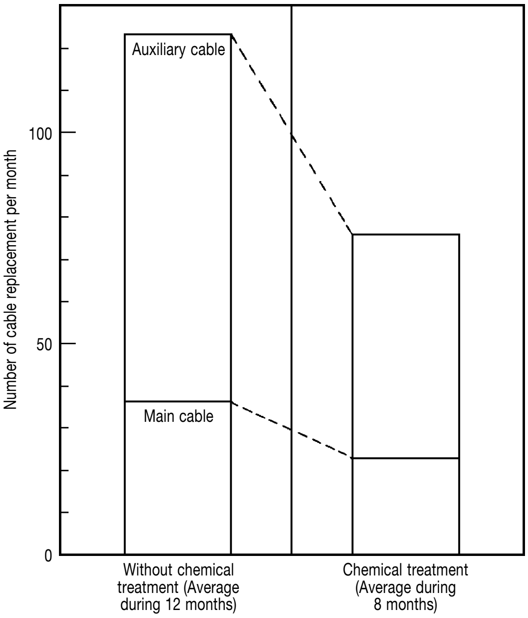


Fig. 10.6 Decrease in the number of cable replacement by applying a chemical treatment

tions of them without scale troubles.

Photographs 10.6 to 10.9 (p. 10-34) show the effect of a polymer based scale inhibitor in a flue gas desulfurization plant. The chemical treatment almost perfectly prevents the nozzle and pipe clogging with scales.

10.5 Scale Inhibitors for Ash Cooling Water Systems in Refuse Incineration Plants

Figure 10.7 shows the flow diagram of a refuse incineration plant and the locations in which scales are formed.

In the plant, SO_X and hydrogen chloride gasses are generated by the refuse incineration, and following methods are employed to remove them or to minimize their generation:

① Blowing of slaked lime or calcium carbonate into the incinerator,

② Spraying of slaked lime slurry or alkaline solution into the gas line,

③ Addition of caustic soda solution into the gas cleaning tower.

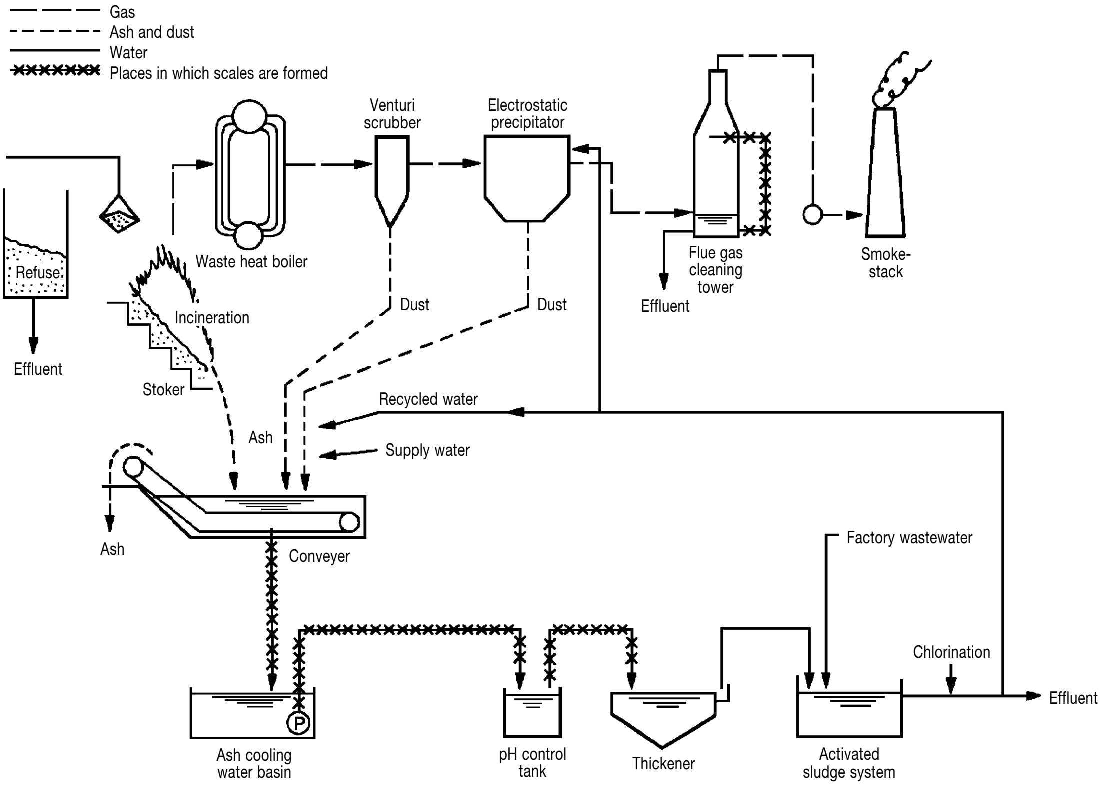


Fig. 10.7 Flow diagram of a continuous refuse incineration plant and the places in which scales are formed.

In case of the method ①, the pH and calcium ion concentration of the ash cooling water are increased to 10 to 12 and 300 to 1,000 mg/*l* respectively. Then a large amount of scale is deposited in the cooling water lines and causes various troubles, such as the pipe clogging.

The use of scale inhibitors, such as phosphonates and polymers, effectively controls those scale troubles. Figure 10.8 shows the inhibition effects of scale inhibitors in the ash cooling water system of a refuse incineration plant. The scale inhibitors show the excellent effects.

10.6 Paint Killers for Paint Spray Booth Circulation Water

Paint spraying is carried out as one process in the production of cars, electrical appliances and so on.

A typical flow diagram of paint spray system with a spray booth is shown in Figure 10.9. This system consists of the air intake part, paint spray booth and exhaust air cleaning part. The circulation water flows on the bottom of the spray booth and is sprayed in the exhaust air cleaning tower to remove the over-spray paint. The over-spray paint is separated from the water in the water pit and the treated water is recycled.

The amount of over-spray paint is generally 10 to 30% of the total sprayed paint for an electrostatic spray coating and 50 to 65% for the other coating methods. This large amount of over-spray paint causes various problems summarized in Table 10.8. Those problems are caused by the adhesion and solidification of over-spray paint, biofouling, etc., in the system.

Paint killers are used to prevent the troubles

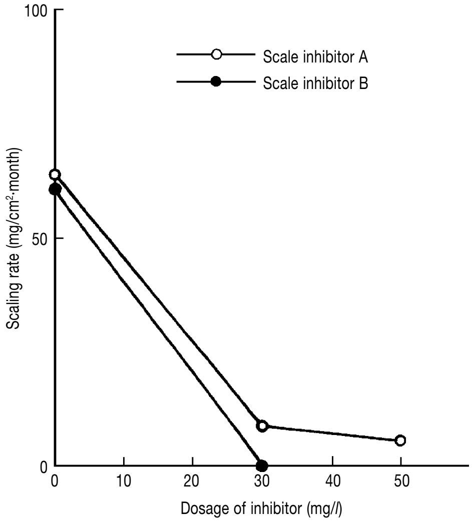


Fig. 10.8 Effects of scale inhibitors on scaling in the ash cooling water line of a refuse incineration plant

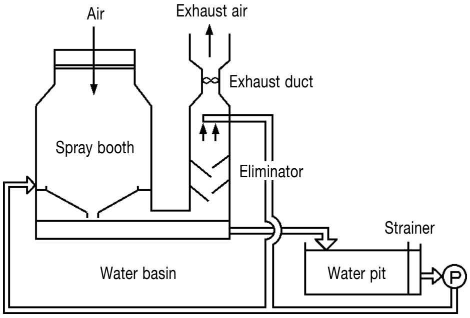


Fig. 10.9 Flow diagram of a paint spray system with a spray booth

Table 10.8 Problems caused by over-spray paint in painting plants

Place	Problem	Cause
Spray booth, Exhaust air duct	Insufficient air exhausting Poor coating	Paint adhesion to spray nozzles, curtains, ducts, etc.
	Cloggings of water spray nozzles Reduction of water circulation rate	Formation of biofouling in the water circulation lines
	Air pollution Deterioration of working environment	Generation of malodor by rotting of organic substances
Circulation water basins and lines	Reduction of water circulation rate	Clogging of strainer with over-spray paint and biofouling Adhesion of paint and fouling in pipings
	Increase in circulation water contamination	Insufficient separation of over-spray paint

caused by the over-spray paint. The paint killers react with the over-spray paint and reduce the stickiness to minimize its adhesion in the system and to promote its separation from the circulation water. Figure 10.10 summarizes the functions of paint killers and the improvements in the paint booth operation under the paint killer treatment.

Formerly, alkalis and surfactants had been used for reducing the stickiness of over-spray paints. Coagulants and flocculants had been applied for improving the separation of paints from water.

In the present, various formulated paint killers composed of polymers, silicates, alkalis, etc., are used to reduce the stickiness of paints and to improve the paint separation.

Table 10.9[1] shows typical case studies of paint killer (KURISTUCK) treatments. In each painting booth, the use of a paint killer remarkably improves the trouble occurrences and reduces the periodical cleaning cost. As the results, the productivity of the booth is improved.

10.7 Antifoaming Agents

10.7.1 Causes of Foaming

A foam generates when a gas is surrounded with a thin liquid film. Even in case of demineralized water, foams are generated by blowing air, but they soon disappear. However, when some substances are present in water, they stabilize the foam films and keep the foams as shown in Figure 6.23(p.6-14). Then various foaming problems occur.

The following substances generally accelerate the foaming.

(1) Surfactants

Since surfactants have hydrophilic and lipophilic groups, they adsorb onto the interface between water and air (gas) as shown in Figure 10.11. Then they lower the surface tension of water to stabilize the foams. Generally, surfactants with larger "Hydrophlic-Lipophilic Balance" (HLB) much more stabilize foams.

(2) Water-soluble high molecular weight compounds

Water-soluble high molecular weight compounds, such as proteins, saponins and starches, stabilize the foam films. Those substances form the gelling films. Synthetic high molecular weight polymers have sticky properties and their stickiness stabilizes the foam films.

(3) Suspended solids

Suspended solids (SS) scarcely generate foams. However, the coexistence of SS with surfactants remarkably stabilizes foams.

(4) Inorganic salts

Inorganic salts themselves rarely generate foams. In some cases, the coexistence of salts with organic substances forms water-insoluble matters and accelerates the foaming.

10.7.2 Functions of Antifoaming Agents

The functions of antifoaming agents are divided into two categories of foam-breaking and foam-inhibiting actions. The foam-breaking action is to destroy foams already generated. The foam-inhibiting action is to minimize the number of foams generating.

Various theories for the foam-breaking action have been proposed but they are not perfectly established. Figure 10.12 shows a typical proposed mechanism for the foam-breaking action of antifoaming agents.

10.7.3 Kinds of Antifoaming Agents

Antifoaming agents are generally classified from their product appearances and the kinds of main ingredients.

Table 10.10 shows the typical classification based on their appearances.

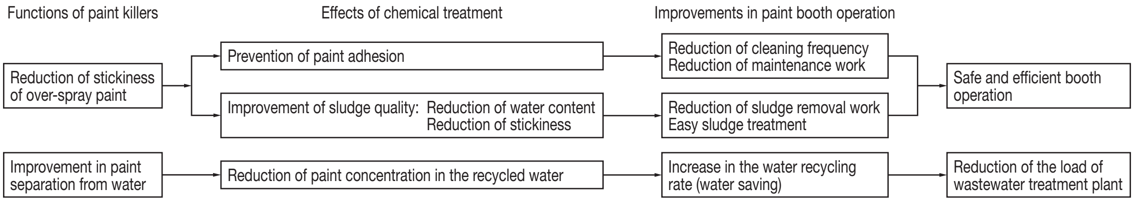


Fig. 10.10 Functions of paint killers and improvements in paint booth operations under the paint killer treatments

Table 10.9 Case studies of paint killer (KURISTUCK) treatments

Plant	Troubles before chemical treatment	Countermeasures before chemical treatment	Effects of paint killer treatment
Final coating booth for refrigerators (Water curtain type)	① Frequent cleaning works for curtains, exhaust air duct, air filters, etc. ② Difficult sludge removal because of paint solidification	Periodical system cleaning, Partial cleaning: once/week Whole system cleaning: twice/year	① Reduction of paint stickiness and paint adhesion ② Minimization of cleaning work Partial cleaning: once/2 weeks
Inner and final coating booth for automatic vending machines (Water curtain type)	① Paint adhesion on curtains and the surrounding ② Clogging of water supply piping for the curtains with paints	Periodical system cleaning: once to twice/2 months	① Improvement in the paint adhesion and the water pipe clogging ② Reduction of cleaning frequency: once to twice/4 months
Paint booth for automobile parts (Water curtain type)	① Paint adhesion on curtains and exhaust air duct ② Difficulty in the sludge and water separation ③ Deterioration of recycled water quality Turbidity: 500 degrees	Periodical cleaning: once*/month * 8 hours work with 6 workers	① Reduction of paint adhesion up to 1/10 ② Reduction of cleaning time: 4 hours cleaning/month ③ Reduction of water turbidity: below 20 degrees
Inner and final coating for automobiles (Venturi scrubber type)	① Paint adhesion and solidification on water curtain wall, water pit, etc. ② Occurrence of poor coating by the disorder of air supply and exhaust caused by the above trouble ③ Low sludge recovery rate ④ Increase in recycled water turbidity: 8,000 degrees	Periodical cleaning, Water curtain trough: once/week Water curtain wall: once/3 months Cleaning of water pit and removal of the sludge	① No poor coating ② No cleaning work for the water curtain wall and troughs during 5 months ③ Easy cleaning work for the water pit ④ Reduction of recycled water turbidity: 80 degrees

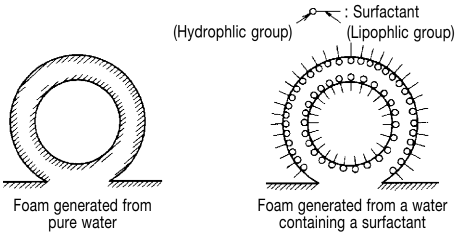


Fig. 10.11 A function of surfactants for the foam stabilization

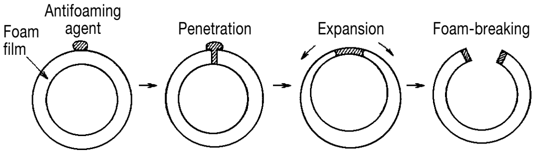


Fig. 10.12 A functional mechanism of foam-breaking by antifoaming agents

From their main ingredients, antifoaminig agents are classified as follows:

① Silicone compound based,
② Fatty acid based,
③ Higher alcohol based,
④ Wax based,
⑤ Nonionic surfactant based.

Antifoaming agents of ② to ⑤ are sometimes called non-silicone compound based ones.

The properties of typical antifoaming agents are outlined below.

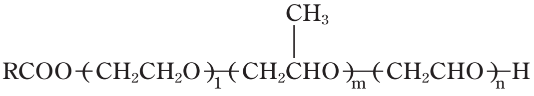
Table 10.10 Classification of antifoaming agents based on their appearances

Appearance	Type	Main ingredient	Feature
Oily liquid	Oil type	Silicone compounds	Insoluble in water
		Non-silicone compounds	
	Self-emulsifying type	Silicone compounds	Dispersing into water as emulsions
		Non-silicone compounds	
Paste or aqueous solution	Water soluble type	Silicone compounds	Strongly hydrophilic Water soluble Effective at a high temperature
		Non-silicone compounds	
Suspension	Emulsion type	Silicone compounds	Dispersing into water
		Non-silicone compounds	

(1) Non-silicone compound based self-emulsifying type

The main ingredients are the nonionic surfactants which are produced by adding polyethylene-oxide and/or polypropylene oxide to fatty acids or higher alcohols. Their HLB are generally low and the appearances are oily liquids.

A typical molecular structure of this type is shown below:

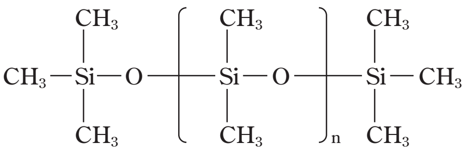


$$\mathrm{RCOO(CH_2CH_2O)_1(CH_2\overset{\displaystyle CH_3}{C}HO)_m(CH_2CHO)_nH}$$

Antifoaming agents of this type show the excellent antifoaming effects and are widely applied for various production processes and wastewater treatment processes.

(2) Silicone compound based emulsion type

Antifoaming agents of this type are produced by emulsifying silicone compounds into water, using emulsifiers. Their appearances are suspensions. A typical molecular structure of a silicone compound is shown below:



$$\mathrm{CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{Si}}-O-\left[\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{Si}}-O\right]_n-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{Si}}-CH_3}$$

These antifoaming agents are most widely applied.

(3) Non-silicone compound based emulsion type

Antifoaming agents of this type are produced by emulsifying fatty acids, higher alcohols, waxes or low HLB surfactants into water, using emulsifiers. Their appearances are suspensions.

These antifoaming agents are used for various production processes, such as paper making and wastewater treatment processes.

(4) Mineral oil type

Those antifoaming agents are produced by blending silicone compounds, metal soaps, silicon dioxide or surfactants with mineral oils.

They are mainly applied for pulping processes where the pH and temperature are high, and the foaming tendency becomes extremely high.

10.7.4 Factors Influencing on the Effects of Antifoaming Agents

The effects of antifoaming agents widely vary depending on the application conditions. In this section, main factors influencing on the effects of self-emulsifying type antifoaming agents are described because they are most widely used.

(1) HLB of antifoaming agents

Since antifoaming agents of self emulsifying type are nonionic surfactants, the antifoaming effect is widely influenced by the HLB as shown in Figure 6.25(p.6-16). The effect is maximized at a specified HLB and it is reduced when the HLB becomes lower or higher.

Therefore, an antifoaming agent having a suitable HLB has to be selected according to the application conditions.

(2) Temperature

The relationship among the effects of antifoaming agents, their HLB and temperature is shown in Figure 6.26(p.6-16). Generally, an antifoaming agent with the higher HLB shows the good effect at the higher temperature and one having the lower HLB shows the good effect at the lower temperature.

In case of a process where the temperature widely varies, it is better to prepare few kinds of antifoaming agents for applying a suitable one according to the temperature change.

10.7.5 Processes Applying Antifoaming Agents

Foaming problems are occurred in various production and wastewater treatment plants where various process fluids and waters containing foaming substances are processed and treated. In this section, typical application methods of antifoaming agents for various processes are outlined.

The use of antifoaming agents in pulp and paper making processes is referred to the section 6.3.5(p.6-13).

(1) Wastewater treatment plants

(a) Aeration tanks (activated sludge tanks)

Foaming problems often occur at the aeration tanks in sewage treatment plants and the wastewater treatment plants of food, pharmaceutical, petrochemical industries and so on. In the aeration tanks, foaming substances in the wastewater and the metabolism products of microorganisms generate a large amount of foams. The generated foams overflow from the aeration tanks and cause various problems, such as the contamination of the surrounding equipment, the deterioration of working environment and the outflow of suspended solids from settling tank, if the foaming is insufficiently controlled.

Self-emulsifying type or emulsion type antifoaming agents are used for the aeration tanks. However, antifoaming agents more or less reduce the air dissolving rate into water. Therefore, a suitable agent and the dosage must be selected to avoid the bad influence of reduced dissolved oxygen concentration on the activated sludges.

(b) Settling tanks

In settling tanks, as foams adhere to suspended solids, they come up and flow out from the tanks. The foaming in the settling tank is caused by a poor foaming control in the aeration tank or a turbulent inflow of the treated water to the settling tank.

In that case, the antifoaming treatment in the aeration tank or the water intake method from the aeration tank to the settling tank must be improved at first. When the foaming is still problem after those improvements, a suitable antifoaming agent is added into the water inlet.

(c) Drainage canals of treated water

Since a low concentration of foaming substances is included not only in a treated wastewater but also in a river water or a seawater, a foaming sometimes occurs in a drainage canal where the treated water is discharged. In that case, antifoaming agents are dosed into the canal to control the foaming.

Generally, a low COD type agent should be used to satisfy the regulation for the effluent. The use of the mineral oil type chemicals should be avoided because they form the oil film and deteriorate the appearance of the effluent.

(2) Production plants

(a) Textile industry

Surfactants, bleaching agents, dyestuffs, dyeing auxiliaries, etc., cause foaming problems in the various production processes in textile industry. Since the foaming causes the unevenness of fibers and cloths in the breaching and dyeing processes, it deteriorates their qualities. In those processes, silicone compound based emulsion type antifoaming agents are used. Before using the agents, it must be confirmed that the agents give no bad influence on the product qualities.

(b) Food industry

Raw materials of food industry, such as starches, proteins and sugars, generate foams in food manufacturing processes and reduce the production efficiencies. The antifoaming agents using in those processes are limited to chemicals approved as food additives.

Generally, fatty acid esters and silicone compound based emulsion type antifoaming agents are used in food industry.

(c) Fermentation industry

In the factories where beverages, gultamic acid, penicillin and so on are produced by utilizing microorganisms and enzymes, the foaming often occurs and reduces the productivity of their fermentation and sterilization processes, etc.

In this field, self-emulsifying type and silicone compound based emulsion type antifoaming agents are used.

(d) Synthetic rubber and resin industry

Since a large amount of surfactants are used in the emulsion polymerization processes of synthetic rubbers, polyvinyl chloride resins, polyvinyl acetate resins and so on, the foaming occurs and reduces their productivity. In those processes, antifoaming agents of silicon compound based emulsion type and self-emulsifying type are mainly applied.

(e) The other industries

In the following processes, foaming problems often occur and antifoaming agents are used:

① Metal finishing processes in iron and steel works, automobile factories, etc.,
② Paint manufacturing processes,
③ Various chemical manufacturing processes.

10.8 Deodorants

10.8.1 Odors and the Strengths

(1) Theory of olfactory sense

Various substances in the air enter to the nasal cavity and contact with the olfactory mucous membrane. The olfactory cells are stimulated with this contact and send the action current to the central brain through the olfactory nerves. Then the brain feels it as an odor.

(2) Standards expressing the strength of odors

For expressing the strength of an odor, some standard must be required. Generally, the following three kinds of standards are used for determining or measuring the strength of an odor:

(a) Threshold values

Two kinds of threshold values are used. The first is the detectable threshold value. This is the minimum concentration of an odor substance, which a person can feel an odor but can not determines the kind of substance, when the concentration of substance is gradually increased.

The second is the recognized threshold value. This is the minimum concentration of an odor substance, which a person identifies the kind of the substance.

Table 10.11 shows the recognized threshold values of eight substances among twelve substances which are regulated by the Offensive Odor Control Law in Japan because they cause the offensive odors.

Table 10.11 Recognized threshold values of eight substances causing offensive odors

Substance	Recognized threshold value (ppm)
H_2S	0.00041
CH_3SH	0.00007
$(CH_3)_2S$	0.003
$(CH_3)_2S_2$	0.0022
NH_3	1.54
$(CH_3)_3N$	0.000027
CH_3CHO	0.00154
$C_6H_5CH = CH_2$	0.033

(b) Six-stage odor strengths

The strength of an odor is divided into six stages as shown in Table 10.12.

(c) Nine-stage comfortable and discomfortable indexes

The kinds and strengths of odors are divided into nine stages from extremely discomfortable to extremely comfortable as shown in Table 10.13.

The relationship between the six-stage odor strength and this index is determined for thirty kinds of offensive odor substances. As the results, the six-stage odor strength of 2 to 3 is equivalent to this index of around -1 and the odor strength of 3 to 4 is in the range of this index of -1 to -2.

(3) Concentrations of odor substances and the olfactory sense

Each person has a different level of the olfactory sense. The sense is influenced by the health condition and the environmental conditions, such as the temperature and humidity. Moreover, the strength of odor generally becomes lower when the same odor is smelled during a long time. Therefore, a screening test is carried out by using standard odors to select testers for the organoleptic test evaluating the strengths of odors. The test environment should be normalized.

The relationship between the concentration of an odor substance, methylmercaptan, and the six-stage odor strength is shown in Figure 10.13. The odor strength is increased in proportion to the logarithm of the concentration of the odor substance. That is, the concentration of an odor substance must be reduced to 1/10 for reducing the odor strength at one stage.

Weber and Fechner proposed the equation (10.1) for representing this relationship between the concentrations of odor substances and their odor strengths.

$$I = K \log C + a \quad \text{..........} \quad (10.1)$$

where

I: odor strength
K, a: constant
C: concentration of an odor substance in air (ppm)

Table 10.12 Six-stage odor strength indication method

Odor strength	Definition	Remarks
0	No odor	
1	Barely detectable odor (detectable threshold value)	
2	Weak odor but determinable for the kind of an odor (recognized threshold value)	
3	Easily recognized odor	Like the odor of a disinfectant which smells in a hospital.
4	Strong odor	
5	Extremely strong odor	Strong odor which makes a person to difficult to remain there

Table 10.13 Nine-stage comfortable and discomfortable indexes

Comfortable and discomfortable index	Definition
-4	Extremely discomfortable
-3	Very discomfortable
-2	Discomfortable
-1	Little discomfortable
0	Neither comfortable nor discomfortable
+1	Little comfortable
+2	Comfortable
+3	Very comfortable
+4	Extremely comfortable

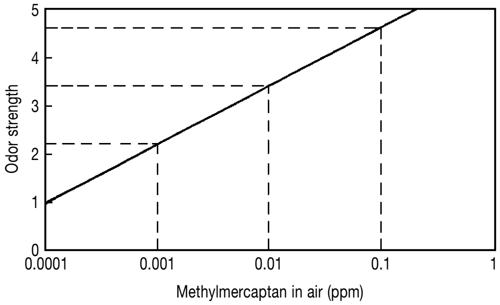


Fig. 10.13 Relationship between the concentration of methylmercaptan and the six-stage odor strength

10.8.2 Measuring Methods of Odors

Odor measuring methods are divided into organoleptic and chemical analysis methods as shown in Figure 10.14.

As the air pollution with odor substances relates to the olfactory sense of the local residents, the both of organoleptic and chemical analysis methods are applied to determine the strengths of odor substances.

(1) Organoleptic methods

(a) Direct method

In this method, the strength of an odor is directly determined by testers at a site. The level of the odor strength is classified by using the six-stage odor strengths shown in Table 10.12 or the nine-stage comfortable and discomfortable indexes shown in Table 10.13.

(b) Air-dilution methods

Even in case of any strong offensive or pleasant odor, the odor becomes not detectable for persons when the air containing the odor substance is diluted with odorless air.

In this method, the odor concentration is indicated the magnification of the dilution, which the odor becomes not detectable. Therefore, the higher magnification value shows the stronger odor.

(i) Odorless room methods

Two kinds of odorless room methods are used. In the first method, testers enter an odorless room which is constructed using stainless steel plates or tiles. A diluted air sample is supplied into the room for measuring the magnification value.

The second method uses an odorless box in which a tester puts the face to smell a diluted sample supplied.

(ii) Smelling bag method

In this method, three smelling bags are used for a tester. Among three bags, only one bag contains the diluted sample and the others include odorless air. Then the tester determines the magnification value of which the odor becomes not detectable.

This test is carried out by six testers. After elimi

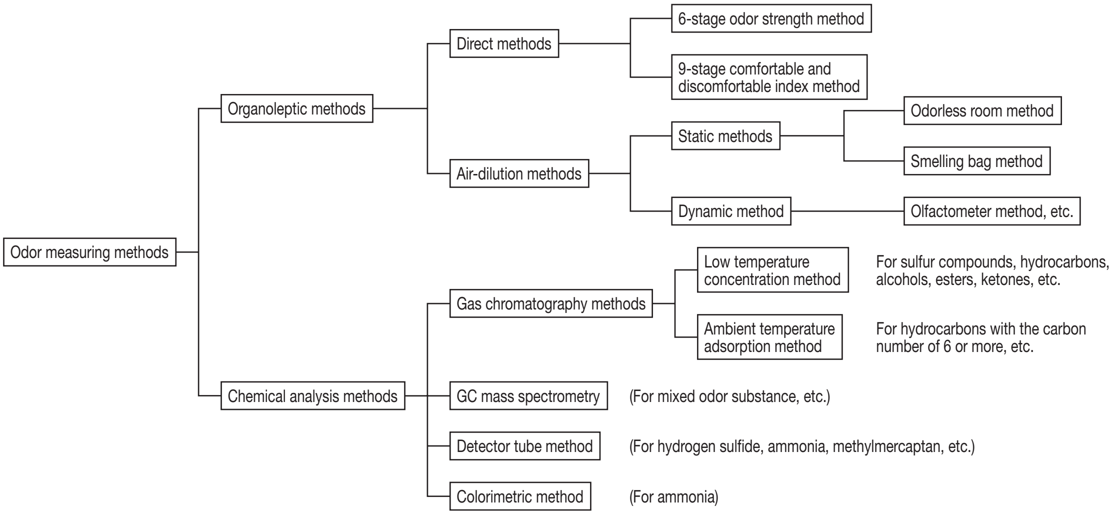


Fig. 10.14 Classification of measuring methods for odor strengths

nating the maximum and minimum magnification values, the logarithmic average value of the remaining four test data is used as the final magnification value. Photograph 10.10 (p. 10-35) shows a view of the smelling bag method testing.

(2) Chemical analysis methods

(a) Gas chromatography

The air sample is supplied to a column filled with an adsorbent, such as diatomaceous earth and synthetic zeolite, to separate and measure the concentration of each fraction. According to the feature of a substance to be measured, either the low temperature concentration or the ambient temperature adsorption method is applied.

(b) Gas chromatography mass spectrometry

This method is applied when the molecular structure and concentration of an odor substance must be determined.

(c) Detector tube method

This is a convenient method for measuring the concentration of an odor substance at site. The kinds of substances to be measured are limited but few ppm to few percent of the concentration is easily measured. A specified amount of a sample air is suctioned into a detector tube containing an adsorbent, and the concentration of an odor substance is measured from the length of the colored adsorbent.

10.8.3 Offensive Odor Control Methods

Offensive odor control methods are summarized in Figure 10.15. The methods are classified into the liquid phase and air phase treatment methods.

In this section, chemical treatment methods are mainly described.

(1) Oxidizing treatment

The oxidizing agents using for the oxidizing treatment of odor substances are described below.

(a) Hydrogen peroxide

Hydrogen peroxide oxidizes and decomposes hydrogen sulfide and methylmercaptan by the following reactions:

$H_2S + H_2O_2 \rightarrow 2H_2O + S$
(in acidic to neutral range) .... (10.2)
$H_2S + 4H_2O_2 \rightarrow 4H_2O + H_2SO_4$
(in alkaline range) .... (10.3)
$CH_3SH + 3H_2O_2 \rightarrow$
$CH_3OH + SO_2 + 3H_2O$ .... (10.4)

(b) Chlorine compounds

Sodium hypochlorite, liquid chlorine, chlorine dioxide, etc., are used to decompose offensive odor substances. Reactions between those compounds and various odor substances are expressed by the following reactions:

$H_2S + 4NaClO \rightarrow H_2SO_4 + 4NaCl$.............. (10.5)
$H_2S + 4Cl_2 + 4H_2O \rightarrow H_2SO_4 + 8HCl$ .... (10.6)

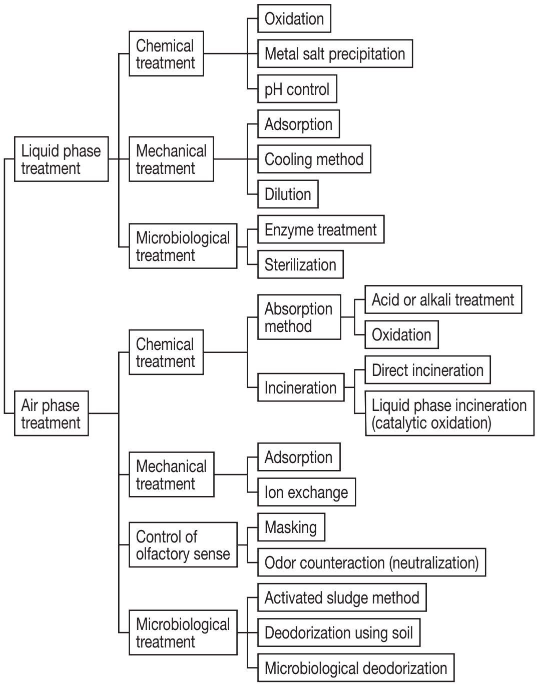


Fig. 10.15 Classification of odor control methods

$$5H_2S + 8ClO_2 + 4H_2O \rightarrow 5H_2SO_4 + 8HCl \quad \text{(10.7)}$$

$$CH_3SH + 2ClO_2 + H_2O \rightarrow HCHO + H_2SO_4 + 2HCl \quad \text{(10.8)}$$

$$8HCHO + 4ClO_2 + 2H_2O \rightarrow 8HCOOH + 4HCl + O_2 \quad \text{(10.9)}$$

$$NH_3 + 3NaClO \rightarrow NCl_3 + 3NaOH \quad \text{(10.10)}$$

(2) pH control

Some offensive odor substances dissociate and are present as stable ions in water when the pH is controlled in the appropriate ranges. Then the releasing of offensive odor gasses from the water to the air is minimized.

In case of hydrogen sulfide, the pH increase at 8 or more promotes the dissociation and the remaining hydrogen sulfide ratio becomes smaller than 10% as shown in Figure 10.16.

$$H_2S \leftrightarrows H^+ + HS^- \quad \text{(10.11)}$$

$$HS^- \leftrightarrows H^+ + S^{2-} \quad \text{(10.12)}$$

By the same way, the pH control by using acids or alkalis minimizes the offensive odors of various substances. The appropriate pH control ranges for ammonia and trimethyl amine are as follows:

Ammonia: pH 6.5–7.5
Trimethyl amine: pH 6.5–7.5

(3) Metal salt precipitation method

Hydrogen sulfide forms the insoluble metallic salt and the salt precipitates in water when the pH is controlled in an appropriate range and a suitable metal salt is added. The following equations show the reactions between sulfide ion and metallic ions, and the solubility products (Ksp) of those metal sulfides:

$$Zn^{2+} + S^{2-} \rightarrow ZnS,\ Ksp = 10^{-21}\text{–}10^{-24} \quad \text{(10.13)}$$

$$Fe^{2+} + S^{2-} \rightarrow FeS,\ Ksp = 10^{-18}\text{–}10^{-22} \quad \text{(10.14)}$$

$$2Fe^{3+} + 3S^{2-} \rightarrow Fe_2S_3,\ Ksp = 10^{-88} \quad \text{(10.15)}$$

(4) Sterilization

The putrefaction or fermentation of organic substances by microorganisms often generates offensive odor substances. Therefore, the sterilization of organic sludges and so on prevents or minimizes the generation of offensive odors.

(5) Odor counteraction (neutralization)

The odor counteraction is a kind of offensive odor control method to chemically lower or eliminate an offensive odor. Generally essential oils are used for this treatment. The various components of the oils react with offensive odor substances to lower or counteract the odors.

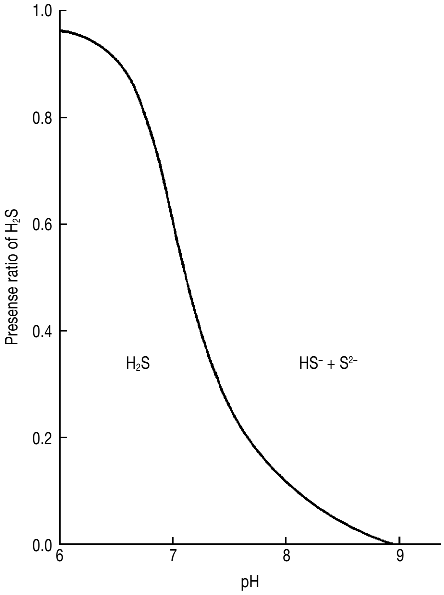


Fig. 10.16 Relationship between pH and the dissociation of hydrogen sulfide

(6) Odor masking

The odor masking is a method that an offensive odor is minimized or changed to an acceptable or a pleasant odor by using aromatic oils, etc.

10.8.4 Case Studies of Offensive Odor Control

(1) A sewage treatment plant

In a sewage treatment plant, strong offensive odors generate from the sludge treatment plant and the sludge itself mainly. The main odor substances are hydrogen sulfide and methylmercaptan.

To prevent the odor in the dehydrator room, various deodorants were added into the sludge tank and the sludge transportation line to evaluate their effects. Figure 10.17 shows the injection points of the deodorants. Figures 10.18 and 10.19 show the effects of an oxidizing type deodorant, KURIRASER, and hydrogen peroxide on methylmercaptan and hydrogen sulfide generations in the sludge dehydrator room. The addition of the deodorant, KURIRASER, with 150 mg/*l*

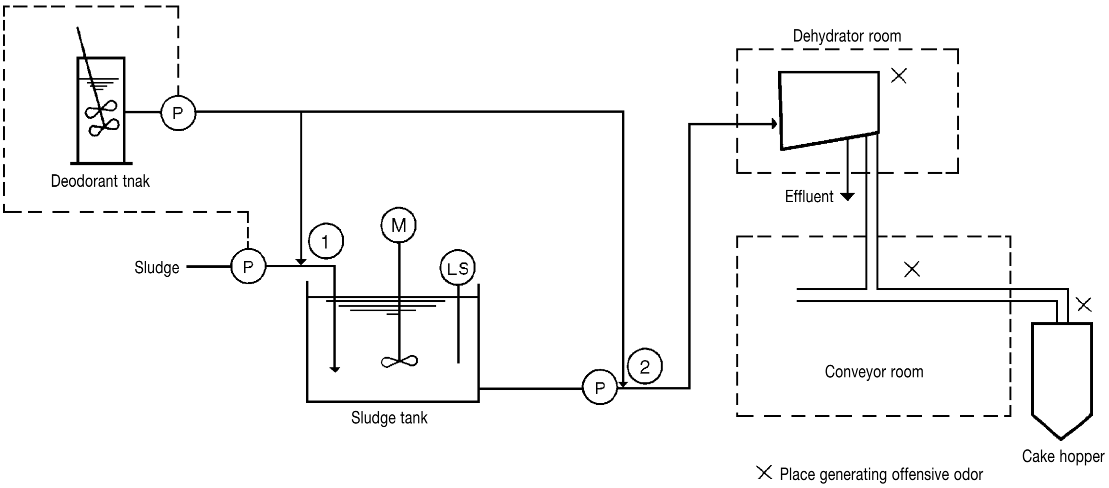


Fig. 10.17 Injection points of a deodorant in a sludge treatment plant

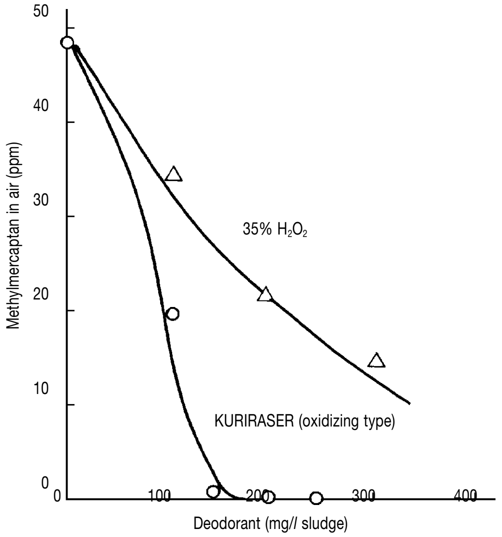


Fig. 10.18 Effects of deodorants on methylmercaptan generation from a sludge

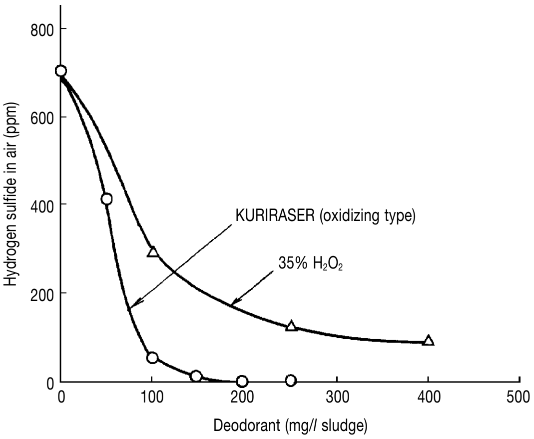


Fig. 10.19 Effects of deodorants on hydrogen sulfide generation from a sludge

sludge perfectly prevents the generation of those odor substances. In this plant, the hydrogen peroxide shows the insufficient effect.

A metallic salt type deodorant shows the sufficient effect on hydrogen sulfide, but it is poor for methylmercaptan. Table 10.14 shows the effect of a ferric salt on the hydrogen sulfide and methylmercaptan generations from the mixed sewage sludge.

The dewatered cake is incinerated or utilized for a land reclamation. During from the dewatering to the final treatment, offensive odors composed of methylmercaptan and hydrogen sulfide are generated by the putrefaction.

The use of a sterilant type deodorant is effective to prevent this type of odor generation. The deodorant was injected into the sludge in the dewatering process. Figure 10.20[2] shows the effect of a sterilant type deodorant on the dewatered cake. This figure shows the relationship between the dosage of the deodorant and the concentration of hydrogen sulfide or methylmercaptan in the air of the cake storage tank after 24 hours from the deodorant addition. The addition of the deodorant with the dosage of 100 mg/l sludge or more shows the excellent inhibition effect on the odor substance generations.

(2) A land reclamation with the cake of sewage sludges

A land reclamation utilizing the dewatered cake of sewage sludges often causes offensive odor problems because the cake generates ammonia at the surface and the underground. In that case, the spraying of deodorants which fix and stabilize ammonia onto the reclaimed land is effective.

Table 10.15 shows the effect of an organic deodorant of this type on a reclaimed land. The use of the deodorant reduces the ammonia in the air and the discomfortable index.

(3) Unloading platform in a refuse incineration plant

At a refuse incineration plant, garbage trucks unload the refuse from the platform to the refuse pit. A mixed offensive odor generates from the pit. To prevent this odor, an essential oil based deodorant is sprayed into the pit. As the result, the odor concentration expressed by the magnification value of the dilution is reduced at the platform as shown in Table 10.16.

10.9 Cleaning Agents for Water Treatment Equipment

10.9.1 Cleaning Agents for Filter Media

(1) Fouling of filter media and its problems

The use of a filter during a long time gradually accumulates a fouling on the surfaces of filter media, which is difficult to be removed by the ordinary back-washing process. This fouling accumulation causes various problems on the filter operation as follows:

① Increase in the pressure difference between the filter inlet and outlet, and the resulting reduction in the filtering rate,
② Increase in the load and the electricity consumption of the pump,
③ Deterioration of the filtered water quality,
④ Increase in the frequency of back-washing and the amount of back-washing water,
⑤ Increase in the frequency of filter media replacement and its cost.

The kinds of fouling matters vary depending on the qualities of waters to be filtered. Typical fouling matters are as follows:

① Mud ball,
② Biofouling (slime),
③ Oils and greases,
④ Metal oxides and hydroxides, such as ferric hydroxide and manganese hydroxide,
⑤ Excess coagulants and flocculants.

Table 10.17 shows the analyses of fouling matters adhered to the filter media using in various manufacturing plants.

(2) Cleaning agents

The kinds of cleaning agents using for filter media cleaning are as follows:

① Acids,
② Alkalis,

Table 10.14 Effects of a ferric salt addition on hydrogen sulfide and methylmercaptan generations from a mixed sludge

Dosage of deodorant (mg/l sludge)	0	50	100	125	200	250
Hydrogen sulfide in air (ppm)	700	300	—	195	—	Not detected
Methylmercaptan in air (ppm)	48	—	47	—	48	—

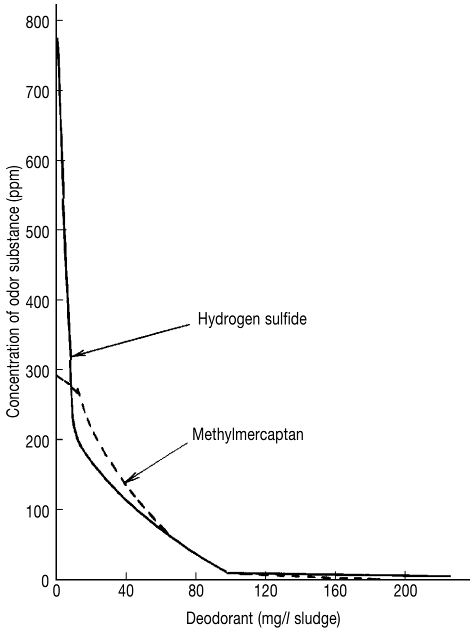


Fig. 10.20 Effect of a sterilant type deodorant on the cake of a mixed sewage sludge

Table 10.15 Effect of an organic deodorant on a reclaimed land utilizing the cake of sewage sludges

Treatment	Ammonia in the air (ppm)	Discomfortable index
None	28	-3
Deodorant	Not detected	-1

Table 10.16 Effect of an essential oil type deodorant in a refuse incineration plant

Deodorant	Odor concentration*
None	1,300
Sprayed	170

* The magnification value of the air dilution at the refuse unloading platform

③ Surfactants,
④ Biocides.

Those chemicals are appropriately used according to the composition of fouling adhering to filter media.

The combination of alkalis and surfactants is generally used for a fouling containing a high concentration of oils and fats. Acids are used together with surfactants to remove the fouling composed of metal oxides, metal hydroxides, mineral scales and so on. The combination of biocides and surfactants is used for biofouling.

(3) Cleaning method

Even though the cleaning methods vary depending on the filter structures, the following procedure is generally applied because the filter media are fouled from the surfaces:

① Backwashing with the ordinary method,
② Draining of the water up to the surface of filter media,
③ Dosing of a cleaning solution to cover the filter media surface,
④ Stirring of the filter media and the cleaning solution with a pressurized air and leaving them under a stagnant condition during a specified period,
⑤ Backwashing with water to discharge the removed fouling.

The cleaning effect is confirmed by measuring the amount of the fouling on the filter media before and after the cleaning.

Photograph 10.11 (p. 10-35) shows the surface conditions of filter media (sands) before and after the cleaning.

10.9.2 Cleaning Agents for Reverse Osmosis (RO) and Ultra-Filtration (UF) Membranes

RO and UF membranes are widely used for the removal of impurities, the concentration and recovery of valuable substances, etc., in various industrial and municipal plants. Those membranes are fouled by various substances and their efficiencies are deteriorated. Various cleaning agents are applied for those membranes to keep their efficiencies. The biofouling of RO and UF membranes using in ultra-pure water production systems and the countermeasures are described in the section 10.2. Cleaning agents for those membranes using in the other processes are described here.

(1) Fouling substances and their problems

Plants utilizing RO and UF membranes equip the pretreatment systems to remove the fouling substances from the supply water. However, those membranes are often fouled with organic substances leaked from the pretreatment systems, biological growth in the plants, and so on.

Typical fouling substances of those membranes are as follows:

① Inorganic scales, such as calcium carbonate

Table 10.17 Analyses of foulings adhering to filter media

Factory		Water to be filtered	Calcium oxide (CaO)	Iron oxide (Fe_2O_3)	Aluminum oxide (Al_2O_3)	Manganese oxide (MnO)	Acid insoluble matter	Ignition loss (600°C)	n-Hexane extract
Filters for service water treatment	A chemical factory	River water	0.7	5.9	16.7	12.0	12.0	44.0	—
	B paper mill	Raw water	0.9	6.9	13.8	Trace	56.4	17.0	—
	C dairy factory	Raw water for boiler feedwater	4.0	17.2	Trace	—	22.4	35.8	—
	D power plant	Supply water for demineralizer	Mainly diatoms, bacterial flocs and filamentous bacteria						
Filters for direct cooling water in iron and steel works	E iron mill	Direct cooling water in hot rolling mill	Trace	91.9	Ttrace	—	Trace	4.4	5
	F iron mill	Direct cooling water in rolling mill	Trace	100.0	Trace	—	3.3	Trace	0.6
	G iron mill	Direct cooling water in continuous casting plant	3.2	43.2	3.1	—	9.6	27.1	3.9
	H iron mill	Direct cooling water in continuous casting plant	1.4	59.6	8.7	Trace	7.6	16.8	1.1
	I iron mill	Direct cooling water in wire rod mill	Trace	91.5	Trace	—	1.4	0.7	0.9
	J iron mill	Direct cooling water in blooming plant	Trace	98.7	Trace	Trace	2.8	Trace	—
	K iron mill	Direct cooling water in hot rolling mill	Trace	96.1	Trace	Trace	3.0	Trace	—
Filters for waste-water treatment	L iron mill	Treated wastewater	Trace	42.0	10.8	—	8.2	38.9	0.5
	M paper mill	Waste white water	0.5	1.0	20.3	—	38.2	31.0	—
	N factory	Smoke washing water of waste incinerator	41.7	3.1	Trace	—	2.8	26.1	—
	O factory	Effluent from wet dust scrubber	38.2	6.2	Trace	1.2	4.9	12.4	—

and silicates,

② Metal hydroxides and metal oxides, such as iron hydroxide and aluminum hydroxide,
③ Microorganisms (biofouling),
④ Organic substances in wastewater, such as oils, fats, proteins, starches and detergents.

Most of those foulings are removed by the routine water flushing. However, they gradually accumulate on the membrane surfaces during a long time operation and cause the following problems:

① Reduction in the flux (product water) by the clogging of the micro-pores of membranes,
② Increase in the pressure drop between the inlet and outlet of the equipment and the resulting increase in the electricity consumption,
③ Deterioration of product water quality,
④ Deterioration of product quality in case of a process fluid treatment,
⑤ Shortening of the service lives of membranes,
⑥ Increase in the operation loads of down flow equipments.

(2) Cleaning agents

The following chemicals are used as cleaning agents for RO and UF membranes:

① Acids; citric acid, oxalic acid, sulfamic acid, hydrochloric acid, etc.,
② Alkalis; sodium hydroxide, sodium carbonate, sodium phosphate, sodium silicate, sodium borate, etc.,
③ Surfactants,
④ Oxidizing agents,
⑤ Reducing agents,
⑥ Polymer based dispersants,

⑦ Enzymes,
⑧ Organic solvents.

A suitable agent or a suitable formulation of those agents must be selected for the membrane cleaning according to the properties and the chemical resistance of a membrane, the amount and the composition of the fouling, etc.

Inorganic foulings, such as mineral scales and iron or aluminum hydroxides, are cleaned by using the mixtures of organic acids, chelating agents, nonionic surfactants, dispersants and so on. Organic foulings like biofouling and oils, are cleaned by using the mixtures of anionic or nonionic surfactants, alkalis, oxidizing or reducing agents, dispersants, enzymes, etc.

As membranes have the different chemical resistances according to their chemical compositions, a suitable cleaning chemical must be selected by considering the kinds of membranes.

(3) Cleaning methods

As the cleaning method varies with the system structure, membrane composition and so on, the cleaning is carried out according to the operation manual of the supplier.

A typical flow diagram of a spiral element type RO membrane system is shown in Figure 10.21.

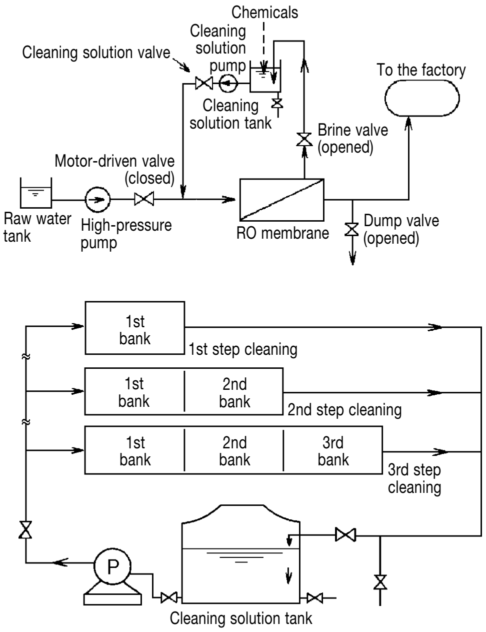


Fig. 10.21 A flow diagram for the cleaning of a spiral element type RO membrane system

The cleaning procedure is described below:

① Add a cleaning solution into the cleaning solution tank.
② Stop the system operation.
③ Open the dump valve and brine valve, and close the feedwater motor driven valve.
④ Open the cleaning solution valve and circulate the solution through the 1st bank using the cleaning pump. The solution is supplied to the 2nd and the 3rd banks in turns.
⑤ Stop the circulation during a specified time.
⑥ Circulate the solution again.
⑦ Discharge the solution from the cleaning solution tank.
⑧ Flush each bank with water.
⑨ Start the normal operation and sufficiently clean up the product water side using the product water.

The cleaning frequency is twice to three times per year for systems treating brackish water, and once to four times per month for systems treating wastewater. However, the cleaning has to be carried out in the following cases:

① When the pressure drop becomes 1.5 times or more of that without fouling.
② When the flux becomes lower than a specified permissible value.
③ After the operation stoppage during a week or more.

The cleaning effect is evaluated by the recovery of the pressure drop or the flux.

Table 10.18 shows the analyses of foulings adhering to RO membranes using for the pretreatment of demineralizers. Table 10.19 shows the recovery in the fluxes of them by the cleaning. The change in the membrane surface condition before and after the cleaning is shown in Photographs 10.12 and 10.13 (p. 10-36).

10.9.3 Cleaning Agents for the Ion Exchange Resins of Softeners

(1) Fouling substances and their problems

Ion exchange resins of softeners are periodically regenerated to recover the performances. However, they are gradually fouled with iron hydroxides and so on. The fouling of resins causes the following problems:

① Reduction in the ion exchange capacity,
② Reduction of softened water production,
③ Increase in the regeneration frequency and the consumption of regeneration chemicals,
④ Hardness leakage caused by a channeling,
⑤ Cracking and break of resins.

(2) Cleaning agents and cleaning methods

As the main component of the resin fouling is generally iron hydroxide, hydrochloric acid shows the best cleaning effect. However, it corrodes the softeners with the pipings, and requires the neutralization of the cleaning solution.

Therefore, neutral and reducing organic compounds are widely used for the resin cleaning. The cleaning agent of 2 to 3% is added into the regeneration chemical solution, and the normal regeneration method is applied to remove the fouling without special cleaning procedures. In the case of a heavy fouling, the dosage of cleaning agent is increased up to 10 to 20%.

Table 10.20 shows the cleaning effects of a cleaning agent on strongly cationic ion exchange resins of softeners for boiler feedwater. Around 70 to 80% of iron is removed from the resins by the cleaning.

10.9.4 Cleaning Agents for the Filter Cloths of Sludge Dehydrators

(1) Fouling substances and their problems

Sludge dehydrators using filter cloths are divided into belt presses, filter presses and vacuum filters. Typical filter cloth materials are polyesters, polyolefins, polyamides and wool.

Those filter cloths are periodically washed with water to keep their functions. However, they are

Table 10.18 Analyses of foulings adhering to RO membranes

(Unit: %)

System	Color	CaO	MgO	Fe_2O_3	Al_2O_3	Acid insoluble matter	MnO	SO_3	P_2O_5	Ignition loss (600° C)
Pretreatment for demineralizer A	Brown	1.4	Trace	7.9	3.4	14.6	—	Trace	4.1	71.3
Pretreatment for demineralizer B	Brown	0.9	0.3	34.8	1.5	17.1	4.1	—	—	25.6

Table 10.19 Recovery in the fluxes of RO membrane systems by the cleaning

System	Dosage of cleaning agent (KURIDINE M) (%)	Flux ($m^3/m^2 \cdot day$)		Salt rejection (%)	
		Before cleaning	After cleaning	Before cleaning	After cleaning
Pretreatment for demineralizer A	5	0.731	0.875	97.5	97.0
Pretreatment for demineralizer B	5	0.553	0.713	97.8	97.0

Table 10.20 Effects of a cleaning agent on fouled cationic exchange resins

Softener	Time of analysis	Ion exchange capacity (meq/m*l* resin)		Fouling amount of resin (%)		Removal rate of Fe_2O_3 (%)	Removed iron content in cleaning solution (mg/*l*)	Iron content in softened water (mg/*l*)
		Neutral salt-splitting capacity	Total ion exchange capacity	Acid insoluble matter (SiO_2)	Fe_2O_3			
A	Before cleaning	1.65	1.67	1.70	0.19	—	—	1.1
	After cleaning	1.67	1.67	0.13	0.04	79	232	Below 0.1 (Raw water 0.1)
B	Before cleaning	1.69	1.70	0.08	0.24	—	—	0.6
	After cleaning	1.74	1.76	0.04	0.07	71	271	0.2 (Raw water 0.2)
C	Before cleaning	1.78	1.79	0.05	0.22	—	—	0.4
	After cleaning	1.79	1.79	0.02	0.07	68	250	0.2 (Raw water 0.2)

gradually fouled with biofouling, oils, fats, calcium scales, iron hydroxides, etc. Those foulings cause the following problems:

① Reduction in the dehydration efficiency and the increase in the water content of cakes,
② Deterioration in the cake removal from the cloths,
③ Reduction in the dewatering capacities of dehydrators,
④ Shortening in the service lives of the cloths,
⑤ Increase in the fuel consumption of cake incineration plants because of the increase in the cake water content.

Therefore, the filter cloths must be periodically cleaned by using cleaning agents to prevent those problems.

(2) Cleaning agents and cleaning methods

In the case of organic fouling (biofouling, oils and fats), alkalis, surfactants, chelating agents, oxidizing agents, reducing agents and enzymes are used as the cleaning agents. For the inorganic fouling like calcium scale, acids, chelating agents and surfactants are used for the cleaning.

A suitable cleaning solution should be selected according to the chemical resistances of the filter cloth materials. Table 10.21 summarizes the chemical resistances of various cloth materials.

The cleaning frequency is once to twice per month, but it becomes once a week in case of a severe fouling condition.

The cleaning effect is evaluated by the following methods:

① Visual inspection of the cloth,
② Measurement of cake moisture contents before and after the cleaning,
③ Visual inspection for the sludge removing condition from the cloth before and after the cleaning,
④ Measurement of the air permeability of the cloth.

(3) A case study

A polyester filter cloth of a belt press dehydrator installed in a sewage treatment facility was cleaned by using a formulated cleaning agent. The cleaning agent solution was sprayed to the cloth under the dehydrator operation at a low speed. After 20 to 30 minutes, the cloth was sprayed with water. Then the excellent cleaning effect was obtained.

Photographs 10.14 to 10.16 (p. 10-36) show the filter cloth conditions before and after the cleaning.

10.10 Synthetic Zeolites

10.10.1 Features of Synthetic Zeolites

(1) Compositions and structures

Synthetic zeolites are crystalline aluminosilicates. They contain alkali and alkali earth metals, like natural zeolites. The chemical composition is expressed by the following formula:

$[M(I)_2 \text{ or } M(II)]O \cdot Al_2O_3 \cdot m\ SiO_2 \cdot n\ H_2O$

where

M(I) = alkali metal (Na or K)
M(II) = alkali earth metal (Mg or Ca)
m, n = integer

Though the crystal structures are divided into three types of A, X and Y, the A and X types are generally used for various industrial processes. Figure 10.22 shows the crystal structures of the A and X types.

The crystals of synthetic zeolites have the uniform pores with the spherical cavities.

(2) Adsorption of various substances

Synthetic zeolites contain water in their cavities under an ambient condition. This water is easily desorbed from the pores by heating or reducing pressure. Then, various substances adsorb into the vacant cavities through the pores. Since the substances with smaller molecular diameter than that of the pore enter into the pores, the substances are sifted by the size of pores. In the case of a Na-A type zeolite, as the pore diameter is around 4 Å as shown in Figure 10.23, substances with the molecular diameter of smaller than 4 Å enter into the cavities through the pores. The synthetic zeolites are called “molecular sieves” because of this function of them..

The size of the pore is controlled by selecting the kind of alkali or alkali earth metals containing in the crystals. The relationship among the kinds of metals, the types of crystals and the pore sizes are shown in Table 10.22.

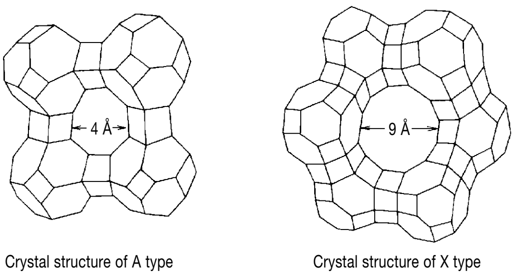
Table 10.23[3)] shows the molecular diameters of various substances. A suitable type of synthetic zeolite to adsorb an aimed substance is selected by using Tables 10.22 and 10.23.

(3) Polar effect

The synthetic zeolite is a kind of polar adsorbents. It strongly adsorbs polar molecules, such as carbon dioxide and unsaturated hydrocarbons. This strong polarity is caused by alkali or alkali earth metals in the crystal structure of the

Table 10.21 Chemical resistances of filter cloth materials using for sludge dehydrators

Material	Polyester	Polypropylene	Polyamide		Polyvinyl alcohol	Wool	Cotton
			Nylon 6	Nylon 6, 6			
Influence of acids	Partly attacked by conc. sulfuric acid	Hardly attacked by acids	Partly attacked by cold conc. hydrochloric, sulfuric or nitric acid	Partly attacked by conc. hydrochloric or sulfuric acid, Deterioration in the strength by benzoic acid or oxalic acid, Dissolved into conc. formic acid, Swelled by glacial acetic acid	Swelled or decomposed by conc. hydrochloric acid, nitric acid or formic acid	Attacked by hot sulfuric acid	Attacked by conc. acids or hot diluted acids
Influence of alkalis	Attacked by hot strong alkalis	Scarcely influenced	Scarcely influenced		Scarcely influenced	Attacked by weak alkalis	Swelled by caustic soda
Influence of organic solvents	Dissolved by some phenolic compounds	Swelled by chlorinated hydrocarbons	Dissolved into some phenolic compounds		Swelled by hot pyridine, phenol or cresol	Not influenced	Not influenced
Influence of other chemicals	—	—	—		—	Breached by oxidizing agents or sulfur dioxide	Breached by hypochlorite or peroxides



Crystal structure of A type

Crystal structure of X type

Fig. 10.22 Crystal structures of synthetic zeolites

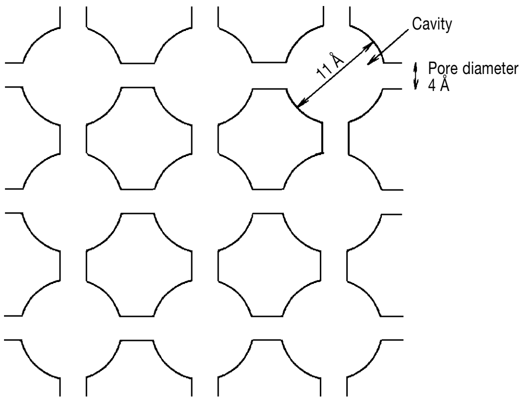


Fig. 10.23 Sizes of the pore and cavity of a Na-A type synthetic zeolite

zeolite. The positive charges of metals electrostatically attract the negative charges of polar substances.

The polar effect of synthetic zeolites is much stronger than that of silica gels or activated aluminas.

(4) Moisture adsorption

When an activated synthetic zeolite contacts with water, it easily adsorbs the water. Figure 10.24[4] shows the adsorption isotherm of water by a Na-A type (4A type) synthetic zeolite at 25°C as compared with those of a silica gel and an activated alumina. The adsorption capacity of the synthetic zeolite is much bigger than those of the other adsorbents at a low partial pressure of water.

(5) Ion exchange property

Alkali metals in the crystal structures of synthetic zeolites are easily exchanged by metallic

Table 10.22 Relationship between the types of synthetic zeolites and their pore sizes

Type		Pore size (Å)
Na-A	(4A)	4
Na-X	(13X)	9
Ca-A	(5A)	5
Ca-X	(10X)	8
K-A	(3A)	3

ions with higher valences in aqueous solutions. The selective orders of the ion exchange by various types of synthetic zeolites are shown below:

① For A-type
$Ag^+ < Tl^+ < Na^+ < K^+ < NH_4^+ < Rb^+$, $Li^+ < Cs^+$
$< Zn^{2+} < Sr^{2+} < Ba^{2+} < Ca^{2+} < Co^{2+} < Ni^{2+} < Cd^{2+}$
$< Hg^{2+} < Mg^{2+}$

② For X-type
$Ag^+ < Tl^+ < Cs^+ < Rb^+ < K^+ < Na^+ < Li^+ < Ba^{2+}$

Table 10.23 Molecular diameters of various substances

Substance	By Pauling		By Lennard-Jones	
	Length (Å)	Width (Å)	γ min.* (Å)	α ** (Å)
He	—	3	3.0	2.6
H_2	3.1	2.4	3.24	2.89
Ne	—	3.2	3.08	2.75
Ar	—	3.84	3.84	3.40
O_2	3.9	2.8	4.02	3.46
N_2	4.1	3.0	4.09	3.64
Kr	—	3.96	3.96	3.60
Xe	—	4.36	4.45	3.96
NO	4.05	3.0	3.58	3.17
N_2O	4.2	3.7	—	3.3
CO	4.2	3.7	4.25	3.76
CO_2	5.1	3.7	—	3.3
Cl_2	5.6	3.6	—	3.2
Br_2	6.2	3.9	—	3.5
H_2O	3.9	3.15	—	2.65
NH_3	4.1	3.8	—	2.6
SO_2	5.28	4.0	—	3.6
CH_4	—	4.2	4.25	3.8
C_2H_2	5.7	3.7	3.7	3.3
C_2H_4	5.0	4.4	—	3.9
C_3H_8	6.5	4.9	—	4.3
n-C_4H_{10}	—	4.9	—	4.3
HCl	4.29	3.6	—	3.2
HBr	4.6	3.9	—	3.5
H_2S	4.36	4.0	—	3.6
Cyclopropane	—	4.75	—	4.23
CS_2	—	4.0	—	3.6
CF_2Cl_2	—	5.0	—	4.4
CCl_4	—	—	6.65	5.9
Propylene	—	—	5.0	4.5
Iso-C_4H_{10}	—	5.6	—	5.0
Butene-1	—	—	5.1	4.5
CF_4	—	4.9	5.28	4.7
SF_6	—	5.8	6.18	5.5
Neopentane	—	7.0	—	6.2
$(C_4H_9)_3N$	—	—	9.1	8.1
$(C_2F_5)_2NC_3F_7$	—	8.7	—	7.7
$(C_4F_9)_3N$	—	11.5	—	10.2
Benzene	—	6.6	—	5.85
$(C_2H_5)_3N$	—	—	8.8	7.8
Cyclohexane	—	6.7	—	6.0

* Average molecular diameter
** Effective molecular diameter

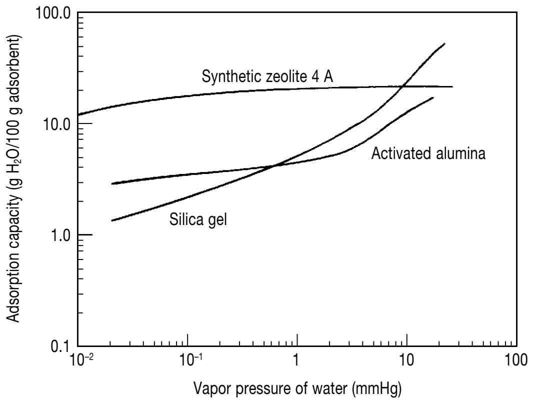


Fig. 10.24 Adsorption isotherms of water by various adsorbents at 25°C

$< Sr^{2+} < Ca^{2+} < Co^{2+} < Mg^{2+}$

③ For Y-type

$Tl^+ < Ag^+ < Cs^+ < Rb^+, NH_4^+ < K^+ < Na^+ < Li^+$

(6) Catalytic action

The X-type and Y-type synthetic zeolites form their strong solid acids when their alkali metals are exchanged with bivalent or trivalent metal ions. Their acidities are much stronger than those of silica-alumina catalysts, typical solid acids. Utilizing this property, synthetic zeolites are used as excellent solid acid catalysts.

10.10.2 Uses of Synthetic Zeolites

(1) Application methods

Utilizing the excellent adsorption ability of synthetic zeolites, they are used for the drying, refining and separation of various gasses and so on. The application methods are divided into the two types as follows:

① Repetition of adsorption and desorption (regeneration),

② Disposable uses (without regeneration).

In case of the large scale application of synthetic zeolites, the first method is used. As the regeneration methods, "thermal swing adsorption (T.S.A.) method" and "pressure swing adsorption (P.S.A.) method" are applied. The outlines of both methods are described below.

(a) T.S.A. method

In the T.S.A. method, two or more adsorption towers are installed. While one tower is in the adsorption process, the other one is in the desorption (regeneration) process. These operations are alternately carried out, then the adsorption process is continued.

In this method, the adsorption process is carried out at an ambient temperature, and the desorption (regeneration) process is carried out at an elevated temperature (heating condition) as shown in Figure 10.25. Since the increase of temperature from T_1 to T_2 reduces the amount of adsorbate from A_1 to A_2, the synthetic zeolite is regenerated.

This method is applied for both of gas phase and liquid phase treatments. As the regeneration process requires at least 2 hours, the adsorption-regeneration cycles of 8 to 48 hours are applied in fields.

(b) P.S.A. method

In this method, the adsorption and desorption are carried out by changing the pressure as shown in Figure 10.26. The adsorption process is carried out under an atmospheric or an increased pressure, and the desorption (regeneration) process is done under a reduced pressure. That is, the reduce of pressure from P_1 to P_2 decreases the amount of adsorbate from A_1 to A_2. This method applies for only gas phase treatment.

In the P.S.A. method, since the change in the pressure requires not so long time, the adsorption and desorption processes are alternated for few minutes to few tens minutes.

(2) Examples of field application

(a) Dehydration of naphtha cracked gas

In an ethylene plant, a naphtha is cracked by

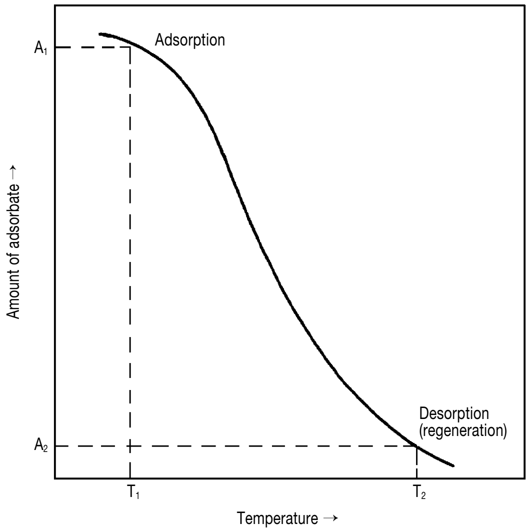


Fig. 10.25 Adsorption-desorption cycle of T.S.A. method

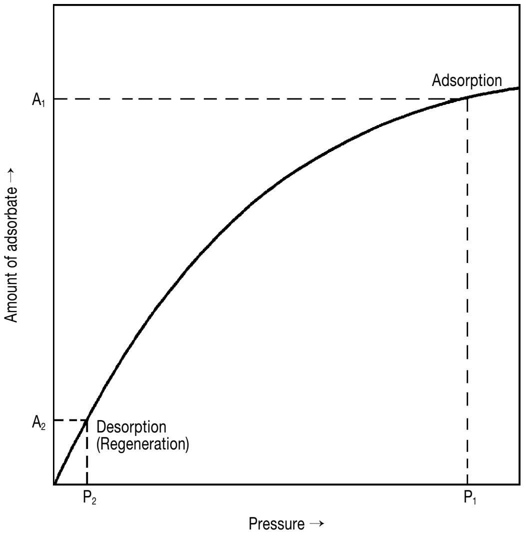


Fig. 10.26 Adsorption-desorption cycle of P.S.A. method

using a high temperature steam. After cooling and pressurizing, the cracked gas is rinsed with an alkaline solution to remove the acidic substances. After those treatments, since the cracked gas is saturated with moisture, it is dried up to the moisture content of below 1 ppm before the low temperature gas separation process.

In this process, a synthetic zeolite is used for drying the gas by a T.S.A. method. Figure 10.27[5] shows a flow diagram of the cracked gas drying process. In this process, a K-A type (3A type) synthetic zeolite is used. The zeolite keeps the higher moisture adsorption capacity than that of an activated alumina after their long term uses as shown in Figure 10.28.

(b) Dehydration of liquid propylene

The dehydration of propylene is carried out in a liquid phase under a high pressure. After the dehydration, the moisture content of propylene must be reduced below 1 ppm. For satisfying this criterion, only a synthetic zeolite is applicable among various adsorbents.

In this process, a K-A type (3A type) synthetic zeolite is used.

(c) Low temperature air separation

Pure oxygen, nitrogen and argon gasses of 99% or more are produced by utilizing the difference in their vaporization temperatures. After compressing and cooling the air repeatedly, it is deeply cooled in an adiabatic expansion process to make the liquid air. Then each substances composing of the liquid air are separated by utilizing the difference of their vaporization temperatures. The evaporation temperatures of nitrogen and oxygen are -196° C and -183° C respectively.

In this low temperature air separation process, synthetic zeolites are used for the following purposes:

(i) Removal of moisture and carbon dioxide from the raw material air

Figure 10.29 shows the flow diagram of a moisture and carbon dioxide removal process using a synthetic zeolite. The moisture and carbon dioxide are removed by the zeolite in the adsorption towers before the adiabatic expansion process. A 13X type synthetic zeolite is used in this process. After the adsorption towers, the moisture of the air is reduced up to the dew point of below -70° C

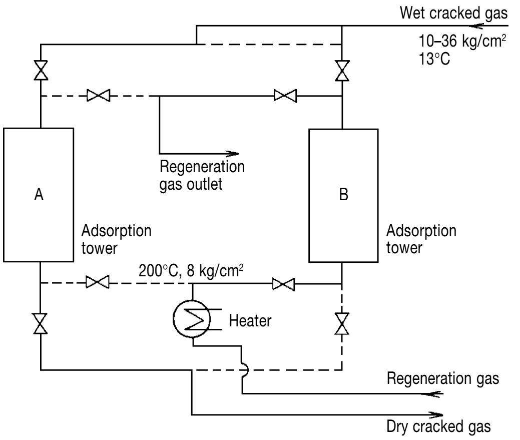


Fig. 10.27 Flow diagram of a naphtha cracked gas dehydration process

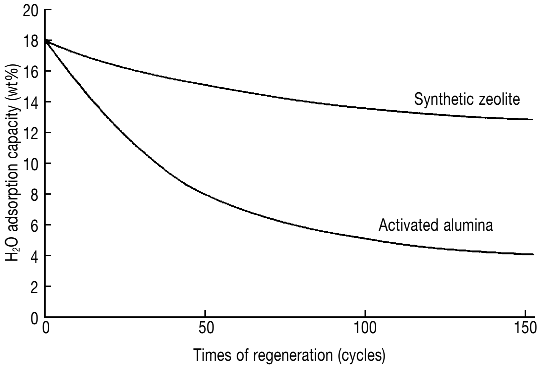


Fig. 10.28 Changes in the water adsorption capacities of adsorbents against the times of regeneration in a naphtha cracked gas drying process

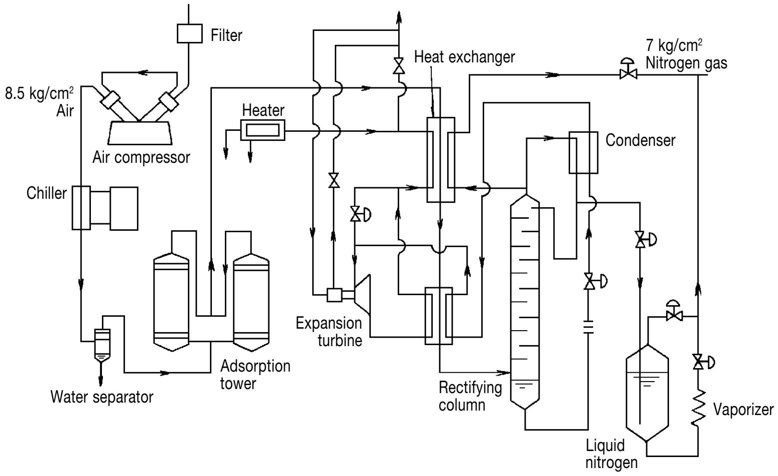


Fig. 10.29 Flow diagram of a low temperature air separation plant equipped with a moisture and carbon dioxide removal system using a synthetic zeolite

and the carbon dioxide concentration is decreased to below 1 ppm.

(ii) Removal of acetylene from the liquid air

The air contains a small amount of hydrogen carbides, such as acetylene, which are finally concentrated in the product liquid oxygen. When the acetylene concentration in the liquid oxygen exceeds a limited value, it may cause an explosion. Therefore, the acetylene is sometimes removed from the liquid air by using synthetic zeolites.

(iii) Drying of argon gas

When the product argon gas is used as an atmospheric gas for the manufacturing processes of electronic components and so on, the gas must have a particularly high purity. In that case, synthetic zeolites are often used to sufficiently purify the product argon gas.

(d) Oxygen production from air by the P.S.A. method

A Ca-A type (5A type) synthetic zeolite is used for the oxygen production. Figure 10.30 shows the adsorption isotherms of the 5A type zeolite for nitrogen and oxygen. This adsorption capacity difference between nitrogen and oxygen is utilized to produce oxygen from the air.

As shown in Figure 10.31, when the air is supplied to an adsorption tower containing a 5A type zeolite under a pressurized condition, nitrogen is preferentially adsorbed by the zeolite. As the result, oxygen is concentrated and discharged from the tower. When the pressure is reduced for the regeneration of the zeolite, a nitrogen rich gas is discharged from the tower.

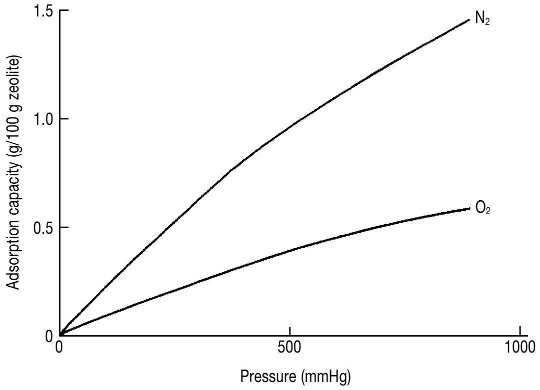


Fig. 10.30 Adsorption isotherms of a 5A type synthetic zeolite for N_2 and O_2 at 30°C

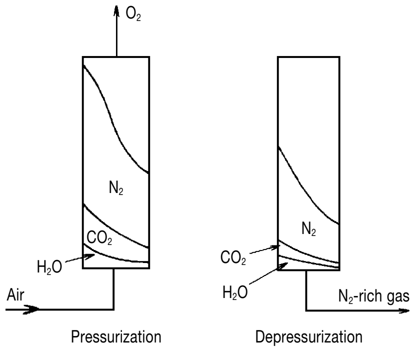


Fig. 10.31 Operation principle of oxygen production by P.S.A. method

The adsorption-desorption cycle of this system is 1 to 10 minutes and the purity of product oxygen is maximum 95%. Table 10.24 shows a typical composition of oxygen produced by this method.

Table 10.24 Composition of an oxygen gas produced by a P.S.A. method

Oxygen	95.0%
Argon	4.5%
Nitrogen	0.5%

Dew point: -70° C

10.11 Dust Blow-Away Preventives

Dust blow-away preventives have been used for reclaimed land, seashores and so on to prevent the troubles caused by the scattering of earth and sands. Recently, their application has been expanded as measures for promoting the germination of grasses on dry lands and the prevention of soil erosion at sloping surfaces. In that case, the dust blow-away preventives are applied by mixing with grass seeds, water retentive agents and so on.

In this section, the application of dust blow-away preventives for civil engineering and construction industry is introduced. The application in the iron and steel works is described in the sections 8.7.1 and 8.7.2(p.8-18).

10.11.1 Prevention of Sloping Soil Surface Erosion

The construction of housing lands, roads, dams and so on, often makes sloping soil surfaces. When the surfaces are left without any protection, wind and rain may cause an accident, such as landslips and falling rocks, because of the surface erosion. For protecting the sloping surfaces, the spraying of mortar or the planting of grasses and trees is carried out.

In the case of the planting, dust blow-away preventives are often utilized.

(1) Planting method

Grass seeds and fertilizers are mixed with a dust blow-away preventive, such as vinyl acetate emulsion. The mixture is sprinkled on sloping surfaces. The preventive bonds the fine earth and soil particles to stabilize them, and prevents the erosion. The sprinkling is carried out by using a pump pressure or air pressure. For a location where the ground work of the sprinkling is difficult, a helicopter is used for the sprinkling.

Photographs 10.17 and 10.18 (p. 10-37) show the sprinkling of the mixture of dust blow-away preventives and grass seeds on sloping surfaces by a pump pressure and a helicopter respectively.

(2) Selection and effect of dust blow-away preventives

The extent of erosion and the effect of dust blow-away preventives vary depending on soil qualities. Therefore, the effects of the preventives are experimentally evaluated by using the earth and sand samples collected at a site to select a suitable one. An artificial rainfall system is used for the testing.

Typical test results are shown in Table 10.25. The use of a dust blow-away preventive reduces the amount of soil washed-away by raining up to around one tenth of non-chemical treatment.

10.11.2 Prevention of Drought Disasters by Using High-Water- Absorbing Polymers

(1) Drought disasters and its prevention

When planting or seeding is carried out in soil which has a poor water-retention capacity, in a high temperature or a dry season, trees will die and seeds scarcely germinate because of a lack of water. To solve this problem, high-water-absorbing polymers, GRASSPOWER, are utilized.

Those polymers are polyacrylates or polyvinyl alcohols with cross-linking structures. They are swelled by absorbing water with the weight of several hundred times of the polymer itself. The absorbed water is scarcely released, even when a pressure is applied to the polymer.

When the planting or seeding is carried out, the polymer is mixed with the soil at the amount of 0.1 to 0.3%. In case of the seeding at a sloping soil surface, after mixing the polymer with a dust blow-

Table 10.25 Effect of a dust blow-away preventive on a soil washed-away by raining

Dosage of preventive (g/m^2)	Amount of soil washed-away (g/m^2)
0	858
100	84
150	75
200	68

Rainfall: 50 mm/h during 1 hour after 24 hours from the preventive solution sprinkling away preventive and seeds, the mixture is sprinkled. Since the polymer remarkably improves the water retention of the soil, it promotes the germination of seeds and their growth.

(2) Effect of high-water-absorbing polymers

The water absorption ability of a cross-linking polyvinyl alcohol is shown in Figure 10.32. This polymer absorbs water at six hundred times of own weight. The mixing of the polymer into the soil improves the germination of lawn grass seeds as shown in Figure 10.33.

After the germination, the polymer keeps the soil moisture and prevents the death of grasses as shown in Photograph 10.19 (p. 10-37).

10.11.3 Prevention of Sand and Soil Blow-Away

(1) Troubles caused by sand and soil blow-away, and their prevention

At reclaimed lands, sandhills, the construction sites of housing lands and roads, etc., fine sand and soil particles are blown away by strong winds to bring various problems to houses in the nearby areas. In those areas, water sprinkling is difficult to apply and the continuation of the effect is limited. Therefore, dust blow-away preventives are widely used to prevent this problem.

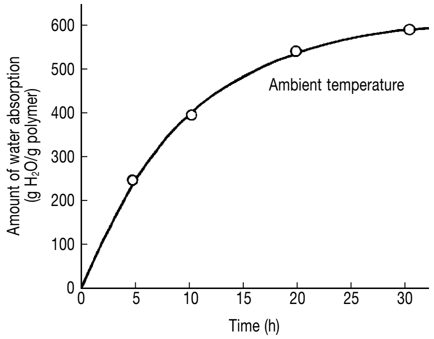


Fig. 10.32 Water absorption by a cross-linking polyvinyl alcohol immersed in water

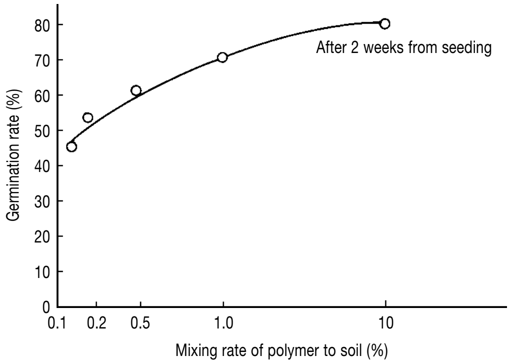


Fig. 10.33 Improvement in the germination of lawn grass seeds by mixing a cross-linking polyvinyl alcohol with soil

The preventives which form the films on the land surfaces are used for this purpose. Generally, polyvinyl acetate based or polyacrylate based emulsions are applied because they form the films with the excellent water resistances and weatherabilities. A suitable preventive is diluted with water to make the 5 to 10% solution, and the solution is sprinkled to the land at the dosage of 50 to 200 g polymer/m^2. The solution permeates into the sand and soil layer. Then the polymer forms the water resistance film by connecting the sand and soil particles together after evaporating the dilution water. Figure 10.34 shows a schematic model of the film formation by the preventive. This film prevents the sand and soil blow-away from the land surface.

When the dust blow-away prevention is required for a long time, a seeding is applied together with dust blow-away preventives. Seeds, fertilizers, soil conditioners and so on are mixed with the soil, then the preventive solution is sprinkled on the surface.

Photograph 10.20 (p. 10-38) shows the sprinkling of a dust blow-away preventive solution on a reclaimed land.

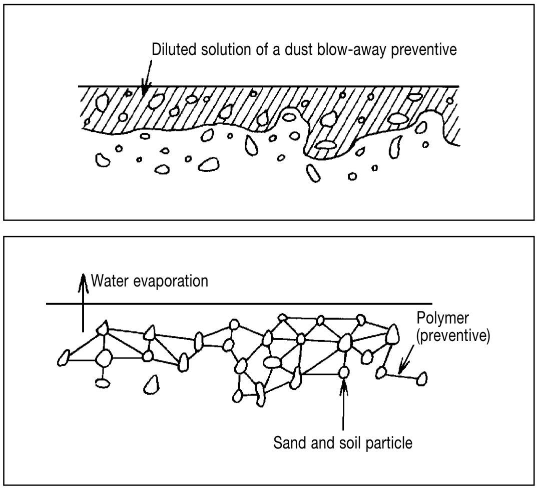


Fig. 10.34 A schematic model of the film formation by a dust blow-away preventive on the surface area of land

(2) Effects of dust blow-away preventives

The effects of dust blow-away preventives are evaluated by using a wind tunnel. Soil samples treated with a preventive solution are placed in the wind tunnel, then the amount of sand and soil blow-away is measured. Typical test results are shown in Figure 10.35. The use of a dust blow-away preventive perfectly prevents the sand and soil blow-away even under the strong wind of 30 m/s.

Photograph 10.21 (p. 10-38) shows a wind tunnel using for the evaluation of dust blow-away preventives. Photograph 10.22 (p. 10-38) shows the grass planting of a reclaimed land, utilizing a dust blow-away preventive.

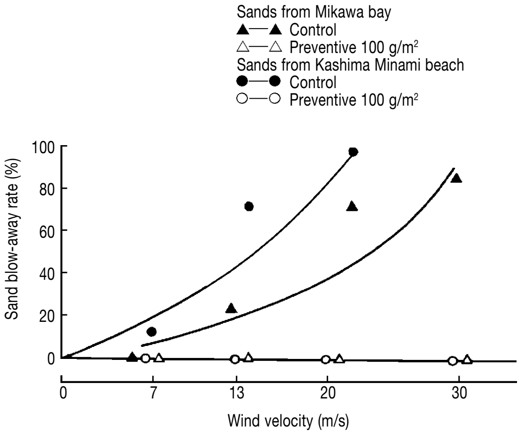


Fig. 10.35 Effect of a dust blow-away preventive on sand blow-away under various wind velocities

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11. Analyses for System Operation Control and Trouble Shooting

11.1 Water Analysis

11.1.1 Meaning of Water Analysis

Bases in the all fields of water treatments including boiler water, cooling water, supply water and wastewater treatments are analytical technologies.

In order to operate various water treatment plants safely and efficiently, the suitable water quality control has to be carried out according to the water analysis data. The water analysis also provides the basic data to determine the causes of various problems occurred in water treatment plants, such as corrosion, scaling and biological fouling.

The purposes of water analysis are divided into two categories:

① for plant operation control,
② for trouble shooting.

The most important point in the water analysis is to select the most suitable analytical method1)–7) including the analytical items, sampling method, the storage method of samples and so on, according to the objective of the analysis.

11.1.2 Sampling and Sample Storage Methods

The sampling is the first step of water analysis. Before sampling, the purpose of analysis has to be fully understood to obtain the samples which represent the characteristics of aimed plant.

For this purpose, the sampling point, sampling time, sampling frequency, etc., are determined by considering the operation conditions of the plant, such as the water flow rate, temperature and the fluctuation of water quality. Since the quality of sample tends to change during the storage, the sample must be carefully stored to maintain its characteristics until the analysis begins.

(1) Sampling and sampling bottle

The sampling is carried out by using a sampling bottle or a water sampler according to the conditions of the sampling point.

The sampling bottle is generally used when the sample is directly taken from the surface of rivers, lakes, etc., or from pipelines. In case of boiler water and cooling water, the sampling bottle is generally used for the sampling.

Water samplers are used to take a sample from a specified depth of a river, a lake or a sea. Turnover sampler, Bandon's sampler or Heyroht-type sampler8) is generally used. The sample taken by the sampler is transferred to a sampling bottle.

A glass or polyethylene made ground stopper bottle must be used as the sampling bottle to prevent the contamination of the sample. Metallic bottles, rubber or cork stoppers are never used for water sampling.

The sampling bottle must be cleaned up before the use and rinsed with the sample water at 4 to 5 times before the sample is taken. The sample water is perfectly filled into the bottle and the bottle is stoppered to eliminate an air space in the bottle.

The sample name, sampling point and so on are noted on the sampling bottle.

(2) Storage of sample8),9)

As the quality of sample tends to change during the storage, the sample should be analyzed as soon as possible.

The following changes in the water quality will happen during the storage:

① change in the concentration of dissolved gasses,
② change in the pH and alkalinity due to the dissolution or releasing of carbon dioxide gas (CO_2),
③ deposition of hard soluble salts, such as calcium carbonate and ferric hydroxide, due to the change in the pH, alkalinity, temperature, the valency of metallic irons and so on,
④ change in the bacterial number due to the growth or the death of microorganisms,
⑤ change in the concentration and structures

of nitrogenous or phosphorous compounds due to the metabolisms or the chemical reactions.

To prevent or minimize these changes, the samples are stored in a cool and dark place. Sometimes, samples are pretreated by using reagents, etc., before the transportation or the storage.

11.1.3 Analytical Items and Methods

(1) General analytical items

Tables 11.1[5,10] and 11.2[1] show the items of water quality control and typical analytical methods for boiler systems and cooling water systems respectively. Those items include the items for the water quality control and chemical injection control for obtaining the appropriate chemical treatment effects.

Even in the case of same analytical item, the most appropriate method has to be selected according to the concentration range to be measured, the kinds and concentrations of coexisting substances, etc.

(2) Analyses of special water treatment chemicals

(a) Polymer dispersants[11]

Various anionic polymer dispersants are widely used to prevent scale problems in boiler, cooling water and gas cleaning water systems, etc. Typical analysis methods used for the polymer dispersants are as follows:

(i) Turbidimetric method

A special cationic surfactant is added into a sample to make a precipitation by reacting with the anionic polymer. The concentration of polymer is obtained from the turbidity of the sample.

(ii) Colorimetric method

A polymer in sample is made to adsorb on an adsorbent. Then a special cationic dyestuff is made to react with the polymer. This reaction product of the polymer with the dyestuff is extracted and the color of the extract is measured by a colorimetric method.

(iii) Detector tube method

A sample water is introduced into an adsorbent packed into a detector tube and a polymer in the

Table 11.1 Analytical items and methods for water quality control in boiler systems

Kind of water to be analyzed		Feedwater		Boiler water			
Kind of feedwater		Raw or softened	Demineralized	Raw or softened			Demineralized
Type of boiler		–	–	Cylindrical	Water tube		
Boiler pressure (kgf/cm^2)		–	–	–	Below 10	10–20	20–30
Analytical item	Electrical conductivity	○	○	○	○	○	○
	pH	○	○	○	○	○	○
	P-alkalinity	–	–	○	○	○	○
	M-alkalinity	○	–	–	–	–	–
	Total hardness	○	–	–	–	–	–
	Chloride ion	○	–	○	○	○	○
	Silica	○	○	○	○	○	△
		–	△	–	–	–	○
	Iron	○	–	○	○	○	–
		–	△	–	–	–	○
	Copper	–	△	–	–	–	–
	Oils and fats	△	△	–	–	–	–
	Dissolved oxygen	△	△	–	–	–	–
	Phosphate ion	–	–	(○)	(○)	(○)	(○)
	Hydrazine	–	(○)	(○)	(○)	(○)	(○)
	Sulfite ion	–	–	(○)	(○)	(○)	(○)

Note: ○ General analytical item
(○) Item analyzed according to the kind of chemical applied
△ Item analyzed if it is required

sample adsorbs on the adsorbent. Then a dyestuff solution is introduced into the tube to react with the polymer adsorbed.

The polymer concentration is determined from the length of colored band in the detector tube.

(b) Azoles

Various azoles, such as benzotriazole, are used as copper corrosion inhibitors for cooling water systems. The concentrations of azoles are generally analyzed by using ultraviolet absorption method.

(c) Non-hydrazine type oxygen scavengers

The use of non- or low-toxic organic oxygen scavengers has become popular year by year. Those chemicals, such as ascorbates, saccharides and alkanol amines, are strong reducing agents. Accordingly, iodometric titration methods are generally used to analyze their concentrations.

11.1.4 Automatic Analysis Systems

Recently, the automatization and computerization of various systems have been progressed to improve the system efficiencies and to save manpower.

In the field of water analysis, a similar trend has been progressed. Especially, in the case that a large number of samples has to be analyzed, the automatization of analysis system is inevitable.

In this section, an automatic analysis system using in KURITA CENTRAL LABOLATORIES is introduced. This system is composed of the automatic titration unit, automatic colorimetric unit and computerized data processing unit. This system has realized the automatic analysis of more than 20 items required for the water quality control of boiler and cooling water systems.

(1) Automatic titration unit

This unit analyzes the pH, P-alkalinity and M-alkalinity. Firstly, the pH is measured by the pH meter. Then the sample is automatically titrated by using sulfuric acid solution. The P- and M-alkalinities are determined from the relationship between the pH and the titer. The analysis results are transmitted to the data processing unit.

Condensate		Analytical method (example)	Standard (for example)
Raw or softened	Demineralized		
–	–		
–	–		
○	○	Conductivity meter	JIS B 8224, 8
○	–	Glass electrode	JIS B 8224, 7
–	–	Sulfuric acid titration	JIS B 8224, 9.2
–	–	Sulfuric acid titration	JIS B 8224, 9.1
–	–	EDTA titration	JIS B 8224, 11.1
○	○	Mercury nitrate titration	JIS B 8224, 19.2
○	–	Molybdenum blue colorimetric	JIS B 8224, 23.1
–	○	Molybdenum blue extraction colorimetric	JIS B 8224, 23.1
○	△	1,10-Phenanthroline colorimetric	JIS B 8224, 32.1
–	△	2,4,6-Tri-2-piridil-1,3,5-triazine colorimetric	JIS B 8224, 23.2
–	○	Diethyl-dithiocarbamate colorimetric	JIS B 8224, 29.1
–	–	N-hexane extraction	JIS B 8224, 15
△	△	Indigocarmine colorimetric	JIS B 8224, 17.2
–	–	Molybdenum blue (ascorbic acid)colorimetric	JIS B 8224, 22.1
–	–	P-dimethylamino-benz-aldehyde colorimetric	JIS B 8224, 24.1
–	–	Iodometric titration	JIS B 8224, 20.1

Table 11.2 Analytical items and methods for water quality control in cooling water systems

Type of system		Open recirculating cooling water	Closed recirculating cooling water	Chiling and heating water	Inorganic brine
Analytical item	Electrical conductivity	○	○	○	–
	pH	○	○	○	○
	M-alkalinity	○	–	○	–
	Calcium hardness	○	△	○	–
	Magnesium hardness	△	–	–	–
	Chloride ion	○	○	○	–
	Sulfate ion	△	△	△	–
	Silica	○	–	–	–
	Iron	○	○	○	○
	Copper	△	△	△	○
	Ammonium ion	△	(△)	–	–
	Turbidity or suspended solids	○	△	△	△
	BOD_5	△	–	–	–
	Total phosphate	(○)	(○)	(○)	–
	Zinc	(○)	(○)	(○)	(○)
	Nitrite	–	(○)	–	–
	Nitrate	–	(○)	–	–
	Number of bacteria	○	△	△	–

Note: ○ General analytical item
(○) Item analyzed according to the kind of chemical applied
△ Item analyzed if it is required

(2) Automatic colorimetric unit

This unit simultaneously analyzes around 20 items required for controlling water qualities in boiler and cooling water systems. Those items include chloride ion, sulfate ion, phosphate ion, silica, calcium hardness and so on.

This unit is composed of the automatic sampler, the injection part of analytical reagents, spectrophotometer, data analysis and transmission part, etc. Figure 11.1 shows the flow diagram of this unit.

(3) Data processing unit

The analysis data obtained by the automatic titration and colorimetric units are transmitted from the sub-computers to the host computer. The host computer prints out the analysis data reports. The host computer accumulates all analysis data and is able to graph the data for each water sample.

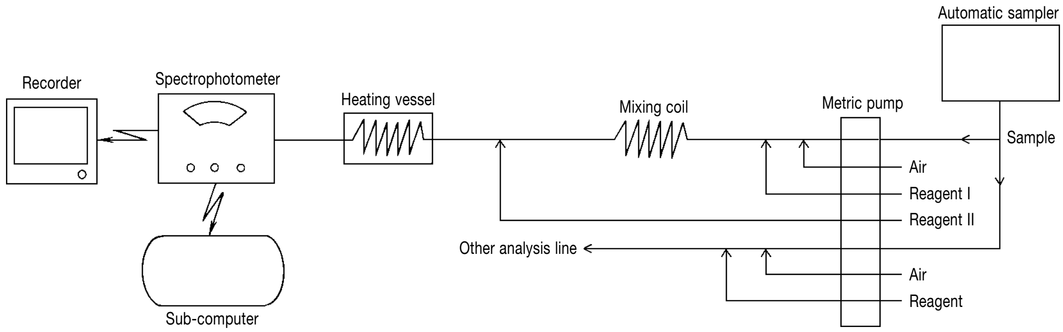


Fig. 11.1 Flow diagram of an automatic colorimetric analysis unit

Organic brine	Analytical method (example)	Standard (for example)
–	Conductivity meter	JIS K0101-86, 12
○	Glass electrode	JIS K0101-86, 11
–	Sulfuric acid titration	JIS K0101-86 , 13.1
–	EDTA titration	JIS K0101-86 , 49.1
–	EDTA titration	JIS K0101-86 , 50.1
–	Silver nitrate titration	JIS K0101-86 , 32.3
–	Barium sulfate tubidimetric	JIS K0101-79, 42.3
–	Molybdenum blue colorimetric	JIS K0101-86, 44.1.2
○	1,10-phenanthroline colorimetric	JIS K0101-86, 60.1
–	Atomic absorption spectrometry	JIS K0101-86, 51.2
–	Indophenol colorimetric	JIS K0101-86, 36.2
–	Turbidimetric or gravimetric	JIS K0101-86, 9.2 or 16.1
–	Oxygen consumption by microorganisms	JIS K0101-86, 19
–	Molybdenum blue colorimetric	JIS K0101-86 , 43.3.1
–	Atomic absorption spectrometry	JIS K0101-86 , 52.2
(○)	Naphthylethlenediamine colorimetric	JIS K0101-86 , 37.1.1
(○)	Naphthylethlenediamine colorimetric	JIS K0101-86 , 37.2.3
–	Agar culture medium	JIS K0101-86, 63.2

The host computer is connected with work stations installed in the all branch offices of KURITA to utilize the those analysis data.

Figure 11.2 shows the flow chart of the data transmission system. Figure 11.3 shows a typical graph of analysis data which is printed out by a work station.

11.1.5 Water Analysis Kits for Job Sites

It is the best to perform the water analysis in a well-equipped laboratory. However, simple analysis kits are often used for quick analyses at job sites. The features of those kits are easy analytical methods, easy handling and easy maintenance.

Photographs 11.1 to 11.4 (p. 11-13) show the Kurita's products for job site analyses. The water analysis kit shown in the Photograph 11.3 is used for boiler and cooling water analysis. The analysis items are alkalinity, total hardness, chloride ion, silica, phosphate ion, sulfate ion, hydrazine, residual chlorine and so on.

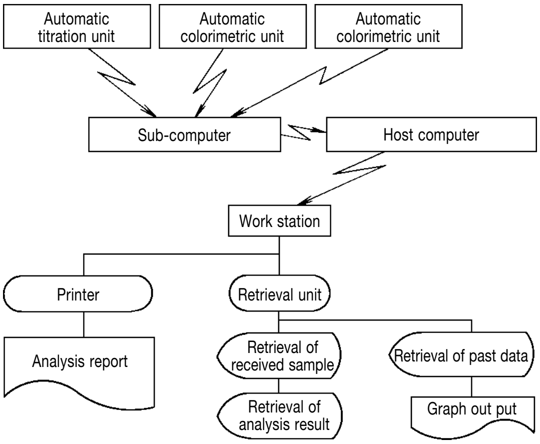


Fig. 11.2 Flow chart of a data transmission and reporting system

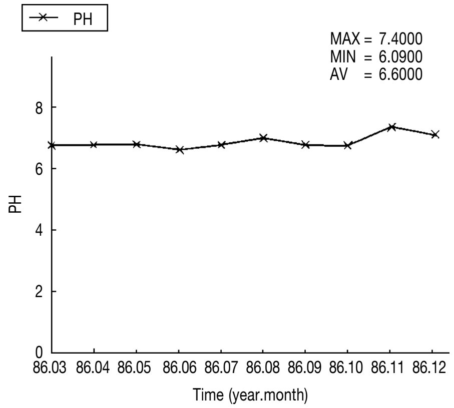


Fig. 11.3 An example of data printout

11.2 Analyses and Examinations for Trouble Shooting

11.2.1 Procedures of Trouble Shooting

Troubles occurred in boiler and cooling water systems are classified into corrosion, scale and slime(biofouling) troubles described in the chapters 2 and 3.

To solve those troubles and to apply an appropriate water treatment program, it is necessary to investigate the causes of troubles. For this purpose, it is required not only to analyze water samples and tube samples with scale, corrosion product, etc., but also to correct the informations relating to the plant operational conditions, such as the temperatures and flow velocities of water and process side fluids, the materials and structures of the equipments, etc.

After analyzing those infomations, the following examinations of tube samples and so on are carried out.

(1) Visual inspection

Firstly, the surface conditions of sample tubes must be closely observed. The kinds, colors, number, sizes and amounts of deposits on the tube surface have to be inspected and recorded. Then, the surface is photographed.

After removing the adhered substances, the surface of the tube is observed and photographed if required.

(2) Measurement of the weight of deposits

The sample tubes, etc., are cut by a saw or a lathe to measure the weights with a chemical balance. The cut sample is dried at 105°C for 2 hours in a drying oven. Then the sample is cooled in a desiccator and is weighed with the chemical balance. The sample is cleaned by using an appropriate cleaning solution to remove the deposits. Table 11.3 shows the kinds of suitable cleaning solutions for various metallic materials. After removing the deposits, the sample is rinsed with running water. Then it is dehydrated by using alcohol and dried with a dryer. The weight of the sample is measured and the amount of the deposits is calculated from equation (11.1).

$$W_D = \frac{a - b}{c} \quad \text{..} \quad (11.1)$$

where

W_D = amount of deposit (mg/cm^2)
a = sample weight before cleaning (mg)
b = sample weight after cleaning (mg)
c = surface area of sample (cm^2)

(3) Measurement of scale(deposit) thickness

The sample is cut to an appropriate size and the cut sample is embedding in a synthetic resin such as an epoxy resin. Then the scale thickness is measured by using a microscope. As the simplified method, the scale thickness on magnetic materials is measured by an electro-magnetic thickness meter. In case of non-magnetic materials, an ultrasonic thickness meter is available to measure the scale thickness.

(4) Measurement of penetration (pitting corrosion) depth

After removing the corrosion product and scale from the surface of the sample tube, the penetration depth is measured by using a micrometer, depth gauge or caliper gauge, based on the height of the uncorroded surface. When no uncorroded surface can be found, the residual tube wall thickness is measured and the penetration depth is cal-

Table 11.3 Kinds of chemical cleaning solutions for various metals

Kind of metal	Cleaning solution
Carbon steels	15% HCl 0.5% inhibitor
Stainless steels	30% HNO_3
Copper and copper alloys	10% H_2SO_4
Aluminum and aluminum alloys	36% HNO_3

culated from the designed wall thickness.

In case that the mechanical measurement of the depth is difficult because of the very minute pit diameter, it is optically measured by using a stereoscopic microscope and so on. The remaining service life of a heat exchanger tube bundle can be estimated by using the penetration depth[12)].

(5) Surface analysis

When the sample surface is covered with a sufficient amount of deposits, the amount and its composition are easily measured and analyzed using the methods described in the sections 11.2.1 (2) and 11.2.3.

When the deposit is present in a limited area with a small amount, surface analysis methods are applied for identifying the deposit composition. Among surface analysis methods, a scanning electron microscope, electron probe X-ray microanalyzer (Photograph 11.5, p. 11-14), Auger electron spectrometer (Photograph 11.6, p. 11-14), and so on are used for the trouble shooting of boiler and heat exchanger tubes.

Table 11.4 summarizes the principle and uses of these analyzers. Some typical surface analysis results are shown in the chapters 2 and 3.

11.2.2 Metallographic Examination

Metal is an aggregate of minute crystals. The crystal structure may be changed by the heat, mechanical treatment, etc. Therefore, the microscopic observation of the crystal structure is useful for obtaining informations to estimate a change in the physical and mechanical properties of a metal, the environmental conditions in the use of the metal and so on.

For the microscopic observation, a metal sample is appropriately processed to clarify the crystals, crystal boundaries and inclusions. Typical processing methods of metal samples for the metallographic examination are summarized below.

(1) Cutting of sample

The sample is cut to an appropriate size including a part where satisfies the test purpose. When the sample is cut, sufficient cares have to be paid

Table 11.4 Principles and uses of surface analyzers

Analyzer	Analytical principle	Characteristic	Use
Scanning electron microscope (SEM)	In a vacuum, a pin point of electron beam scans on a sample surface. The secondary electron beam generating from the irradiated portion is converted to electric signals to make a magnified image of the sample surface on a cathode ray tube.	The sample surface is observed at a high magnification rate of few tens thousands times.	Observation of minute structure of sample surface, such as metals, scales, ores and membranes
Electron probe X-ray micro-analyzer (EPMA or XMA)	In a vacuum, a pin point of electron beam scans on a sample surface. X-rays generating from the irradiated portion are separated into a particular X-ray for each element. This particular X-ray is converted to electric signals to make a magnified image showing the presence of an element on the sample surface, using a cathode ray tube.	Detection of the distributions of all elements, except H, He, Li and Be. Detection of element distributions on a sample surface with the depth of 1 to 2 μm.	Measurement of element distributions of sample surface, such as metals, scales, ores and membranes
Auger electron spectrometer (AES) Scanning Auger microscope (SAM)	In a vacuum, a pin point of electron beam scans on a sample surface. The kinetic energy of Auger electrons generated from the irradiated portion are analyzed to identify the kinds of elements and their presence ratios. Using the ion-spattering method, the change in the elemental composition in the vertical direction from the surface is also analyzed.	Detection of the distributions and presence ratios of all elements, except H and He in a very minute area (50 nm diameter) to a relatively wide area (300 μm square) Detection of element distributions on a just sample surface with the depth of only 0.3 to 3 nm.	Measurement of element distributions of the surface or the vertical direction from the surface of sample, such as metals, scales, ores and membranes.

for preventing the transformation of the sample by a heat generated from the cutting and so on.

(2) Mounting of sample

Generally, the sample is mounted in a resin or an alloy with a low melting point to handle it easily in the following processes, such as polishing and etching.

(3) Polishing

The surface of sample is firstly polished with abrasive papers under water spraying. The polishing is started using the No. 120 abrasive paper and finished with the No. 600 one. Then the sample is again polished by using alumina, chromium or diamond pastes to obtain a specular surface.

(4) Etching

The etching means to partially corrode the sample surface for clarifying the crystal boundaries. The etching is divided into two methods, chemical and electrochemical methods. Suitable etching method and etching solution are selected according to the kind of a sample metal.

Table 11.5 shows the typical etching solutions for metals in a wide use.

Table 11.5 Kinds of metals and their suitable etching solutions

Metal	Etching solution
Carbon steels	Ethyl alcohol with 2–5% nitric acid
Stainless steels	10–20% nitric acid solution including 0.1–3% hydrofluoric acid
Copper and copper alloys	3–10% ammonium water solution including a small amount of 30% hydrogen peroxide solution
Aluminum and aluminum alloys	2–10% sodium hydroxide solution

(5) Microscopic observation and photographing

After the etching, the metallurgical structure of sample surface is observed by using a metallurgical microscope at the magnification of 10 to 400 times. Then the photographs are taken. In the microscopic observation, the field of view is limited in a small part. Therefore, the whole surface of sample should be observed and a sufficient number of photographs should be taken.

11.2.3 Analysis of Deposits

The identification of a deposit composition is required to confirm the causes of a trouble and to determine the adequate countermeasures. Generally, the deposits are composed of scales, corrosion products, slime (biofouling) and so on.

Figure 11.4 shows a typical procedure of deposit analysis.

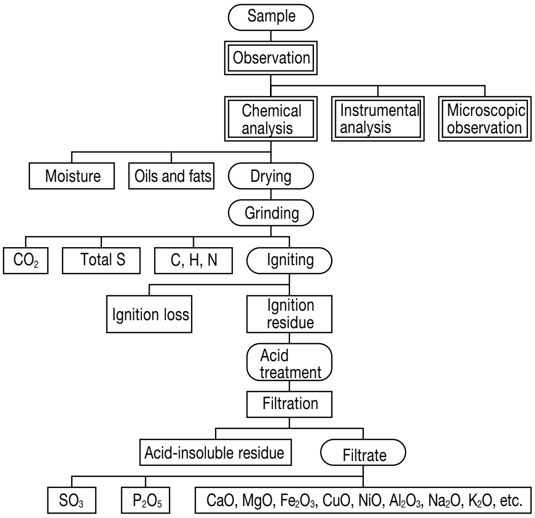


Fig. 11.4 Typical procedure of deposit analysis

(1) Chemical analysis

The outline of a deposit analysis for boiler and cooling water systems is described below.

(a) Ignition loss

After drying a sample at 105°C, it is ground to the fine powder. Around 0.25 g of sample powder is taken into a 50 m*l* crucible of which weight is already measured. Then the sample weight is accurately measured by using a chemical balance. The crucible is put in an electric furnace and the sample is ignited at 600 ± 25°C for 1 hour. After cooling the crucible in a desiccator, the weight of the crucible is measured and the ignition loss of sample is calculated from the equation (11.2).

$$IL = \frac{w_1 - w_2}{w_s} \times 100 \quad \text{..................................} \quad (11.2)$$

where

IL = ignition loss of sample (%)

w_1 = weight of the crucible including the sample before ignition (mg)

w_2 = weight of the crucible after ignition (mg)

w_S = weight of the sample (mg)

(b) Acid-insoluble residue

Around 15 m*l* of (1 + 1) hydrochloric acid is added into the crucible containing the ignition residue. The crucible is heated on a sand bath to dry up. After cooling, about 10 m*l* of nitric acid is added into the crucible and it is dried up again on the sand bath. These acid treatment is repeated more than two times.

Finally, 10 m*l* of (1 + 1) hydrochloric acid is added into the acid treatment residue. It is slightly heated and stirred with a glass rod. The sample is filtered with No. 6 filter paper and the insoluble matter on the filter paper is sufficiently washed with water.

The all filtrate is received with a 250 m*l* volumetric flask and demineralized water is added to make the volume to 250 m*l*.

The insoluble matter is transferred into a crucible together with the filter paper. The crucible is put in a drying oven to dry the sample at 105° C. Then the crucible is transferred into an electric furnace and the sample is ignited at 800° C for 1 hour. After cooling the crucible in a desiccator, the weight is measured.

The amount of acid-insoluble residue is calculated by using the equation (11.3).

$$AR = \frac{w_3 - w_4}{w_s} \times 100 \quad \text{.................................} \quad (11.3)$$

where

AR = amount of acid-insoluble residue (%)

w_3 = weight of crucible including the residue after ignition (mg)

w_4 = weight of the crucible (mg)

(c) Metallic components

Metallic components including in the filtrate are analyzed by using an atomic absorptiometry or emission spectrometry.

(i) Atomic absorptiometry

Accurately 10 m*l* of the filtrate in the section (b) is taken into a 100 m*l* volumetric flask. The 10 m*l* of 4% strontium chloride solution and demineralized water is added into the flask to make the volume to 100 m*l*. The metallic ion concentrations are analyzed by using an atomic absorption spectrophotometer. The concentrations of metallic components are generally expressed as the concentrations of the metallic oxides. Table 11.6 shows the conversion factors calculating the metallic oxide concentrations from the metallic ion concentrations.

Table 11.6 Conversion factors calculating metallic oxide concentrations from the ion concentrations

Metallic oxide		Conversion factor from the ion concentration
CaO	(%)	1.40
MgO	(%)	1.66
Fe_2O_3	(%)	1.43
CuO	(%)	1.25
ZnO	(%)	1.25
MnO	(%)	1.29
Al_2O_3	(%)	1.89
Na_2O	(%)	1.35
K_2O	(%)	1.20

(ii) Emission spectrometry

When the concentrations of various metallic elements are analyzed at the same time, the use of an emission spectrometry is convenient. An inductive couple plasma emission spectrometer (IPC) analyzes not only metallic elements but also sulfur and phosphorous.

Photograph 11.7 (p. 11-15) shows an inductive coupled plasma emission spectrometer.

(d) Phosphoric acid anhydride (P_2O_5)

The phosphorous compounds are present as phosphate ions in the filtrate. This phosphate ion concentration is analyzed by a colorimetric method or IPC method.

The P_2O_5 content is calculated from the equation (11.4).

$$P_2O_5\ (\%) = 0.747 \times PO_4^{3-}\ (\%) \quad \text{.....................} \quad (11.4)$$

(e) Sulfuric acid anhydride (SO_3)

In the filtrate, sulfur compounds are present as sulfate ion. After appropriately diluting the sample with water, 0.1 g of barium chloride and the other reagents are added into the sample to make fine barium sulfate particles. Then the sample becomes turbid. The turbidity of the sample is measured by a colorimetric method and determined the sulfate ion concentration from the calibration curve previously prepared.

The sulfuric acid anhydride contents is calculated from the equation (11.5).

$$SO_3\ (\%) = 0.83 \times SO_4^{2-}\ (\%) \quad \text{........................} \quad (11.5)$$

(f) Moisture

The sample of around 1 g is taken and the weight is exactly measured. The sample is transferred to an 100 m*l* evaporating dish with the known weight and dried at 105 to 110°C in a drying oven for 2 hours or more. After cooling it in a desiccator, the weight of the dish including sample is measured.

The moisture content of sample is calculated by using the equation (11.6).

$$M = \frac{w_5 - w_6}{S_1} \times 100 \quad \text{.................................} \quad (11.6)$$

where

M = moisture content (%)

w_5 = weight of evaporating dish with sample before drying (mg)

w_6 = weight of evaporating dish with sample after drying (mg)

S_1 = weight of sample before drying (mg)

(g) N-hexane extract (oils and fats)

After drying a sample at lower than 80°C, the sample of around 1g is taken and the weight is exactly measured. The sample is transferred to an extraction thimble and extracted with n-hexane by using a Soxhlet's extractor.

After finishing the extraction, the n-hexane is transferred to a beaker of the known weight and evaporated at 80 ± 5°C on a hot plate. After cooling the beaker in a desiccator, the weight of beaker with the extract is measured.

The amount of the extract (oils and fats) is calculated from the equation (11.7).

$$OF = \frac{w_7 - w_8}{S_2} \times 100 \quad \text{...............................} \quad (11.7)$$

where

OF = amount of oils and fats (%)

w_7 = weight of beaker with extract (mg)

w_8 = weight of beaker (mg)

S_2 = weight of sample (mg)

(h) Total sulfur

The dried sample of around 0.5 g is taken and the weight is exactly measured. The sample is transferred to a porcelain crucible. The Eschka's mixture of 2 g is added to the sample and they are thoroughly mixed. Another 1 g of Eschka's mixture is added to cover the sample surface perfectly.

The crucible is transferred to an electric furnace and ignited at 600 ± 25°C for 30 to 60 minutes. After cooling, the crucible is transferred to a 200 m*l* beaker containing around 50 m*l* of hot demineralized water on a sand bath and the content in the beaker is dissolved into the water. The water is filtered with a No. 6 filter paper to remove the insoluble matter. The filtrate is collected to 300 m*l* conical beaker. The 3% bromine water of 20 m*l* and the hydrochloric acid (1 + 1) of 10 m*l* are added into the filtrate. Then it is heated on a sand bath to remove the bromine. After cooling, the solution is transferred to a 500 m*l* measuring flask and demineralized water is added to make the total volume to 500 m*l*.

The sample of 50 m*l* is taken into a color comparison tube with a ground stopper, and the sulfate ion concentration is determined by the turbidimetry using barium chloride.

The total sulfur content is calculated from the equation (11.8).

$$TS = \frac{SO_4}{60 \times S_3} \times 100 \quad \text{................................} \quad (11.8)$$

where

TS = total sulfur (%)

SO_4 = sulfate ion concentration (mg/*l*)

S_3 = amount of sample (g)

(i) Carbonic acid anhydride (CO_2)

The amount of carbonate in a scale is analyzed as the amount of carbonic anhydride (CO_2) by using a Schroetter's alkalimeter. Figure 11.5 shows a Schroetter's alkalimeter.

After drying and cooling the alkalimeter, Vaseline is applied to the ground joints of (C), (D), (E) and (F) to prevent a gas leakage. Then hydrochloric acid (1 + 1) and concentrated sulfuric acid are added into (A) and (B) up to the heights of around 80% and 30% respectively. The weight of the alkalimeter is measured. A sample of 500 to 1,000 mg is put into the meter inside through (C) and the weight of the meter is measured again.

The stop cock (D) is slowly opened to introduce the hydrochloric acid into the reaction chamber for reacting with the sample. The reaction between the sample and hydrochloric acid forms carbon dioxide gas. The gas is released to the air from the (E) through the sulfuric acid in the (B).

When all hydrochloric acid is entered into the chamber and the formation of carbon dioxide gas is perfectly stopped, the weight of the alkalimeter is measured.

The amount of carbonic acid anhydride is calculated by using equation (11.9).

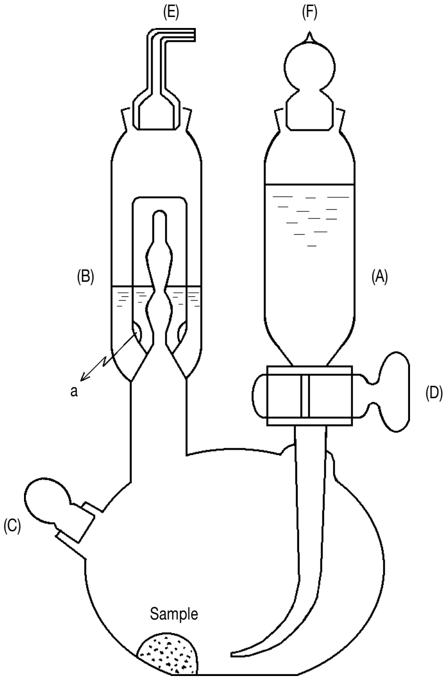


Fig. 11.5 Schroetter's alkalimeter

$$CA = \frac{Y - Z}{Y - X} \times 100 \quad \text{.................................} \quad (11.9)$$

where

CA = amount of carbonic anhydride (%)

X = weight of alkalimeter including hydrochloric and sulfuric acids (mg)

Y = weight of alkalimeter after adding sample (mg)

Z = weight of alkalimeter after finishing CO_2 gas generation (mg)

(j) Carbon, hydrogen and nitrogen (C, H, N analysis)

To determine the kind of organic substances in the deposit, the contents of carbon, hydrogen and nitrogen is sometimes analyzed. Photograph 11.8 (p. 11-15) shows a C, H, N-analyzer using for the analysis of carbon, hydrogen, and nitrogen. Total organic carbon analyzer shown in photograph 11.9 (p. 11-15) is also used for analyzing the organic carbon content.

(2) Instrumental analysis

Chemical analyses determine the kinds of elements or ions composed of deposits. However, the determination of molecular structure of substances composed of the deposit is sometimes required for a trouble shooting. In that case, various instrumental analyzers are used. Photographs 11.10 to 11.16 (p. 11-16 and p. 11-17) show the typical instrumental analyzers.

X-ray diffractometer and infrared spectrophotometer are generally used for determining the structures of inorganic substances. For determining the structures of organic substances, gas chromatograph, Furrier transform infrared spectrometer, gas chromatograph mass-spectrometer, nuclear magnetic resonance spectrometer and so on are used.

(3) Microbiological testing methods

Whether a deposit originates from biological fouling or not is determined by the microscopic observation and chemical analysis. Samples using for the microbiological testing should be preserved at 2 to 5°C using a refrigerator, etc. The testing has to be carried out as soon as possible.

(a) Microscopic observation

A drop of sample is placed on a slide glass using a pipette or a micro-spatula. Then it is covered with a cover glass to make no air bubble mixing in. The cover glass is lightly pressed and the water oozing is absorbed by a filter paper to make the sample as thin as possible.

The specimen is observed by using a microscope at the magnification of 100 to 400 times generally. Then the representative parts are photographed.

The kinds of microorganisms composing of the deposit are determined by referring to the standard photographs of suitable reference books.[4),13)]

Photographs 11.17 to 11.23 (p. 11-17 and p. 11-18) show the typical microorganisms growing up in cooling water systems and so on.

(b) Chemical analysis

Most of biological foulings include microorganisms and inorganic substances. Large-size inorganic substances are easily defined by microscopic observation, while fine inorganic substances are difficult to identify.

In that case, the measurement of protein content and/or ignition loss is carried out to determine the microorganism content of the deposit.

Table 11.7 shows a determination method for the kinds of biofouling (slime) including microorganisms from the chemical analysis.

Table 11.7 Identification for the types of biofouling (slime) from the chemical analysis

Type of slime	Protein content (%)	Ignition loss (%)
Sedimented sludge	Below 5	Below 20
Adhesion type slime including inorganic matter	5–15	20–40
Slime composed of microorganisms	Over 15	Over 40

Reference

1) Japanese Industrial Standard (JIS) K0101, “Testing Methods for Industrial Water” (1986)
2) JIS K0102, “Testing Methods for Industrial Wastewater” (1993)
3) Testing Method for Drinking Water: Japan Water Works Association (1978)
4) Testing Methods for Sewage: Japan Sewage Works Association (1974)
5) JIS B 8224, “Testing Methods for Boiler Feedwater and Boiler Water” (1993)
6) Standard Methods for the Examination of Water and Wastewater: APHA, AWWA, WPCF (1979)
7) Water Analysis: ASTM Standard, Part 31 (1980)
8) JIS K0094, “Sampling Method for Industrial Water and Industrial Wastewater” (1980)
9) K. Sakai, M. Sakata: “Instrumental Analysis for Environmental Analysis”, p.51, Japan Assoc. of Environmental Analysis (1980)
10) JIS B 8223, “Water Conditioning for Boiler Feedwater and Boiler Water” (1989)
11) M. Wakamatsu, H. Matsui: Journal of Japan Water Works Association, **5**, No. 524, 15, (1978)
12) Japan Soc. of Corrosion Eng.: “The Prediction of Service Lives of Materials for Process Plants” (Japanese), Maruzen (1984)
13) H. Mizuno: “Japanese Plankton in Fresh Water” (Japanese), Hoiku-sha (1975)

Appendices

A1 Conversion factors for measurement units

A1.1 Units of length

cm	m	in	ft	yd	mile
1	0.01	0.3937	0.03281	0.01094	6.2137 x 10^{-6}
100	1	39.370	3.2808	1.0936	6.2137 x 10^{-4}
2.54	0.0254	1	0.08333	0.02778	1.5783 x 10^{-5}
30.48	0.3048	12	1	0.3333	1.8939 x 10^{-4}
91.44	0.9144	36	3	1	5.6818 x 10^{-4}
1.6093 x 10^{5}	1.6093 x 10^{3}	6.336 x 10^{4}	5,280	1,760	1

A1.2 Units of area

cm^2	m^2	in^2	ft^2	yd^2	$mile^2$
1	10^{-4}	0.1550	1.07639 x 10^{-3}	1.1960 x 10^{-4}	3.8610 x 10^{-11}
10^{4}	1	1,550	10.7639	1.1960	3.8610 x 10^{-7}
6.4516	6.4516 x 10^{-4}	1	6.9444 x 10^{-3}	7.7160 x 10^{-4}	2.4910 x 10^{-10}
929.03	0.092903	144	1	0.1111	3.5870 x 10^{-8}
8,361.27	0.836127	1,296	9	1	3.2283 x 10^{-7}
2.5900 x 10^{10}	2.5900 x 10^{6}	4.0145 x 10^{9}	2.7878 x 10^{7}	3.0976 x 10^{6}	1

A1.3 Units of volume

m^3	cm^3	liter	in^3	ft^3	qt	gal (U.S.)
1	10^{6}	10^{3}	6.1024 x 10^{4}	35.3147	1.0567 x 10^{3}	264.17
10^{-6}	1	10^{-3}	0.061024	3.53147 x 10^{-5}	1.0567 x 10^{-3}	2.6417 x 10^{-4}
10^{-3}	1,000	1	61.024	0.0353147	1.0567	0.26417
1.6387 x 10^{-5}	16.387	0.016387	1	5.7870 x 10^{-4}	0.01732	4.3290 x 10^{-3}
2.8317 x 10^{-2}	28,317	28.317	1,728	1	2.9922	7.4805
9.4635 x 10^{-4}	946.35	0.94635	57.75	0.03420	1	0.25
3.785 x 10^{-3}	3,785	3.785	231	0.13368	4	1

A1.4 Units of weight

g	kg	oz	lb	metric ton	ton (U.S.)
1	10^{-3}	0.035274	2.2046 x 10^{-3}	10^{-6}	1.1023 x 10^{-6}
1,000	1	35.274	2.2046	10^{-3}	1.1023 x 10^{-3}
28.3495	0.0283495	1	0.0625	2.83495 x 10^{-5}	5 x 10^{-4}
453.592	0.453592	16	1	4.53592 x 10^{-4}	0.0005
10^{6}	1,000	35,274	2,204.6	1	1.1023
907,184	907.184	32,000	2,000	0.907184	1

A1.5 Units of density

g/cm^3	g/l (kg/m^3)	oz/in^3	lb/in^3	lb/ft^3	lb/gal
1	1,000	0.57804	0.036127	62.4280	8.3454
10^{-3}	1	5.7804 x 10^{-4}	3.6127 x 10^{-5}	0.062428	8.3454 x 10^{-3}
1.7230	1,723.0	1	0.0625	108	14.4375
27.6799	27,679.9	16	1	1,728	231
0.016018	16.018	9.2593 x 10^{-3}	5.7870 x 10^{-4}	1	0.1337
0.1198	119.8	4.7495 x 10^{-3}	4.3290 x 10^{-3}	7.4805	1

A1.6 Units of pressure

Pa (N/m^2)	dyn/cm^2	bar	atm	kg/cm^2	mmHg	in Hg	lb/in^2
1	10	10^{-5}	9.8692 x 10^{-6}	1.0197 x 10^{-5}	7.5006 x 10^{-3}	2.9530 x 10^{-4}	1.4504 x 10^{-4}
0.1	1	10^{-6}	9.8692 x 10^{-7}	10197 x 10^{-6}	7.5006 x 10^{-4}	2.9530 x 10^{-5}	1.4504 x 10^{-5}
10^5	10^6	1	0.98692	1.0197	750.06	29.530	14.504
101,325	1,013,250	1.01325	1	1.03323	760	29.921	14.6960
98,066.5	980,665	0.980665	0.96784	1	735.56	28.959	14.223
133.322	1,333.22	1.33322 x 10^{-3}	1.3158 x 10^{-3}	1.35951 x 10^{-3}	1	0.03937	0.01934
3,386.4	33,864	0.033864	0.03342	0.03453	25.4	1	0.4912
6,894.8	68,948	0.068948	0.06805	0.07031	51.715	2.0360	1

A1.7 Units of flow rate

m^3/h	m^3/min	m^3/s	L/s	ft^3/h	ft^3/min	ft^3/s	gal (UK)/ min	gal (U.S.)/ min
1	0.01667	2.778 x 10^{-4}	0.2778	35.31	0.5886	9.810 x 10^{-3}	3.667	4.403
60	1	0.01667	16.67	2.119	35.31	0.5886	220.0	264.2
3,600	60	1	1,000	1.271 x 10^5	2,119	35.31	1.320 x 10^4	1.585 x 10^4
3.6	0.06	0.001	1	127.1	2.119	0.03531	13.20	15.85
0.02832	4.719 x 10^{-4}	7.866 x 10^{-6}	7.866 x 10^{-3}	1	0.01667	2.778 x 10^{-4}	0.1038	0.1247
1.699	0.02832	4.719 x 10^{-4}	0.4719	60	1	0.01667	6.229	7.481
101.9	1.699	0.02832	28.32	3,600	60	1	373.7	448.8
0.2728	4.546 x 10^{-3}	7.577 x 10^{-5}	0.07577	9.632	0.1605	2.676 x 10^{-3}	1	1.201
0.2271	3.785 x 10^{-3}	6.309 x 10^{-5}	0.06309	8.021	0.1337	2.228 x 10^{-3}	0.8327	1

A1.8 Units of energy

J	kg·m	ft·lb	kcal	Btu	kWh	PSh	HPh	MeV
1	0.10197	0.7376	2.3885 x 10^{-4}	9.4782 x 10^{-4}	2.7778 x 10^{-7}	3.7767 x 10^{-7}	3.7251 x 10^{-7}	6.2419 x 10^{12}
9.8067	1	7.2330	2.3423 x 10^{-3}	9.2949 x 10^{-3}	2.7241 x 10^{-6}	3.7037 x 10^{-6}	3.6530 x 10^{-6}	6.1212 x 10^{13}
1.3582	0.13826	1	3.2383 x 10^{-4}	1.2851 x 10^{-3}	3.7662 x 10^{-7}	5.1206 x 10^{-7}	5.0505 x 10^{-7}	8.4629 x 10^{12}
4.1868 x 10^{3}	4.2694 x 10^{2}	3.0880 x 10^{3}	1	3.9683	1.163 x 10^{-3}	1.5812 x 10^{-3}	1.5596 x 10^{-3}	2.6134 x 10^{16}
1.0551 x 10^{3}	1.0759 x 10^{2}	7.7817 x 10^{2}	0.2520	1	2.9307 x 10^{-4}	3.9847 x 10^{-4}	3.9302 x 10^{-4}	6.5856 x 10^{15}
3.6 x 10^{6}	3.6710 x 10^{5}	2.6552 x 10^{6}	8.5985 x 10^{2}	3.4121 x 10^{3}	1	1.3596	1.3410	2.2471 x 10^{19}
2.6478 x 10^{6}	2.7 x 10^{5}	1.9529 x 10^{6}	6.3241 x 10^{2}	2.5096 x 10^{3}	0.7355	1	0.9863	1.6527 x 10^{19}
2.6845 x 10^{6}	2.7375 x 10^{5}	1.98 x 10^{6}	6.4119 x 10^{2}	2.5444 x 10^{3}	0.7457	1.0139	1	1.6757 x 10^{19}
1.6021 x 10^{-13}	1.6337 x 10^{-14}	1.1816 x 10^{-13}	3.8265 x 10^{-17}	1.5185 x 10^{-16}	4.4502 x 10^{-20}	6.0506 x 10^{-20}	5.9678 x 10^{-20}	1

A1.9 Units of heat flux

w/cm^2	kcal/m^2·h	Btu/ft^2·h	Btu/in^2·h
1	8.598 x 10^{3}	3.170 x 10^{3}	22.01
1.163 x 10^{-4}	1	0.3687	2.560 x 10^{-3}
3.155 x 10^{-4}	2.712	1	6.944 x 10^{-3}
4.543 x 10^{-2}	3.906 x 10^{2}	1.44 x 10^{2}	1

A1.10 Units of heat transfer coefficient

w/cm^2·°C	kcal/m^2·h·°C	Btu/ft^2·h·°F	Btu/in^2·h·°F
1	8.598 x 10^{3}	1.761 x 10^{3}	12.23
1.163 x 10^{-4}	1	0.2048	1.422 x 10^{-3}
0.5678 x 10^{-3}	4.882	1	6.944 x 10^{-3}
0.08177	7.031 x 10^{2}	1.44 x 10^{2}	1

A1.11 Units of thermal conductivity

w/cm·°C	kcal/m·h·°C	Btu/ft·h·°F	Btu/in·h·°F
1	85.98	57.78	4.815
1.163 x 10^{-2}	1	0.6720	0.0560
0.01731	1.488	1	0.08333
0.2077	17.86	12	1

A2 Atomic weights of elements

Element	Symbol	Atomic number	Atomic weight	Element	Symbol	Atomic number	Atomic weight
Actinium	Ac	89	—	Mercury	Hg	80	200.5_9
Aluminum	Al	13	26.98154	Molybdenum	Mo	42	95.9_4
Americium	Am	95	—	Neodymium	Nd	60	144.2_4
Antimony	Sb	51	121.7_5	Neon	Ne	10	20.17_9
Argon	Ar	18	39.95	Neptunium	Np	93	237.0482
Arsenic	As	33	74.9216	Nickel	Ni	28	58.7_1
Astatine	At	85	—	Niobium	Nb	41	92.9064
Barium	Ba	56	137.3_4	Nitrogen	N	7	14.0067
Berkelium	Bk	97	—	Nobelium	No	102	—
Beryllium	Be	4	9.01218	Osmium	Os	76	190.2
Bismuth	Bi	83	208.9806	Oxygen	O	8	15.999_4
Boron	B	5	10.81	Palladium	Pd	46	106.4
Bromine	Br	35	79.904	Phosphorus	P	15	30.9738
Cadmium	Cd	48	112.40	Platinum	Pt	78	195.0_9
Calcium	Ca	20	40.08	Plutonium	Pu	94	—
Californium	Cf	98	—	Polonium	Po	84	—
Carbon	C	6	12.011	Potassium	K	19	39.102
Cerium	Ce	58	140.12	Praseodymium	Pr	59	140.9077
Cesium	Cs	55	132.9055	Promethium	Pm	61	—
Chlorine	Cl	17	35.453	Protactinium	Pa	91	231.0359
Chromium	Cr	24	51.996	Radium	Ra	88	226.0254
Cobalt	Co	27	58.9332	Radon	Rn	86	—
Copper	Cu	29	63.54_6	Rhenium	Re	75	186.2
Curium	Cm	96	—	Rhodium	Rh	45	102.9055
Dysprosium	Dy	66	162.5_0	Rubidium	Rb	37	85.467_8
Einsteinium	Es	99	—	Ruthenium	Ru	44	101.0_7
Erbium	Er	68	167.2_6	Samarium	Sm	62	150.4
Europium	Eu	63	151.96	Scandium	Sc	21	44.9559
Fermium	Fm	100	—	Selenium	Se	34	78.9_6
Fluorine	F	9	18.9984	Silicon	Si	14	28.08_6
Francium	Fr	87	—	Silver	Ag	47	107.868
Gadolinium	Gd	64	157.25	Sodium	Na	11	22.9898
Gallium	Ga	31	69.72	Strontium	Sr	38	87.62
Germanium	Ge	32	72.5_9	Sulfur	S	16	32.06
Gold	Au	79	196.9665	Tantalum	Ta	73	180.947_9
Hafnium	Hf	72	178.4_9	Technetium	Tc	43	98.9062
Helium	He	2	4.00260	Tellurium	Te	52	127.6_0
Holmium	Ho	67	164.9303	Terbium	Tb	65	158.9254
Hydrogen	H	1	1.0080	Thallium	Tl	81	204.3_7
Indium	In	49	114.82	Thorium	Th	90	232.0381
Iodine	I	53	126.9045	Thulium	Tm	69	168.9342
Iridium	Ir	77	192.2_2	Tin	Sn	50	118.6_9
Iron	Fe	26	55.84_7	Titanium	Ti	22	47.9_0
Krypton	Kr	36	83.80	Tungsten	W	74	183.8_5
Lanthanum	La	57	138.905_5	Uranium	U	92	238.029
Lawrencium	Lr	103	—	Vanadium	V	23	50.941_4
Lead	Pb	82	207.2	Xenon	Xe	54	131.30
Lithium	Li	3	6.94_1	Ytterbium	Yb	70	173.0_4
Lutetium	Lu	71	174.97	Yttrium	Y	39	88.9059
Magnesium	Mg	12	24.305	Zinc	Zn	30	65.3_8
Manganese	Mn	25	54.9380	Zirconium	Zr	40	91.22
Mendelevium	Md	101	—				

A3 Saturation state steam table (temperature base)

Temp.	Saturation pressure		Specific volume (m^3/kg)		Enthalpy (kcal/kg)			Entropy (kcal/kg·°K)	
(°C)	(atm)	(mmHg)	v'	v''	h'	h''	r = h'' - h'	s'	s''
0.01	0.00623	4.6	0.0010002	206.16	0.00	597.5	597.5	0.0000	2.1872
5	0.00889	6.5	0.0010000	147.16	5.02	599.7	594.7	0.0182	2.1560
10	0.01251	9.2	0.0010003	106.43	10.03	601.9	591.8	0.0361	2.1262
15	0.01738	12.8	0.0010008	77.98	15.03	604.1	589.0	0.0536	2.0977
20	0.02383	17.5	0.0010017	57.84	20.03	606.2	586.2	0.0708	2.0704
25	0.03228	23.7	0.0010029	43.40	25.02	608.4	583.4	0.0877	2.0443
30	0.04325	31.8	0.0010043	32.93	30.01	610.6	580.6	0.1043	2.0193
35	0.05732	42.2	0.0010060	25.24	35.00	612.7	577.7	0.1206	1.9954
40	0.07520	55.3	0.0010078	19.55	40.00	614.9	574.9	0.1366	1.9725
45	0.09771	71.9	0.0010099	15.28	44.99	617.0	572.0	0.1525	1.9504
50	0.12578	92.5	0.0010121	12.05	49.98	619.1	569.1	0.1680	1.9293
55	0.16051	118.1	0.0010145	9.579	54.97	621.2	566.3	0.1834	1.9090
60	0.20313	149.4	0.0010171	7.679	59.97	623.3	563.3	0.1985	1.8895
65	0.2550	187.6	0.0010199	6.202	64.97	625.4	560.4	0.2134	1.8707
70	0.3178	233.7	0.0010228	5.046	69.98	627.4	557.5	0.2281	1.8526
75	0.3931	289.1	0.0010259	4.134	74.98	629.5	554.5	0.2425	1.8352
80	0.4829	355.2	0.0010292	3.409	79.99	631.4	551.5	0.2568	1.8184
85	0.5894	433.6	0.0010326	2.829	85.01	633.4	548.4	0.2709	1.8022
90	0.7149	525.9	0.0010361	2.361	90.03	635.4	545.3	0.2848	1.7865
95	0.8619	634.0	0.0010399	1.982	95.06	637.3	542.2	0.2986	1.7714
100	1.0332	760.0	0.0010437	1.673	100.1	639.2	539.1	0.3121	1.7568
110	1.4609	—	0.0010519	1.210	110.2	642.8	532.6	0.3388	1.7290
120	2.0246	—	0.0010606	0.8915	120.3	646.3	526.0	0.3649	1.7028
130	2.7546	—	0.0010700	0.6681	130.5	649.6	519.2	0.3904	1.6781
140	3.685	—	0.0010801	0.5085	140.7	652.8	512.1	0.4154	1.6548
150	4.854	—	0.0010908	0.3924	151.0	655.7	504.7	0.4399	1.6327
160	6.303	—	0.0011022	0.3068	161.3	658.4	497.1	0.4640	1.6116
170	8.076	—	0.0011145	0.2426	171.8	660.9	489.1	0.4876	1.5914
180	10.224	—	0.0011275	0.1938	182.3	663.1	480.8	0.5110	1.5721
190	12.799	—	0.0011415	0.1563	192.9	665.0	472.1	0.5340	1.5534
	15.855								
200	23.656	—	0.0011565	0.1272	203.6	666.6	463.0	0.5567	1.5352
220	34.138	—	0.0011900	0.08604	225.4	668.7	443.4	0.6014	1.5004
240	47.869	—	0.0012291	0.05965	247.8	669.3	421.5	0.6454	1.4667
260	65.468	—	0.0012756	0.04213	271.1	667.9	396.8	0.6890	1.4333
280		—	0.0013324	0.03013	295.4	664.1	368.1	0.7329	1.3993
	87.621								
300	115.12	—	0.0014041	0.02165	321.3	657.1	335.8	0.7775	1.3634
320	148.93	—	0.0014995	0.01548	349.3	645.8	296.4	0.8240	1.3238
340	190.43	—	0.0016387	0.01078	381.1	627.2	246.2	0.8746	1.2761
360	225.56	—	0.0018959	0.006940	421.4	593.6	172.3	0.9365	1.2086
374.15		—	0.003170	0.003170	503.3	503.3	0	1.0612	1.0612

A4 Saturation state steam table (pressure base)

Pressure	Saturation temperature	Specific volume (m^3/kg)		Enthalpy (kcal/kg)			Entropy (kcal/kg·°K)	
(atm)	(°C)	v'	v''	h'	h''	r = h'' - h'	s'	s''
0.01	6.70	0.0010001	131.62	6.72	600.4	593.7	0.0243	2.1457
0.03	23.76	0.0010026	46.52	23.80	607.9	584.1	0.0836	2.0506
0.05	32.55	0.0010051	28.72	32.56	611.7	579.1	0.1126	2.0070
0.07	38.66	0.0010073	20.91	38.66	614.3	575.6	0.1324	1.9785
0.10	45.45	0.0010101	14.95	45.44	617.2	571.8	0.1539	1.9485
0.2	59.67	0.0010170	7.791	59.64	623.2	563.5	0.1975	1.8907
0.3	68.68	0.0010221	5.326	68.65	626.9	558.2	0.2242	1.8573
0.5	80.86	0.0010298	3.300	80.86	631.8	550.9	0.2593	1.8156
0.7	89.47	0.0010357	2.408	89.47	635.1	545.7	0.2833	1.7882
1.0	99.09	0.0010430	1.725	99.17	638.8	539.6	0.3097	1.7594
2	119.62	0.0010603	0.9018	119.9	646.2	526.3	0.3639	1.7038
3	132.88	0.0010728	0.6168	133.4	650.6	517.1	0.3976	1.6713
4	142.92	0.0010831	0.4708	143.7	653.7	510.0	0.4226	1.6482
5	151.11	0.0010920	0.3816	152.1	656.0	503.9	0.4426	1.6303
6	158.08	0.0011000	0.3213	159.3	657.9	498.6	0.4594	1.6156
7	164.17	0.0011072	0.2778	165.7	659.5	493.8	0.4739	1.6031
8	169.61	0.0011140	0.2448	171.3	660.8	489.5	0.4867	1.5922
10	179.04	0.0011262	0.1979	181.3	662.9	481.6	0.5087	1.5739
12	187.08	0.0011373	0.1663	189.8	664.5	474.7	0.5273	1.5588
14	194.13	0.0011476	0.1434	197.3	665.7	468.4	0.5434	1.5458
16	200.43	0.0011572	0.1260	204.1	666.7	462.6	0.5577	1.5345
18	206.15	0.0011663	0.1124	210.2	667.4	457.2	0.5705	1.5243
20	211.93	0.0011749	0.1015	215.9	668.0	452.1	0.5822	1.5152
25	222.91	0.0011953	0.08147	228.6	668.9	440.3	0.6078	1.4954
30	232.76	0.0012142	0.06794	239.6	669.3	429.7	0.6295	1.4788
35	241.42	0.0012321	0.05817	249.4	669.3	419.8	0.6485	1.4643
40	249.18	0.0012494	0.05076	258.4	668.9	410.5	0.6654	1.4514
45	256.22	0.0012662	0.04494	266.6	668.3	401.7	0.6808	1.4396
50	262.69	0.0012826	0.04025	274.3	667.6	393.3	0.6949	1.4288
60	274.28	0.0013149	0.03313	288.3	665.5	377.2	0.7203	1.4091
70	284.47	0.0013469	0.02798	301.0	662.8	361.8	0.7427	1.3915
80	293.61	0.0013791	0.02406	312.8	659.7	346.9	0.7631	1.3752
100	309.53	0.0014457	0.01848	334.3	652.3	318.0	0.7993	1.3451
120	323.15	0.0015177	0.01466	354.0	643.5	289.4	0.8316	1.3170
140	335.10	0.0015985	0.01183	372.8	632.8	259.9	0.8616	1.2890
160	345.75	0.0016935	0.009615	391.3	619.7	228.4	0.8905	1.2595
180	355.35	0.0018139	0.007794	410.8	603.7	192.9	0.9205	1.2274
200	364.07	0.0019902	0.006187	431.6	582.8	151.1	0.9520	1.1892
220	372.05	0.0023688	0.004423	462.7	545.8	83.1	0.9988	1.1276
225.56	374.15	0.003170	0.003170	503.3	503.3	0	1.0612	1.0612

A5 Compressed water and superheated steam table (1)

Pressure (atm) [Saturation temp. (°C)]		Temperature (°C)										
		150	200	250	300	350	400	450	500	550	600	650
0. 05 [32.6]	v	39.81	44.52	59.23	53.94	58.65	63.35	68.06	72.77	77.47	82.18	86.89
	h	664.8	687.8	711.2	734.9	758.9	783.3	808.2	833.4	859.0	885.1	911.5
	s	2.1540	2.2055	2.2523	2.2956	2.3358	2.3735	2.4090	2.4428	2.4749	2.5056	2.5351
0. 1 [45.5]	v	19.90	22.26	24.61	26.97	29.32	31.67	34.03	36.38	38.74	41.09	43.44
	h	664.7	687.8	711.2	734.8	758.9	783.3	808.1	833.4	859.0	885.1	911.5
	s	2.0775	2.1290	2.1759	2.2191	2.2594	2.2971	2.3326	2.3664	2.3985	2.4292	2.4587
0. 2 [59.7]	v	9.941	11.122	12.302	13.480	14.658	15.835	17.013	18.190	19.367	20.544	21.710
	h	664.6	687.7	711.1	734.8	758.8	783.3	808.1	833.3	859.0	885.0	911.5
	s	2.0007	2.0524	2.0994	2.1427	2.1829	2.2206	2.2562	2.2899	2.3221	2.3528	2.3822
0. 5 [80.9]	v	3.966	4.442	4.916	5.388	5.860	6.332	6.803	7.274	7.745	8.216	8.687
	h	664.0	687.3	710.8	734.6	758.7	783.2	808.0	833.3	858.9	885.0	911.4
	s	1.8988	1.9508	1.9980	2.0414	2.0817	2.1195	2.1551	2.1888	2.2210	2.2517	2.2812
0. 7 [89.4]	v	2.828	3.170	3.509	3.847	4.184	4.521	4.858	5.195	5.532	5.868	6.205
	h	663.7	687.1	710.7	734.5	758.6	783.1	808.0	833.2	858.9	884.9	911.4
	s	1.8610	1.9134	1.9607	2.0042	2.0446	2.0823	2.1179	2.1517	2.1839	2.2146	2.2441
1 [99.1]	v	1.975	2.215	2.454	2.691	2.927	3.164	3.400	3.636	3.871	4.107	4.343
	h	663.1	686.8	710.5	734.3	758.5	783.0	807.9	833.1	858.8	884.9	911.4
	s	1.8207	1.8735	1.9211	1.9647	2.0051	2.0429	2.0785	2.1123	2.1445	2.1752	2.2047
2 [119.6]	v	0.9788	1.1019	1.2227	1.3422	1.4612	1.5798	1.6982	1.8164	1.9345	2.0526	2.1706
	h	661.3	685.6	709.7	733.8	758.1	782.6	807.6	832.9	858.6	884.7	911.2
	s	1.7409	1.7953	1.8436	1.8875	1.9282	1.9661	2.0018	2.0357	2.0679	2.0987	2.1282
3 [132.9]	v	0.6466	0.7307	0.8123	0.8927	0.9724	1.0518	1.1310	1.2100	1.2889	1.3677	1.4465
	h	659.4	684.5	708.9	733.2	757.6	782.3	807.3	832.6	858.4	884.5	911.0
	s	1.6927	1.7487	1.7978	1.8421	1.8830	1.9210	1.9568	1.9907	2.0230	2.0538	2.0833
5 [151.1]	v	.0010908	0.4336	0.4840	0.5330	0.5814	0.6294	0.6772	0.7249	0.7724	0.8198	0.8672
	h	151.0	682.1	707.3	732.1	756.7	781.6	806.7	832.1	857.9	884.1	910.7
	s	0.4399	1.6884	1.7392	1.7843	1.8256	1.8639	1.8999	1.9339	1.9663	1.9972	2.0268
7 [164.2]	v	.0010906	0.3061	0.3432	0.3788	0.4138	0.4484	0.4827	0.5169	0.5510	0.5850	0.6190
	h	151.0	679.5	705.7	730.9	755.8	780.8	806.1	831.6	857.5	883.7	910.4
	s	0.4398	1.6471	1.6997	1.7458	1.7875	1.8261	1.8622	1.8963	1.9288	1.9597	1.9894
10 [179.0]	v	.0010904	0.2103	0.2375	0.2632	0.2881	0.3126	0.3369	0.3610	0.3850	0.4089	0.4328
	h	151.1	675.4	703.1	729.1	754.5	779.8	805.2	830.8	856.8	883.2	909.9
	s	0.4397	1.6010	1.6566	1.7041	1.7466	1.7856	1.8220	1.8563	1.8889	1.9199	1.9497
15 [197.4]	v	.0010901	0.1353	0.1552	0.1732	0.1903	0.2070	0.2234	0.2397	0.2559	0.2720	0.2880
	h	151.1	668.0	698.6	726.0	752.2	777.9	803.6	829.5	855.7	882.2	909.0
	s	0.4396	1.5437	1.6052	1.6554	1.6992	1.7389	1.7758	1.8104	1.8432	1.8744	1.9043

v: Specific volume (m^3/kg), h: Enthalpy (kcal/kg), s: Entropy (kcal/kg·°K)

A5 Compressed water and superheated steam table (2)

Pressure (atm) [Saturation temp. (°C)]		Temperature (°C)										
		150	200	250	300	350	400	450	500	550	600	650
20 [211.4]	10^3 v	1.0898	1.1561	113.9	128.1	141.4	154.2	166.7	179.1	191.3	203.5	215.6
	h	151.2	203.6	693.6	722.8	749.8	776.1	802.1	828.2	854.6	881.2	908.2
	s	0.4395	0.5565	1.5661	1.6194	1.6647	1.7052	1.7425	1.7774	1.8104	1.8418	1.8719
30 [232.8]	10^3 v	1.0891	1.1551	72.18	82.91	92.42	101.4	110.0	118.4	126.8	135.0	143.2
	h	151.4	203.7	682.6	715.8	744.9	772.3	799.0	825.6	852.4	879.3	906.5
	s	0.4392	0.5562	1.5046	1.5653	1.6140	1.6563	1.6946	1.7302	1.7637	1.7955	1.8258
50 [262.7]	10^3 v	1.0877	1.1531	1.2496	46.37	53.09	59.02	64.57	69.90	75.10	80.20	85.24
	h	151.6	203.9	259.3	699.6	734.1	764.3	792.7	820.4	847.9	875.4	903.2
	s	0.4387	0.5554	0.6667	1.4867	1.5445	1.5911	1.6318	1.6688	1.7033	1.7358	1.7667
70 [284.5]	10^3 v	1.0864	1.1511	1.2461	30.26	36.06	40.80	45.08	49.09	52.96	56.73	60.42
	h	151.9	204.1	259.3	679.7	721.9	755.7	786.0	815.0	843.3	871.6	899.8
	s	0.4382	0.5547	0.6656	1.4214	1.4921	1.5443	1.5878	1.6265	1.6621	1.6953	1.7268
100 [309.5]	10^3 v	1.0844	1.1482	1.2409	1.3987	23.02	27.03	30.41	33.47	36.35	39.11	41.80
	h	152.4	204.4	259.3	320.9	700.4	741.4	775.5	806.6	836.4	865.7	894.8
	s	0.4374	0.5536	0.6639	0.7762	1.4251	1.4885	1.5373	1.5790	1.6163	1.6509	1.6833
140 [335.1]	10^3 v	1.0819	1.1444	1.2344	1.3827	13.71	17.69	20.55	23.02	25.26	27.37	29.40
	h	153.0	204.8	259.4	319.9	661.3	719.9	760.0	794.7	826.8	857.6	887.9
	s	0.4364	0.5522	0.6618	0.7722	1.3354	1.4256	1.4837	1.5301	1.5703	1.6067	1.6404
170 [350.7]	10^3 v	1.0800	1.1417	1.2298	1.3719	1.7372	13.43	16.16	18.39	20.36	22.19	23.92
	h	153.4	205.1	259.5	319.3	399.0	700.2	747.4	785.3	819.4	851.5	882.8
	s	0.4357	0.5512	0.6603	0.7694	0.9023	1.3808	1.4485	1.4993	1.5420	1.5799	1.6147
200 [364.1]	10^3 v	1.0781	1.1390	1.2253	1.3619	1.6728	10.303	13.050	15.129	16.925	18.559	20.091
	h	153.9	205.5	259.5	318.7	393.9	677.1	733.8	775.5	811.7	845.3	887.5
	s	0.4350	0.5502	0.6588	0.7668	0.8922	1.3341	1.4156	1.4714	1.5168	1.5564	1.5923
250 [—]	10^3 v	1.0751	1.1347	1.2182	1.3467	1.6052	6.367	9.454	11.416	13.023	14.444	15.752
	h	154.6	206.0	259.7	318.0	388.6	623.9	708.3	758.0	798.4	834.6	868.7
	s	0.4338	0.5485	0.6564	0.7627	0.8805	1.2407	1.3624	1.4288	1.4795	1.5223	1.5602
300 [—]	10^3 v	1.0722	1.1305	1.2115	1.3331	1.5587	3.045	6.979	8.923	10.418	11.701	12.861
	h	155.4	206.6	259.9	317.4	384.9	526.1	678.7	739.1	784.5	823.7	859.7
	s	0.4326	0.5469	0.6541	0.7589	0.8716	1.0875	1.3082	1.3892	1.4461	1.4923	1.5325
350 [—]	10^3 v	1.0693	1.1265	1.2051	1.3207	1.5229	2.155	5.166	7.133	8.558	9.746	10.801
	h	156.1	207.2	260.2	317.0	382.2	479.0	644.3	719.0	770.0	812.5	850.6
	s	0.4314	0.5454	0.6519	0.7554	0.8643	1.0131	1.2509	1.3511	1.4151	1.4652	1.5077
400 [—]	10^3 v	1.0665	1.1226	1.1990	1.3094	1.4937	1.931	3.838	5.795	7.169	8.285	9.261
	h	156.9	207.7	260.5	316.6	380.0	463.6	606.6	697.7	755.1	801.1	841.5
	s	0.4303	0.5438	0.6497	0.7521	0.8580	0.9867	1.1914	1.3138	1.3859	1.4401	1.4851

v: Specific volume (m^3/kg), h: Enthalpy (kcal/kg), s: Entropy (kcal/kg·°K)

A6 Constants of saturated water and steam

Temp. (°C)	Sp. heat at constant pressure (kcal/kg·°C)		Viscosity (cP)		Kinematic viscosity (cSt)		Thermal conductivity (kcal/m·h·°C)		Prandtl number	
	C'p (Water)	C"p (Steam)	μ' (Water)	μ" (Steam)	ν' (Water)	ν" (Steam)	λ' (Water)	λ" (Steam)	Pr' (Water)	Pr" (Steam)
0	1.0073	0.4429	1.750	0.00802	1.750	1,655	0.4893	0.01565	13.0	0.815
10	1.0014	0.4441	1.300	0.00842	1.300	896	0.5047	0.01617	9.29	0.831
20	0.9989	0.4457	1.000	0.00882	1.002	510	0.5184	0.01668	6.94	0.847
30	0.9981	0.4477	0.797	0.00922	0.800	304	0.5314	0.01720	5.39	0.863
40	0.9981	0.4503	0.651	0.00962	0.656	188	0.5434	0.01771	4.30	0.883
50	0.9987	0.4535	0.544	0.01002	0.551	121	0.5529	0.01823	3.54	0.896
60	0.9995	0.4575	0.463	0.01042	0.471	80.0	0.5623	0.01883	2.96	0.913
70	1.0007	0.4615	0.400	0.01082	0.409	54.6	0.5692	0.01935	2.53	0.930
80	1.0023	0.4685	0.351	0.01122	0.361	38.2	0.5761	0.01995	2.20	0.947
90	1.0043	0.4758	0.311	0.01162	0.322	27.4	0.5813	0.02064	1.94	0.966
100	1.0069	0.4844	0.279	0.01202	0.291	20.1	0.5856	0.02132	1.73	0.984
110	1.0100	0.4945	0.252	0.01242	0.265	15.0	0.5881	0.02201	1.56	1.00
120	1.0138	0.5063	0.230	0.01280	0.244	11.4	0.5907	0.02279	1.42	1.02
130	1.0183	0.5198	0.211	0.01317	0.226	8.80	0.5915	0.02365	1.31	1.04
140	1.0234	0.5352	0.195	0.01354	0.211	6.89	0.5916	0.02451	1.21	1.06
150	1.0294	0.5528	0.181	0.01390	0.197	5.45	0.5907	0.02545	1.14	1.08
160	1.0362	0.5726	0.169	0.01425	0.186	4.37	0.5881	0.02649	1.07	1.11
170	1.0440	0.5950	0.159	0.01461	0.177	3.54	0.5856	0.02760	1.02	1.13
180	1.0527	0.6200	0.149	0.01496	0.168	2.90	0.5821	0.02889	0.970	1.15
190	1.0627	0.6479	0.141	0.01530	0.161	2.39	0.5770	0.03018	0.935	1.18
200	1.0740	0.6790	0.134	0.01565	0.155	1.99	0.5718	0.03164	0.904	1.21
210	1.0870	0.7136	0.127	0.01599	0.149	1.67	0.5649	0.03328	0.881	1.24
220	1.1018	0.7523	0.122	0.01634	0.145	1.41	0.5572	0.03500	0.864	1.26
230	1.1190	0.7956	0.116	0.01670	0.140	1.19	0.5494	0.03697	0.853	1.29
240	1.1390	0.8447	0.111	0.01707	0.136	1.02	0.5400	0.03912	0.846	1.33
250	1.1624	0.9010	0.107	0.01745	0.134	0.873	0.5314	0.04162	0.842	1.36
260	1.1901	0.9666	0.103	0.01785	0.131	0.752	0.5185	0.04445	0.848	1.40
270	1.2233	1.0446	0.0994	0.01828	0.129	0.651	0.5073	0.04772	0.868	1.44
280	1.2635	1.1387	0.0961	0.01875	0.128	0.565	0.4944	0.05159	0.883	1.49
290	1.3133	1.2546	0.0930	0.01927	0.127	0.492	0.4798	0.05632	0.916	1.54
300	1.3762	1.4008	0.0901	0.01984	0.127	0.430	0.4652	0.06208	0.958	1.61
310	1.4579	1.5884	0.0865	0.0207	0.125	0.379	0.4497	0.06930	1.00	1.71
320	1.5680	1.8443	0.0830	0.0217	0.124	0.336	0.4368	0.07438	1.07	1.94
330	1.7243	2.2359	0.0794	0.0231	0.124	0.300	0.4145	0.08255	1.19	2.24
340	1.9663	2.9165	0.0754	0.0247	0.124	0.266	0.3955	0.09200	1.35	2.82
350	2.4135	4.0963	0.0709	0.0266	0.123	0.234	0.3758	0.1023	1.64	3.83
360	3.4820	5.9989	0.0653	0.0292	0.124	0.203	0.3431	0.1178	2.38	5.34
370	10.310	18.371	0.0560	0.0340	0.124	0.169	0.2992	0.1427	6.95	15.7
374.15	∞	∞	0.0450	0.0450	0.143	0.143	0.2046	0.2046	∞	∞

A7 Constants of water

Temp. (°C)	Density (g/cc)	Vapor pressure (mmHg)	Sp. heat (kcal/kg·°C)	Viscosity (cp)	Thermal conductivity (kcal/m·h·°C)	*Pr* (—)	Enthalpy (kcal/kg)	Temp. (°C)	Density (g/cc)	Vapor pressure (mmHg)	Sp. heat (kcal/kg·°C)	Viscosity (cp)	Thermal conductivity (kcal/m·h·°C)	*Pr* (—)	Enthalpy (kcal/kg)
0	0.99987	4.579	1.008	1.792	0.500	13.0	0	50	0.9881	92.51	0.999	0.549	0.550	3.59	49.96
2	0.99997	5.294	1.006	1.673	—	12.1	2.00	52	0.9872	102.09	0.999	0.532	0.552	3.47	51.96
4	0.99000	6.101	1.005	1.567	—	11.3	4.01	54	0.9862	112.51	0.999	0.515	0.554	3.34	53.95
6	0.99997	7.013	1.003	1.473	—	10.6	6.01	56	0.9853	123.80	0.999	0.499	0.556	3.22	55.95
8	0.99988	8.045	1.002	1.386	—	10.0	8.02	58	0.9843	136.08	1.000	0.483	0.558	3.12	57.94
10	0.99973	9.209	1.002	1.308	0.498	9.48	10.02	60	0.9832	149.38	1.000	0.469	0.560	3.02	59.94
12	0.99952	10.518	1.001	1.236	0.501	8.91	12.02	62	0.9822	163.77	1.000	0.455	0.562	2.91	61.94
14	0.99927	11.987	1.000	1.171	0.504	8.37	14.02	64	0.9811	179.31	1.000	0.442	0.563	2.82	63.94
16	0.99897	13.634	1.000	1.111	0.508	7.87	16.02	66	0.9800	196.09	1.000	0.429	0.565	2.74	65.94
18	0.99862	15.477	0.999	1.056	0.512	7.32	18.01	68	0.9790	214.17	1.001	0.417	0.567	2.64	67.94
20	0.9982	17.535	0.999	1.005	0.515	7.03	20.01	70	0.9778	233.7	1.001	0.406	0.568	2.57	69.94
22	0.9978	19.827	0.999	0.958	0.518	6.69	22.01	72	0.9767	254.6	1.001	0.395	0.570	2.50	71.94
24	0.9973	22.377	0.999	0.914	0.520	6.32	24.01	74	0.9755	277.2	1.002	0.385	0.571	2.43	73.94
26	0.9968	25.209	0.999	0.874	0.523	6.01	26.01	76	0.9743	301.4	1.002	0.375	0.573	2.36	75.94
28	0.9963	28.349	0.998	0.836	0.525	5.72	28.00	78	0.9731	327.3	1.002	0.366	0.574	2.30	77.95
30	0.9957	31.824	0.998	0.801	0.528	5.49	30.00	80	0.9718	355.1	1.003	0.357	0.575	2.24	79.95
32	0.9951	35.663	0.998	0.768	0.530	5.21	32.00	82	0.9706	384.9	1.003	0.348	0.576	2.19	81.95
34	0.9944	39.898	0.998	0.737	0.532	5.00	33.99	84	0.9693	416.8	1.003	0.340	0.577	2.13	83.96
36	0.9937	44.563	0.998	0.709	0.535	4.77	35.99	86	0.9680	450.9	1.004	0.332	0.578	2.08	85.96
38	0.9930	49.692	0.998	0.681	0.537	4.56	37.98	88	0.9667	487.1	1.004	0.324	0.580	2.02	87.97
40	0.9922	55.324	0.998	0.656	0.539	4.38	39.98	90	0.9653	525.76	1.005	0.317	0.581	1.98	89.98
42	0.9915	61.50	0.998	0.632	0.541	4.20	41.97	92	0.9640	566.99	1.005	0.310	0.582	1.93	91.99
44	0.9901	68.26	0.998	0.610	0.543	4.06	43.97	94	0.9626	610.90	1.006	0.303	0.583	1.88	94.00
46	0.9898	75.65	0.999	0.588	0.545	3.88	45.97	96	0.9612	657.62	1.006	0.296	0.584	1.84	96.02
48	0.9890	83.71	0.999	0.568	0.548	3.73	47.96	98	0.9598	707.27	1.007	0.290	0.585	1.80	98.03
								100	0.9584	760.00	1.007	0.284	0.586	1.75	100.04

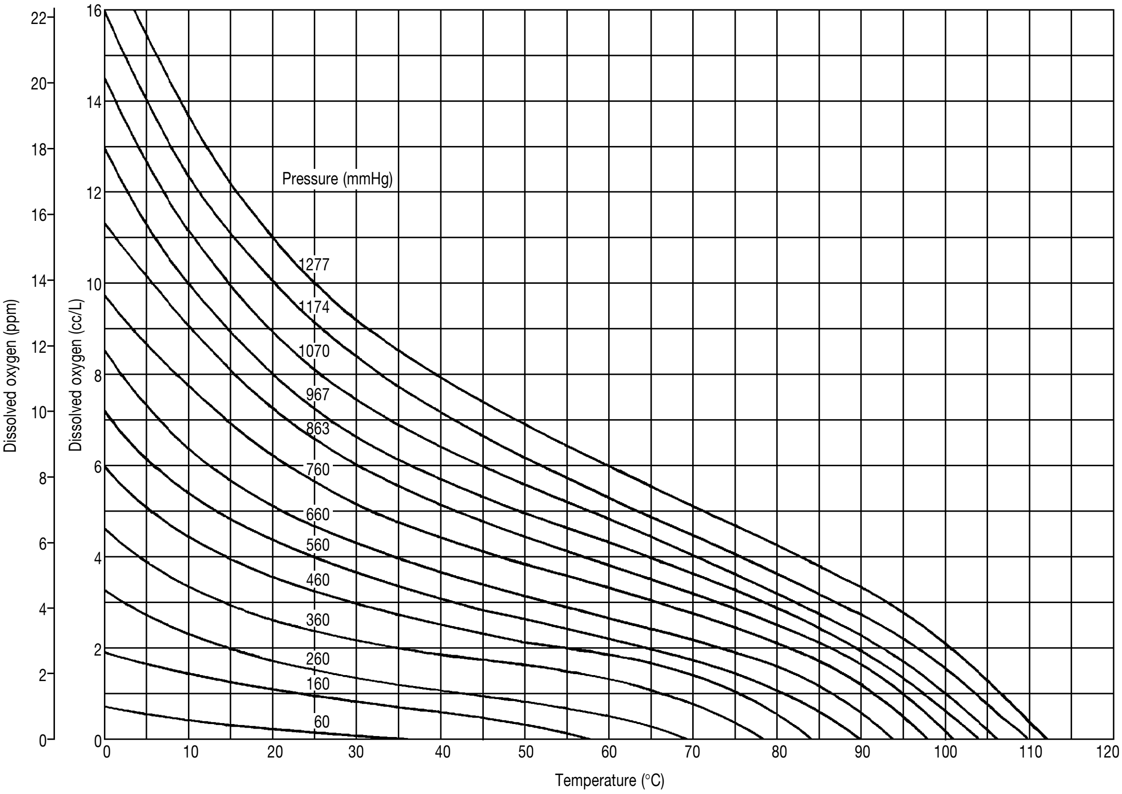
A8 Solubilities of gasses in water

Temp. (°C)	Air		N_2 (containing 1.2% Ar)		O_2		H_2	
	N_2 (m*l*/m*l*) (x 10^3)	O_2 (m*l*/m*l*) (x 10^3)	(m*l*/m*l*) (x 10^3)	(g/100 g) (x 10^3)	(m*l*/m*l*) (x 10^3)	(g/100 g) (x 10^3)	(m*l*/m*l*) (x 10^3)	(g/100 g) (x 10^3)
0	18.4	10.2	23.5	2.94	48.9	6.95	21.4	0.193
5	16.3	8.9	20.9	2.60	42.9	6.07	20.4	0.184
10	14.5	7.9	18.6	2.31	38.0	5.37	19.5	0.176
15	13.1	7.0	16.9	2.09	34.2	4.80	18.8	0.169
20	11.9	6.4	15.5	1.90	31.0	4.34	18.2	0.162
25	11.0	5.7	14.3	1.75	28.3	3.93	17.5	0.156
30	10.3	5.1	13.4	1.62	26.1	3.59	17.0	0.147
35	—	—	12.6	1.50	24.4	3.32	16.7	0.143
40	8.7	4.5	11.8	1.39	23.1	3.08	16.4	0.139
45	—	—	11.3	1.30	21.9	2.86	16.2	0.134
50	7.5	3.9	10.9	1.22	20.9	2.66	16.1	0.129
60	6.5	3.3	10.2	1.05	19.5	2.27	16.0	0.119
70	—	—	9.8	0.85	18.3	1.86	16.0	0.102
80	4.0	2.0	9.6	0.66	17.6	1.38	16.0	0.079
90	—	—	9.5	0.38	17.2	0.79	16.0	0.046
100	0.0	0.0	9.5	0.00	17.0	0.00	16.0	0.000

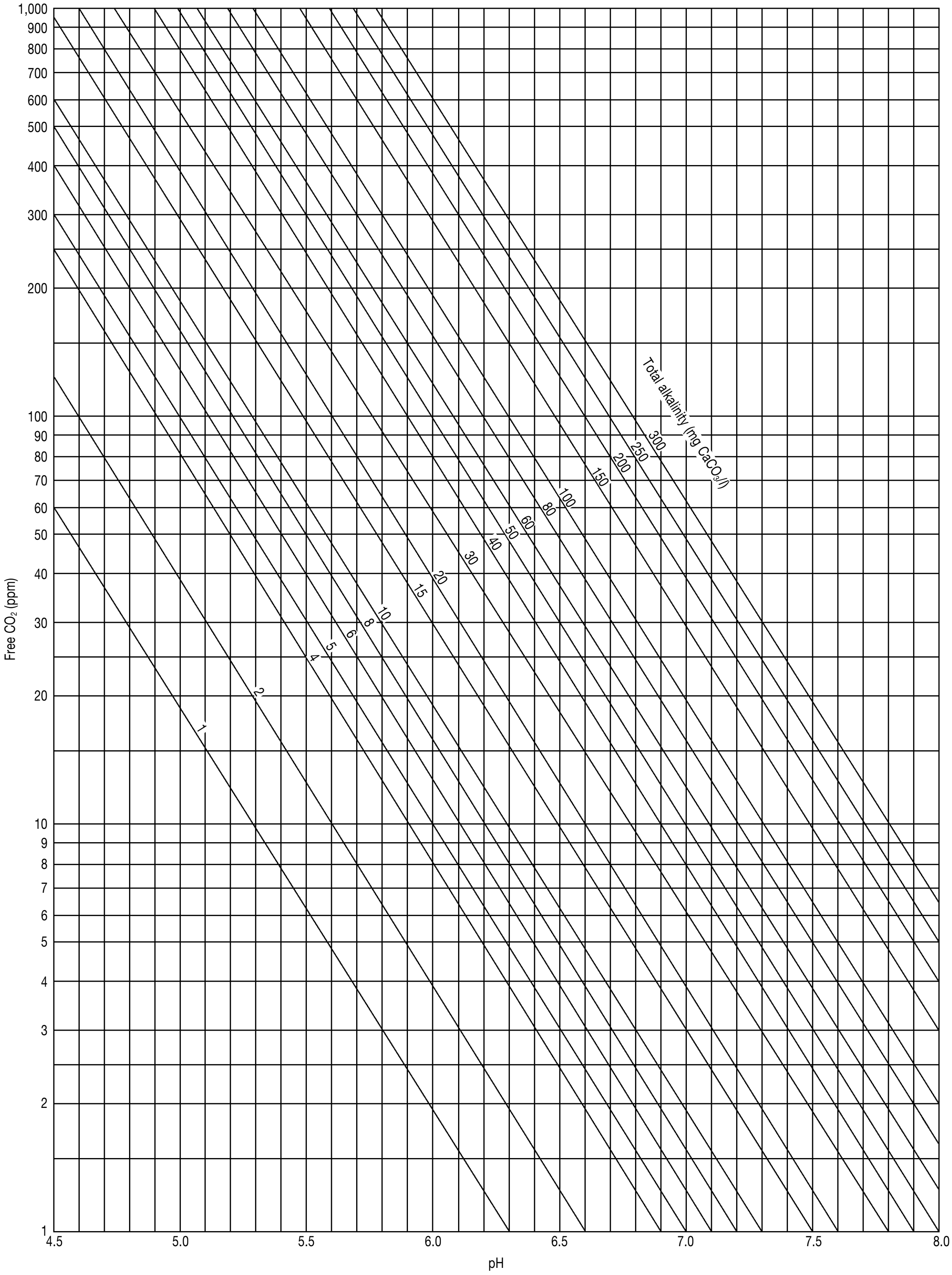
Temp. (°C)	H_2S		HCl		NH_3		Cl_2	O_3
	(m*l*/m*l*)	(g/100 g) (x 10^3)	(m*l*/m*l*)	(g/100 g)	(g/100 g)	(m*l*/g)	(g/100 g) (x 10^3)	(g/100 g) (x 10^3)
0	4.621	699	517	82.3	87.5	1,299	1,460	3.94
5	3.935	593	—	79.7	77.5	1,019	—	3.43
10	3.362	505	474	76.3	67.9	910	997	2.99
15	2.913	436	—	74.9	60.0	802	850	2.59
20	2.554	380	442	71.9	52.6	710	729	—
25	2.257	334	—	—	46.0	635	641	1.39
30	2.014	295	412	67.3	40.3	—	572	0.77
35	1.811	262	—	—	35.5	—	510	—
40	1.642	233	386	63.3	30.7	—	459	0.42
45	1.499	209	—	—	27.0	—	423	—
50	1.376	186	362	59.6	22.9	—	393	0.06
60	1.176	146	339	56.1	—	—	330	0
70	1.010	109	—	—	—	—	279	—
80	0.906	76	—	—	—	—	223	—
90	0.835	41	—	—	—	—	127	—
100	0.800	0	—	—	—	—	0	—

Temp. (°C)	CO		CO_2		N_2O	NO	SO_2	
	(m*l*/m*l*) (x 10^3)	(g/100 g) (x 10^3)	(m*l*/m*l*)	(g/100 g) (x 10^3)	(m*l*/m*l*)	(m*l*/m*l*) (x 10^3)	(m*l*/m*l*)	(g/100 g)
0	35.4	4.40	1.713	334.6	—	73.8	79.789	22.83
5	31.5	3.90	1.424	277.4	1.1403	64.6	67.485	19.31
10	28.2	3.48	1.194	231.8	0.9479	57.1	56.647	16.21
15	25.4	3.13	1.019	197.0	0.7896	51.5	47.276	13.54
20	23.2	2.84	0.878	168.8	0.6654	47.1	39.374	11.28
25	21.4	2.60	0.759	144.9	0.5752	43.0	32.786	9.41
30	20.0	2.41	0.665	125.7	—	40.0	27.161	7.80
35	18.8	2.23	0.592	110.5	—	37.3	22.489	6.47
40	17.8	2.08	0.530	97.3	—	35.1	18.766	5.41
45	16.9	1.93	0.479	86.0	—	33.1	—	—
50	16.2	1.80	0.436	76.1	—	31.5	—	—
60	14.9	1.52	0.365	57.6	—	29.5	—	—
70	14.4	1.28	0.319	—	—	28.1	—	—
80	14.3	0.98	—	—	—	27.0	—	—
90	14.2	0.57	—	—	—	26.5	—	—
100	14.1	0.00	—	—	—	26.3	—	—

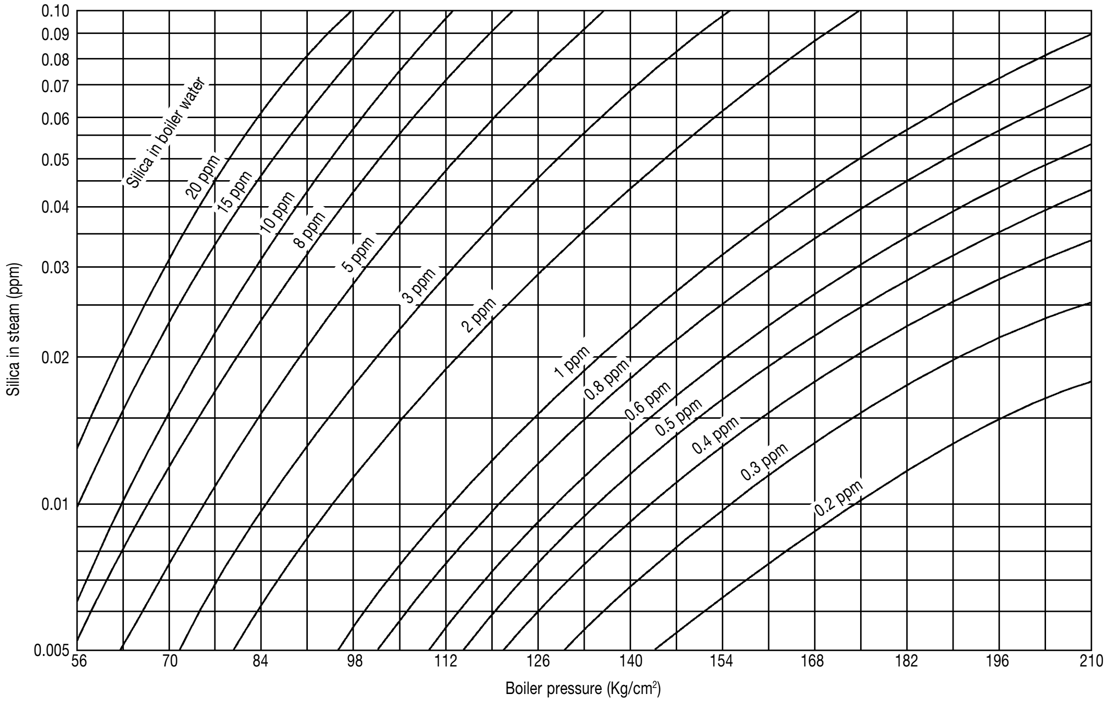
A9 Solubility of oxygen in pure water



A10 Relationship among the pH, free CO_2 and alkalinity of water



A11 Relationship between silica concentrations in boiler water and in steam under various boiler pressures



A12 Specific gravity of sodium chloride solution

NaCl (%)	Specific gravity (15/4°C)
1	1.0071
2	1.0144
3	1.0218
4	1.0292
5	1.0366
6	1.0441
8	1.0591
10	1.0742
20	1.1525

A13 Specific gravity of sodium hydroxide solution

NaOH (%)	Specific gravity (15/4°C)
1	1.0106
2	1.0219
4	1.0444
6	1.0666
8	1.0889
10	1.1111
22	1.2440
40	1.4333
45	1.4822

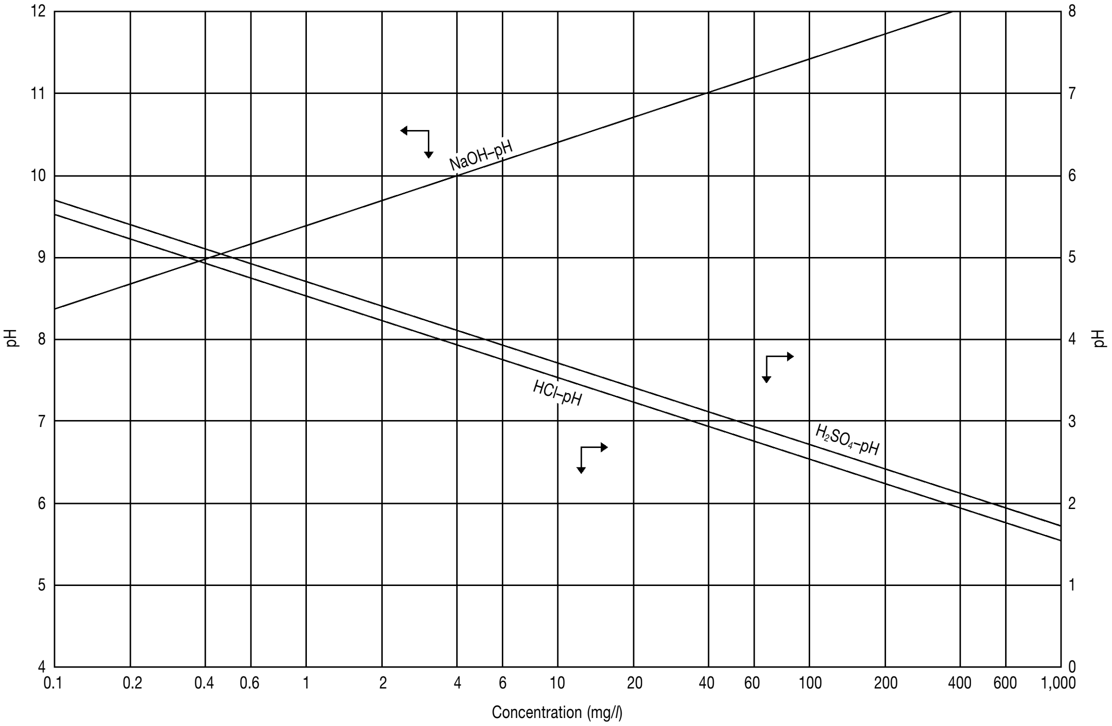
A14 Specific gravity of hydrochloric acid solution

HCl (%)	Specific gravity (15/4°C)
1	1.0043
2	1.0093
4	1.0194
6	1.0293
8	1.0392
10	1.0492
35	1.1780
40	1.1990

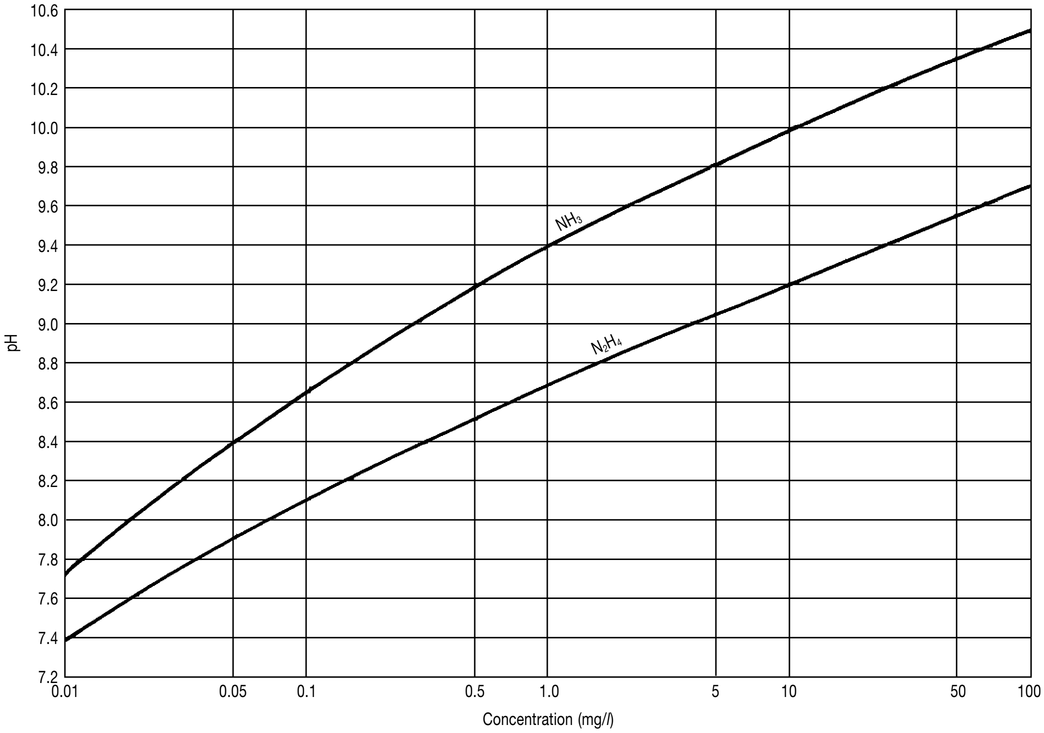
A15 Specific gravity of sulfuric acid solution

H_2SO_4 (%)	Specific gravity (15/4°C)
1	1.0054
2	1.0102
3	1.0198
4	1.0266
5	1.0334
6	1.0403
8	1.0545
10	1.0687
20	1.1430
30	1.2213
50	1.3989
70	1.6150
90	1.8198
96	1.8406
98	1.8411

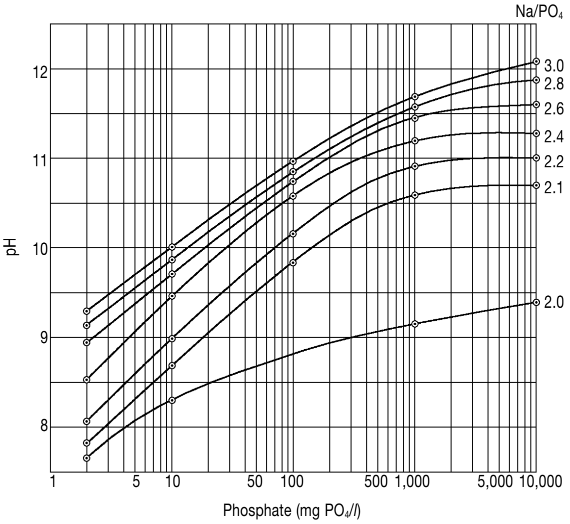
A16 Relationship between the pH and concentration of HCl, H_2SO_4 or NaOH solution



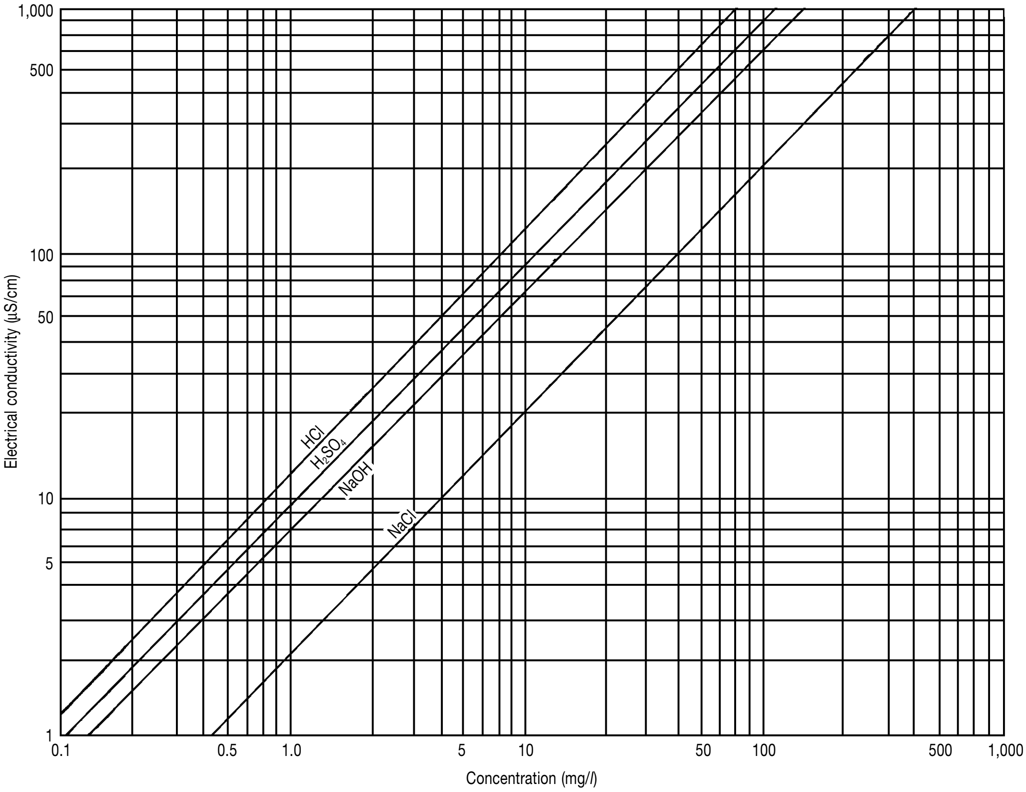
A17 Relationship between the pH and concentration of ammonia or hydrazine solution



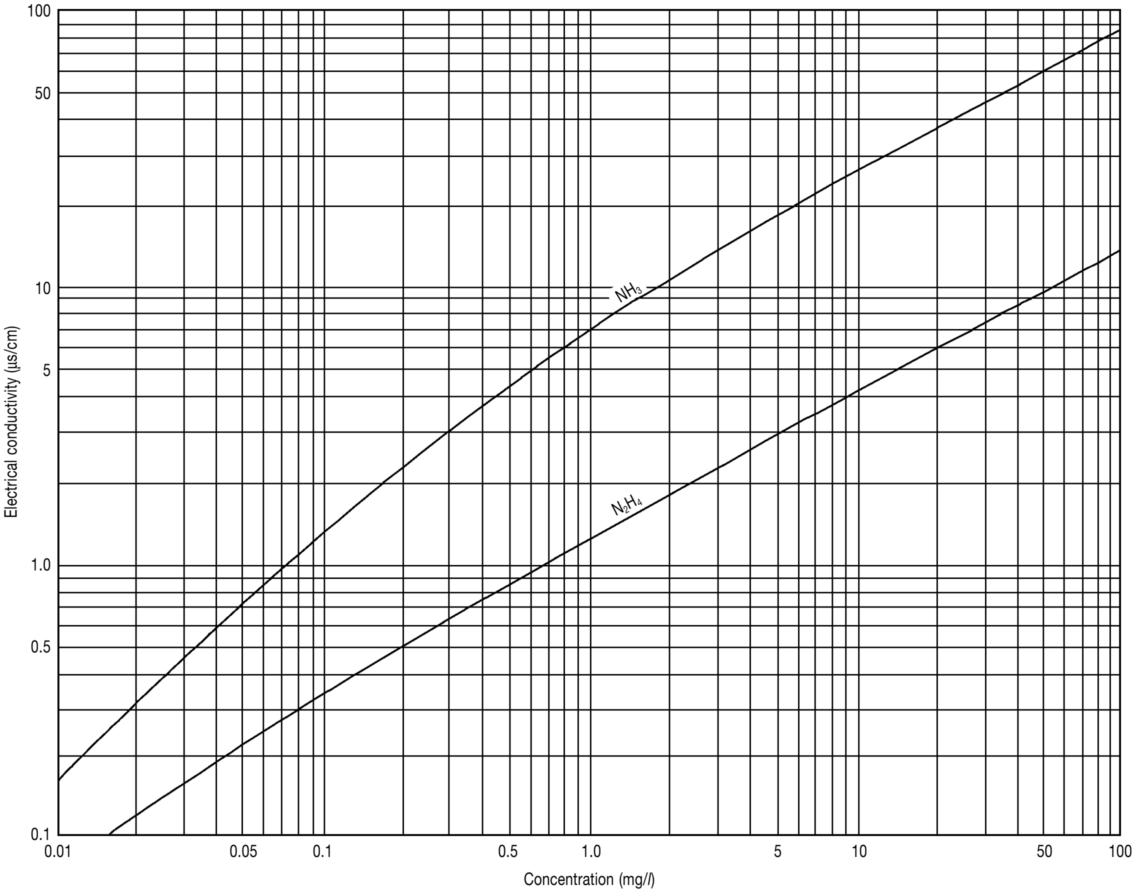
A18 Relationship among the pH, concentration and Na/PO_4 ratio of sodium phosphate solution



A19 Relationship between the electrical conductivity and concentration of HCl, H_2SO_4, NaOH or NaCl solution



A20 Relationship between the electrical conductivity and concentration of ammonia or hydrazine solution

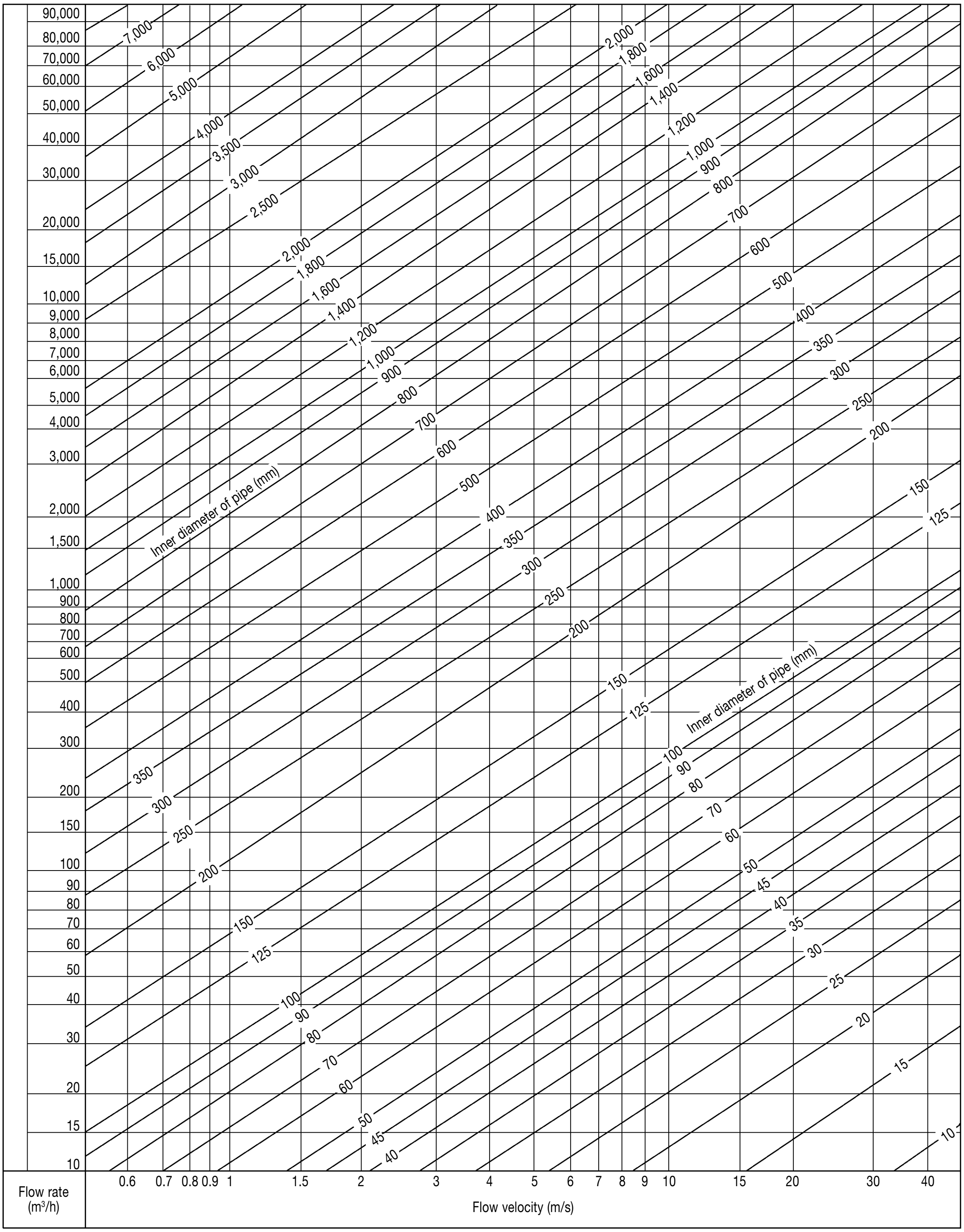


A21 Freezing points of organic brines

Brine Concentration (%)	Ethylalcohol	Glycerine	Ethyleneglycol
10	- 4.3	- 1.6	—
20	- 10.0	- 4.8	- 8
40	- 29.5	- 15.4	- 24
60	- 44.0	- 34.7	- 47
80	- 58	- 20.7	- 43
100	- 117	+ 17.0	- 15

(°C)

A22 Nomogram for converting flow rate into flow velocity (flow velocity into flow rate) in piping



A23 Properties of pure metals

Symbol of element	Density (20°C) (kg/l)	Melting point (°C)	Specific heat (20°C) (kcal/kg·°C)	Coeff. of linear expansion (20–40°C) (x 10^{-6})	Thermal conductivity (20°C) (kcal/m·h·°C)	Electric resistance (20°C) (μΩ/cm)
Ag	10.49	960.5 ± 0.0	0.056 (0°C)	19.7	360	1.59
Al	2.699	660.2 ± 1.0	0.215	23.9	190.8	2.655
Au	19.32	1,063.0 ± 0.0	0.031	14.2	255.6	2.19 (0°C)
C	2.22	3,700 ± 100	0.165	0.6–4.3	20.5	1,375 (0°C)
Ca	1.55	850 ± 20	0.149	22	108.0	3.43 (0°C)
Nb	8.57	2,415 ± 15	0.065 (0°C)	7.1	—	13.1 (18°C)
Co	8.9	1,495 ± 1	0.099	12.3	59.4	6.24
Cr	7.19	1,890 ± 10	0.11	6.5–8.5	57.6	14.1 (28°C)
Cu	8.96	1,083.0 ± 0.1	0.092	16.5	338.4	1.673
Fe	7.87	1,539 ± 3	0.11	11.7	64.8	9.71
Ga	5.91	29.78 ± 0.02	0.079	18	—	53.4 (0°C)
Hg	13.55	38.87 ± 0.02	0.033	—	7.2	94.1 (0°C)
In	7.31	156.4 ± 0.1	0.057	33	20.5	8.37 (0°C)
Ir	22.5	2,454 ± 3	0.031	6.8	50.4	5.3
Li	0.53	186 ± 5	0.79	56	61.2	8.55 (0°C)
Mg	1.74	650 ± 2	0.25	26	136.8	4.46
Mn	7.43	1,245 ± 10	0.115	22	—	185
Mo	10.2	2,625 ± 50	0.061	4.9	126.0	5.17 (0°C)
Na	0.97	97.7 ± 0.2	0.295	71	115.2	4.2 (0°C)
Ni	8.90	1,455 ± 1	0.105	13.3	79.2	6.84
Pb	11.34	327.4 ± 0.1	0.031	29.3	29.9	20.65
Pd	12.0	155.4 ± 1	0.058 (0°C)	11.8	61.2	10.8
Pt	21.45	1,773.5 ± 1	0.032	8.9	61.2	9.83 (0°C)
Se	4.81	220 ± 5	0.084	37	—	—
Si	2.33	1,430 ± 20	0.162 (0°C)	2.8–7.3	72.0	10.5 (0°C)
Sn	7.298	231.9 ± 0.1	0.054	23	57.6	11.5
Ti	4.507	1,670 ± 20	0.126	8.2	—	54.98
U	18.7	1,180	0.028	—	23.0	60 (18°C)
V	6.0	1,735 ± 50	0.120	7.8	—	26
W	19.3	3,410 ± 20	0.032	4.3	172.8	5.5
Zn	7.133	419.46	0.0915	39.7	97.2	5.916

A24 Properties of alloys

Alloy	Chemical composition (%)	Specific gravity	Melting point (°C)	Thermal conductivity (20°C) (kcal/m·h·°C)	Coefficient of thermal expansion (20°C) (x 10^{-6})	Specific heat (20°C) (kcal/kg·°C)
Mild steel	C 0.12–0.20	7.855–7.863	1,470–1,490	43–52	11.16–11.28	0.1136–0.1146
Semi-hard steel	C 0.30–0.45	7.836–7.854	1,420–1,450	36.5–43.5	10.73–10.92	0.1158–0.1168
High-carbon steel	C 0.8–1.6	7.810–7.833	1,335–1,540	32–37	9.58–10.87	0.1210–0.1240
Silicon steel	C < 0.08, Si 0.8–4.3, Mn < 0.35	7.8–7.6	1,430–1,530	0.5–1.2 (vertical) 0.013–0.014 (horizontal)	12–15	—
Ni-Cr steel	C 0.25–0.55, Ni 1.0–5.0, Cr 0.03–2.0	7.8	1,450–1,510	29–38	13.3 (20–400°C)	—
Ni steel	C 0.08–0.25, Ni 1.5–5.0	7.87 (Ni 3%)	—	36–38 (Ni 1.07–1.93)	10.354	0.1162–0.1170 (Ni 1.07–1.93)
Cr-Mo steel	C 0.35, Cr 0.9, Mo 0.2, C < 0.2, Mn < 0.5	7.85	—	36.7	17.2	0.122
13% Cr stainless steel	Cr 11–15, Ni < 1.0, C < 0.08, Si < 1.0	7.60–7.75	1,510–1,532	21.5 (200°C)	11.0	0.11
18-8 stainless steel	Ni 8–11, Cr 17–19	7.91	1,400–1,420	14	17.1	0.12
Gray cast iron	C 2.8–3.8	7.05–7.30	1,145–1,275	27–48	9.2–11.8	0.1285–0.1350
Ni-Cr-Fe alloy	Ni 76, Cr 15.5, Fe 7	8.51	1,390–1,430	—	11.5 (38–93°C)	0.109
9-1 brass	Cu 90, Zn 10	8.8	1,045	—	18.2 (25–300°C)	0.09
7-3 brass	Cu 69–72, Zn 28–31	8.54	950	96	19	0.09
Gun metal	Cu 88, Sn 10, An 2	8.7	—	41	18.3	—
Al bronze	Al 9–10, Mn < 0.6, Fe < 0.25 remaining Cu	7.6	1,040	—	17	0.104
70-30 cupro-nickel	Cu 70, Ni 30	8.94	1,170–1,240	—	16.2	0.09
German silver	Cu 60–65, Ni 12–22, Zn 18–23	8.3–8.7	950–1,180	215–360	18–21	0.095–0.106
Phosphorus bronze	Sn < 10, P < 0.5, remaining Cu	8.90–8.95	—	68	16.8	—
White metal	Sn 80–90, Sb 4–10, Cu 2–7	7.38	240–355	—	20	—

A25 Chemical resistant materials for tank, pump and piping

Chemical	Pipe	Valve	Tank	Pump (compressor)	Strainer
HCl	Hard rubber, glass, rubber-lining steel, tile	—	Rubber-lining steel, pitch or asphalt-coating steel	Rubber lining steel	Rubber-lining steel
HF	Lead, rubber-lining steel, bakelite	—	Lead	Lead, rubber-lining steel	—
Conc. H_2SO_4	Cast iron, steel, wrought iron	—	Steel	Iron, steel, 14% Si-iron, 18-8 Ni-Cr-steel	—
HNO_3	14% Si-iron, Cr-steel	—	Aluminum, glass	Si-iron, Cr-steel	—
H_3PO_4	Lead, rubber-lining steel	—	Lead-lining steel, Ni-Cr-steel, rubber-lining steel	—	—
Cl_2 (dry)	Steel, Si-iron, rubber-lining steel	Monel metal, steel	Iron, steel	Cast iron, steel (compressor)	—
Cl_2 (wet)	Lead-lining steel, ceramics	Stellite	—	—	—
NH_3 (dry)	Wrought iron, steel, Cr-steel	Monel metal	—	Monel metal (compressor)	—
H_2 (cold)	Carbon steel, Cr-steel, Cr-Mo-steel	Carbon steel	Ni-steel	Cr-V steel (compressor)	—
O_2 (cold)	Wrought iron	Bronze	Steel	Iron, steel (compressor)	—
NH_4OH	Iron, steel, nickel	—	Steel, cast iron, lead	Monel metal	—
Coal	Wrought iron, steel	Cast iron	Iron, steel	Cast iron	—
NaOH	Iron, steel, nickel, monel metal, Al-bronze	Cast iron	—	Iron, steel, Ni, monel metal, Al-bronze	Iron
$Al_2(SO_4)_3$	Lead-lining steel, rubber-lining steel	—	—	Iron, Ni-iron, steel	Cast iron
NH_4Cl	Cast iron, steel, wrought iron, rubber-lining steel	—	Rubber-lining steel	Iron, Ni-iron, steel	Iron
Na_2SO_3	Ni-Cr-steel, lead, rubber-lining steel	—	Lead, rubber-lining steel	Rubber-lining steel, zinc	Lead
Na_2CO_3	Steel	—	Iron, steel	Iron, steel, 18-8 Ni-Cr-steel	Iron, steel
NaCl	Cast iron, copper, monel metal	—	Steel, cement, enamel	Cast iron, steel, monel metal	—
Na_3PO_4	Iron, steel, lead	—	Steel, iron	Iron, Si-iron	Iron
Na_2SO_4	Steel, lead, Cr-Ni-steel	—	Steel, lead, Cr-Ni-steel	Iron, bronze	Cast iron

A26 Chemical resistant lining materials

Material / Temp. (°C) / Chemical	Ebonite		Soft rubber		Neoprene rubber		Hard PVC		Soft PVC		Saran		Polyethylene		Fiber reinforced polyester		Epoxy resin		Fluorocarbon resin	
	24	66	24	66	24	71	24	71	24	66	25	66	24	52	24	93	24	93	24	121
37% HCl	E	E	E	E	N	N	E	E	E	N	E	E	E	E	E	G	E	E	E	E
50% H_2SO_4	E	E	E	E	E	F	E	E	E	F	E	E	E	E	E	G	E	E	E	E
70% H_2SO_4	F	N	F	N	N	N	E	E	N	N	E	E	E	F	G	P	F	N	E	E
93% H_2SO_4	N	N	N	N	N	N	E	F	N	N	P	N	F	N	F	N	N	N	E	E
85% H_3PO_4	E	E	E	E	E	F	E	E	E	E	E	E	E	E	E	G	E	E	E	E
28% NH_4OH	E	F	G	F	E	E	E	E	G	G	N	N	E	E	G	F	E	E	E	E
25% NaOH	E	E	E	E	E	E	E	E	G	F	F	N	E	E	N	N	E	E	E	E
10% $FeCl_3$ or $Fe_2(SO_4)_3$	E	E	E	E	F	N	E	E	E	E	E	E	E	E	E	E	E	E	E	E
10% Na_2CO_3	E	E	E	E	E	E	E	E	E	G	E	E	E	E	E	E	E	E	E	E
10% Na_3PO_4	E	E	E	E	E	E	E	E	G	F	E	E	E	E	G	F	E	E	E	E
10% $CaCl_2$, $MgCl_2$, KCl or NaCl	E	E	E	E	E	E	E	E	E	E	E	E	E	E	E	E	E	E	E	E
10% $Ca(NO_3)_2$, $Mg(NO_3)_2$, KNO_3 or $NaNO_3$	E	E	E	E	E	E	E	E	E	E	E	E	E	E	E	E	E	E	E	E
10% $MgSO_4$, K_2SO_4 or Na_2SO_4	E	E	E	E	E	E	E	E	E	E	E	E	E	E	E	E	E	E	E	E
Wet Cl_2	G	F	F	N	N	N	E	G	F	F	E	E	N	N	F	N	P	N	E	E
Dry Cl_2	F	N	N	N	N	N	E	E	G	F	E	E	P	N	G	F	F	N	E	E
Gasoline	G	N	N	N	G	F	—	—	E	F	E	E	P	—	—	—	E	G	E	E

E: Excellent, G: Good, F: Fairly good, P: Partly applicable, N: Not applicable

A27 Comparison of Japanese Industrial Standards (JIS) with foreign standards for steel products

A27.1 Steel bars, sections and plates

JIS			Foreign standards
No. of JIS	Name of standard	Symbol of material	
G3101	Rolled steel for general structure	SS 330, 400, 490, 540	ASTM A36-89b ASTM A283-88
G3103	Carbon steel and molybdenum alloy steel plates for boilers and other pressure vessels	SB 410, 450, 480, 450M, 480M	ASTM A204-88 ASTM A285-82
G3119	Manganese-molybdenum and manganese-molybdenum-nickel alloy steel plates for boilers and other pressure vessels	SBV 1A, 1B, 2, 3	ASTM A302-82 ASTM A533-87
G4109	Chromium-molybdenum alloy steel plates for boilers and pressure vessels	SCMV 1, 2, 3, 4, 5, 6	ASTM A387-89 BS 1501/2-88 DIN 17155-83 NF A36-206-83 ISO 2604/4-75

A27.2 Steel pipes and tubes (1)

JIS			Foreign standards
No. of JIS	Name of standard	Symbol of material	
G3452	Carbon steel pipes for ordinary piping	SGP	ASTM A53-89a API 5L BS 1387-85 DIN 1615-84 DIN 2440-78 DIN 2441-78 ISO 68-51 ISO 559
G3454	Carbon steel pipes for pressure service	STPG 370, 410	ASTM A135-89a ASTM A53-89a API PL BS 3601-87 BS 3602(1)-87 DIN 1625-84 DIN 1629-84 DIN 2448-81 DIN 2442-63 ISO 2604(II)-75 ISO 2604(III)-75 ISO 9329(I)-89 ISO 9330(I)-90
G3455	Carbon steel pipes for high pressure service	STS 370, 410, 480	BS 778-66 DIN 1628-84 DIN 1630-84 ISO 2604(II)-75 ISO 9329(I)-89
G3456	Carbon steel pipes for high temperature service	STPT 370, 410, 480	ASTM A160-89a DIN 17175-79 DIN 17177-79 BS 3602(I)-87 ISO 2604(II)-75 ISO 2604(III)-75 ISO 9329(I)-89 ISO 9330(I)-90

A27.2 Steel pipes and tubes (2)

JIS			Foreign standards
No. of JIS	Name of standard	Symbol of material	
G3461	Carbon steel boiler and heat exchanger tubes	STB 340, 410, 510	ASTM A178/A178M-89 ASTM A179/A179M-88a ASTM A192/A192M-88 ASTM A210/A210M-88 ASTM A214/A214M-88 ASTM A226/A226M-88 BS 3059(1)-87, (2)-78 BS 3606-78 DIN 17175-79 DIN 17177-79 ISO 2604(II)-75 ISO 2604(III)-75
G3462	Alloy steel boiler and heat exchanger tubes	STBA 12, 13, 20, 22, 23, 24, 25, 26	ASTM A199/A199M-89 ASTM A209/A209M-88 ASTM A213/A213M-89a ASTM A250/A250M-89a ASTM A423/A423M-89 BS 3059(2)-78 BS 3606-78 DIN 17175-79 DIN 17177-79 ISO 2604(II)-75 ISO 2604(III)-75
G3463	Stainless steel boiler and heat exchanger tubes	SUS 410TB, 430TB, 304HTB, 304LTB, 304TB, 321TB, 321HTB, 316TB, 316HTB, 316LTB, 309STB, 310STB, 347TB, 347HTB, 329J1TB, 309TB, 310TB, 317TB, 317LTB, XM15J1TB, 329J2LTB, 405TB, 409TB, 410TiTB, 444TB, XM8TB, XM27TB	ASTM A213/A213M-88a ASTM A249/A249M-88b ASTM A268/A268M-88b ASTM A269-88a ASTM A789/A789M-89a BS 3059(2)-78 BS 3606-78 DIN 17455-85 DIN 17456-85 DIN 17457-85 DIN 17458-85 ISO 2604(II)-75 ISO 2604(III)-75 ISO 2604(V)-75

A28 Densities of various metals and the conversion factors of corrosion rates

Kind of metal	Density (g/cm^3)	Conversion factors of corrosion rate	
		mdd[*1] → mpy[*2]	mdd → mm/y
Aluminum	2.72	0.528	0.0135
Admiral brass	8.54	0.168	0.00427
Carbon steel	7.87	0.183	0.00464
Cast iron	7.20	0.200	0.00508
Copper	8.95	0.161	0.00408
Cupro-nickel	8.94	0.161	0.00408
Stainless steel (SUS304)	7.93	0.181	0.00460
Titanium	4.54	0.317	0.00804
Zinc	7.14	0.201	0.00511

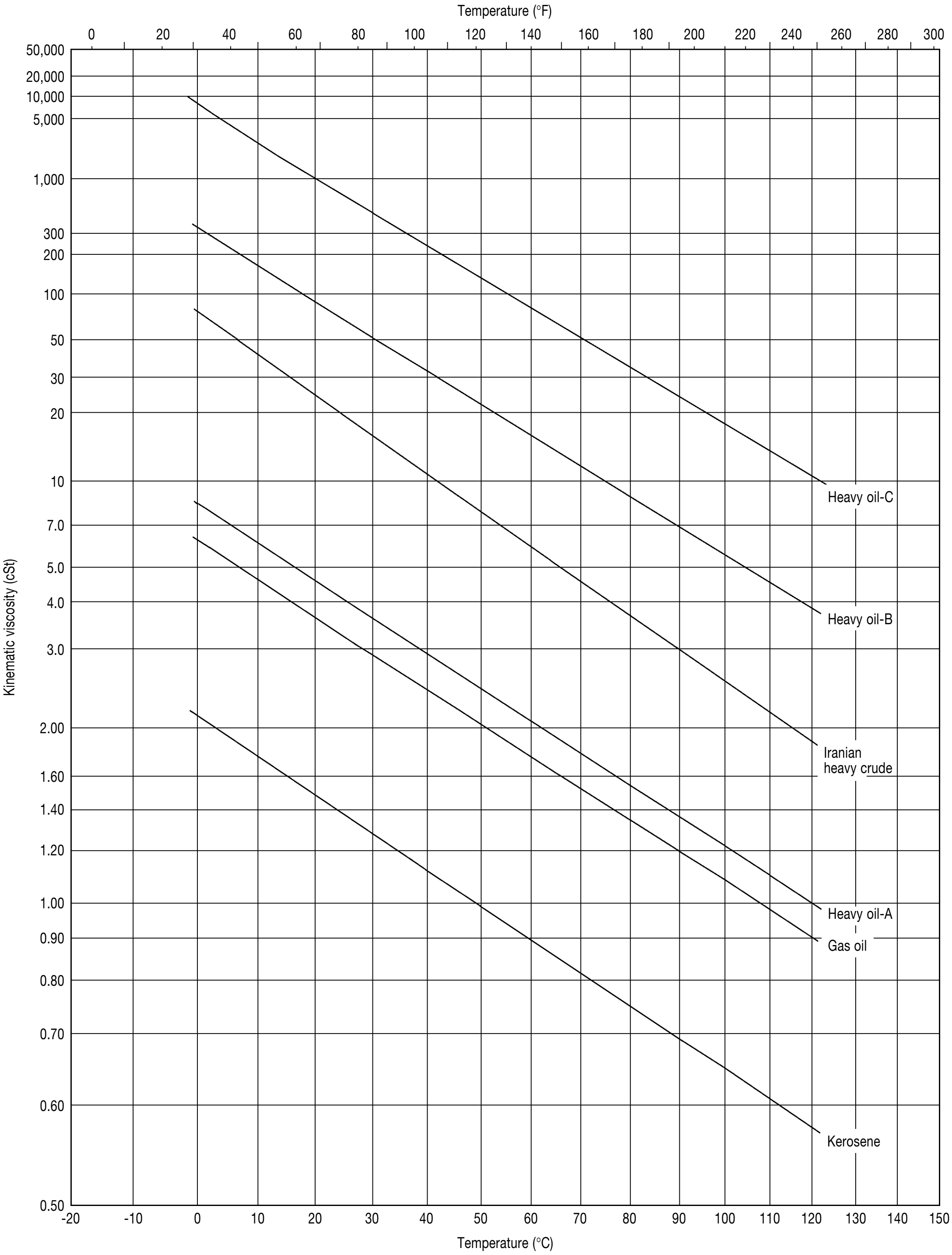
[*1] mdd: mg/dm^2·day

[*2] mpy: mil/y

A29 Compositions and calorific values of various fuels

Kind of fuel	Composition (%)							Calorific value (kcal/kg)	
	C	H	O	S	N	Ash	Moisture	High	Low
Carbon	100.0	—	—	—	—	—	—	8,100	8,100
Coke	75.7	0.4	0.0	1.0	0.0	19.0	3.9	6,250	6,200
Anthracite	79.6	1.5	1.3	0.4	0.4	13.3	3.5	6,920	6,810
Bituminous coal	62.3	4.7	11.6	2.2	1.3	16.8	0.9	6,190	5,930
Brown coal	52.8	4.8	14.6	0.6	0.9	8.6	17.7	5,240	4,890
Lignite	47.7	3.7	19.9	0.5	0.7	8.8	18.7	4,470	4,160
Minus crude	86.6	13.2	—	0.1	—	0.0	0.1	11,040	10,380
Iranian heavy crude	85.6	12.7	—	1.6	—	0.0	0.1	10,790	10,140
Khafji crude	84.8	12.3	—	2.9	—	0.0	0.0	10,650	10,040
Light naphtha	84.3	15.7	—	0.0	—	0.0	0.0	11,320	10,570
Naphtha	84.6	15.4	—	0.0	—	0.0	0.0	11,270	10,520
Kerosene	86.0	14.0	—	0.0	—	0.0	0.0	11,150	10,390
Gas oil	85.8	13.7	—	0.5	—	0.0	0.0	10,990	10,300
Heavy oil - A	86.2	13.2	—	0.6	—	0.0	0.0	10,890	10,200
Heavy oil - B	89.8	11.9	—	2.2	—	0.0	0.1	10,550	9,940
Heavy oil - C	86.7	12.0	—	1.3	—	0.0	0.1	10,650	10,040

A30 Relationship between the temperatures and viscosities of various fuel oils



A31 Compositions and calorific values of various fuel gasses

Fuel gas	Composition (%)										Calorific value (kcal/Nm^3)	
	H_2	CH_4	C_2H_6	C_3H_8	C_4H_{10}	C_5C_{12}	CO_2	CO	O_2	N_2	High	Low
Natural gas (Brunei)	—	88.2	5.0	4.9	1.8	0.1	0	—	—	0	10,950	9,920
Natural gas (Niigata)	—	96.4	2.4	0.4	0.3	0.1	0.4	—	—	—	9,780	8,820
Natural gas (Texas)	—	71.5	7.0	4.4	1.0	0	—	—	—	15.5	9,310	8,440
Blast furnace gas	2.7	—	—	—	—	—	19.3	23.3	—	54.7	790	770
Coke oven gas	55.2	28.1	3.1				2.7	8.0	0.3	2.6	5,100	4,500
Coal gas	51.8	30.8	3.2				2.5	10.3	0.4	1.0	5,300	4,730
Producer gas	12.1	3.6	0.4				4.8	25.5	0.2	53.4	1,550	1,450
Domestic liquid petroleum gas	—	—	2.0	87.2	10.8	—	—	—	—	—	11,920	10,980
Industrial liquid petroleum gas	—	—	—	1.2	98.6	0.2	—	—	—	—	11,730	10,830

A32 Typical seawater analysis

Ion	Concentration (mg/*l*)
Cl^-	18,980
SO_4^{2-}	2,690
HCO_3^-	140
Br^-	65
BO_3^{3-}	26
SiO_3^{2-}	1.5
F^-	1.4
Na^+	10,560
Mg^{2+}	1,270
Ca^{2+}	400
K^+	380
Sr^{2+}	13

A33 Typical qualities of Japanese industrial waters

Location	Turbidity (degree)	pH	E. conductivity (μS/cm)	M-alkalinity (mg $CaCO_3/l$)	Ca-hardness (mg $CaCO_3/l$)	Chloride (mg Cl^-/l)	Sulfate (mg SO_4^{2-}/l)	Silica (mg SiO_2/l)	Total iron (mg Fe/l)
Sendai	1.8	6.6	149	28	24	13	22	16	0.19
Kashima	6.5	7.4	387	69	40	65	21	7	0.27
Chiba	3.3	6.8	284	74	61	22	24	21	0.27
Kawasaki	< 1.0	7.1	322	60	63	31	27	20	0.10
Yokkaichi	1.6	6.8	125	43	31	7	11	9	0.11
Chita	3.1	6.8	74	27	14	3	6	11	0.12
Senhoku	< 1.0	6.5	209	30	33	20	—	7	0.08
Niihama	3.1	7.0	85	31	24	3	9	6	0.15
Matsuyama	< 1.0	6.7	271	67	66	15	38	19	0.16
Mizushima	10.1	7.3	111	33	34	7	—	9	0.55
Iwakuni	—	6.9	57	14	11	5	5	1	< 0.05
Ube	2.1	7.3	187	60	44	12	13	6	0.16
Onoda	2.5	7.4	166	74	48	8	7	6	0.09
Kitakyushu	1.0	7.3	254	73	56	12	31	10	0.24
Oita	3.6	6.9	151	60	33	5	9	47	—

A34 Feedwater and boiler water quality standards

A34.1 Feedwater and boiler water qualities for cylindrical boilers (JIS B8223-1989)

Division	Maximum operating pressure	(MPa)	Below 1			Above 1 to 2
		(kgf/cm^2)	Below 10			Above 10 to 20
	Evaporation rate per heating surface area (kg/m^2·h)		Below 30*1	Above 30 to 60	Above 60	—
	Kind of feedwater		Fresh water	Softened water		
Feedwater	pH (25°C)		7–9	7–9	7–9	7–9
	Hardness (mg $CaCO_3$/*l*)		Below 60	Below 1	Below 1	Below 1
	Oils and fats (mg/*l*)*2		*3	*3	*3	*3
	Dissolved oxygen (mg O/*l*)		*3	*3	*3	*3
Boiler water	Treatment method		Alkaline phosphate treatment			
	pH (25°C)		11.0–11.8	11.0–11.8	11.0–11.8	11.0–11.8
	Acid consumption (pH 4.8) (mg $CaCO_3$/*l*)*4		100–800	100–800	100–800	Below 600
	Acid consumption (pH 8.3) (mg $CaCO_3$/*l*)*5		80–600	80–600	80–600	Below 500
	Total evaporation residue (mg/*l*)		Below 4,000	Below 3,000	Below 2,500	Below 2,300
	Electrical conductivity (μS/cm) (25°C)		Below 6,000	Below 4,500	Below 4,000	Below 3,500
	Chloride ion (mg Cl^-/*l*)		Below 600	Below 500	Below 400	Below 350
	Phosphate ion (mg PO_4^{3-}/*l*)*6		20–40	20–40	20–40	20–40
	Sulfite ion (mg SO_3^{2-}/*l*)*7		10–50	10–50	10–50	10–50
	Hydrazine (mg N_2H_4/*l*)*8		0.1–1.0	0.1–1.0	0.1–1.0	0.1–1.0

*1: Apply for cast iron boilers which the feedwater is continuously supplied because of continuous use of the raw steam.

*2: N-Hexane or carbon tetrachloride extractive matter (refer to JIS B8224)

*3: Keep possibly low.

*4: M-alkalinity

*5: P-alkalinity

*6: Apply when phosphates are used as boiler compounds.

*7: Apply when sulfite is used as an oxygen scavenger. Control the sulfite ion concentration in the range of 10 to 20 mg SO_3^{2-}/*l* when a deaerator is operated.

*8: Apply when hydrazine is added into feedwater as an oxygen scavenger. When a deaerator is operated, it is desirable to control the hydrazine concentration in the range of 0.1 to 0.5 mg N_2H_4/*l*.

A34.2 Feedwater and boiler water qualities for water tube boilers (JIS B8223-1989)

Division	Maximum operating pressure	(MPa)	Below 1		Above 1 to 2			Above 2 to 3		Above 3 to 5		Above 5 to 7.5			Above 7.5 to 10		Above 10 to 15		Above 15 to 20	
		(kgf/cm^2)	Below 10		Above 10 to 20			Above 20 to 30		Above 30 to 50		Above 50 to 75			Above 75 to 100		Above 100 to 150		Above 150 to 200	
	Evaporation rate per heating surface area ($kg/m^2 \cdot h$)		Below 50	Above 50	—	—		—		—		—			—		—		—	
	Kind of feedwater		Softened water		Softened water	Demineralized water		Demineralized water		Demineralized water		Demineralized water			Demineralized water		Demineralized water		Demineralized water	
Feedwater	pH (25°C)		7–9	7–9	7–9	8.0–9.5		8.0–9.5		8.0–9.5		8.5–9.5^{*9}			8.5–9.5^{*9}		8.5–9.6^{*9}		8.5–9.6^{*9}	
	Hardness (mg $CaCO_3/l$)		Below 1	Below 1	Below 1	0		0		0		0			0		0		0	
	Oils and fats (mg/l)^{*2}		^{*3}	^{*3}	^{*3}	^{*3}		^{*3}		^{*3}		^{*3}			^{*3}		^{*3}		^{*3}	
	Dissolved oxygen (mg O/l)		^{*3}	^{*3}	Below 0.5	Below 0.5		Below 0.1		Below 0.03		Below 0.007			Below 0.007		Below 0.007		Below 0.007	
	Iron (mg Fe/l)		—	Below 0.3	Below 0.3	Below 0.1		Below 0.1		Below 0.1		Below 0.05			Below 0.03^{*10}		Below 0.03^{*10}		Below 0.02^{*11}	
	Copper (mg Cu/l)		—	—	—	—		—		Below 0.05		Below 0.03			Below 0.02		Below 0.01		Below 0.005	
	Hydrazine (mg N_2H_4/l)		—	—	—	—		Above 0.2		Above 0.06		Above 0.01			Above 0.01		Above 0.01		Above 0.01	
	Electrical conductivity (μS/cm) (25°C)		—	—	—	—		—		—		—			—		Below 0.5^{*12}		Below 0.5^{*12}	
Boiler water	Treatment method		Alkaline phosphate treatment		Alkaline phosphate treatment	Alkaline phosphate treatment	Coordinated phosphate treatment	Alkaline phosphate treatment	Coordinated phosphate treatment	Alkaline phosphate treatment	Coordinated phosphate treatment	Alkaline phosphate treatment	Coordinated phosphate treatment	Volatile treatment	Coordinated phosphate treatment	Volatile treatment	Coordinated phosphate treatment	Volatile treatment	Coordinated phosphate treatment	Volatile treatment
	pH (25°C)		11.0–11.8	11.0–11.8	11.0–11.8	10.5–11.5	9.8–10.8	10.0–11.0	9.4–10.5	9.6–10.8	9.4–10.5	9.6–10.5	9.2–10.2^{*13}	8.5–9.5	9.0–10.0^{*13}	8.5–9.5	8.5–9.8	8.5–9.6	8.5–9.8	8.5–9.6
	Acid consumption (pH 4.8) (mg $CaCO_3/l$)^{*4}		100–800	100–800	Below 600	Below 250	Below 130	Below 150	Below 100	—	—	—	—	—	—	—	—	—	—	—
	Acid consumption (pH 8.3) (mg $CaCO_3/l$)^{*5}		80–600	80–600	Below 500	Below 200	Below 100	Below 120	Below 80	—	—	—	—	—	—	—	—	—	—	—
	Total evaporation residue (mg/l)		Below 3000	Below 2500	Below 2000	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
	Electrical conductivity (μS/cm) (25°C)		Below 4500	Below 4000	Below 3000	Below 1500	Below 1200	Below 1000	Below 800	Below 800	Below 600	Below 500	Below 400	Below 60^{*12}	Below 150	Below 60^{*12}	Below 60	Below 20^{*12}	Below 60	Below 20^{*12}
	Chloride ion (mg Cl^-/l)		Below 500	Below 400	Below 300	Below 150	Below 150	Below 100	Below 100	Below 80	Below 80	Below 50	Below 50	Below 2	Below 10	Below 2	Below 2	Below 1	Below 2	Below 1
	Phosphate ion (mg PO_4^{3-}/l)^{*6}		20–40	20–40	20–40	10–30	10–30	5–15	5–15	5–15	5–15	3–10	3–10^{*13}	^{*14}	2–6^{*13}	^{*14}	0.1–3	^{*14}	0.1–3	^{*14}
	Sulfite ion (mg SO_3^{2-}/l)		10–50^{*7}	10–50^{*7}	10–20	10–20	10–20	5–10	5–10	5–10	5–10	—	—	—	—	—	—	—	—	—
	Hydrazine (mg N_2H_4/l)^{*8}		0.1–1.0	0.1–1.0	0.1–0.5	0.1–0.5	0.1–0.5	—	—	—	—	—	—	—	—	—	—	—	—	—
	Silica (mg SiO_2/l)		—	—	—	Below 50	Below 50	Below 50	Below 50	Below 20	Below 20	Below 5^{*15}	Below 5^{*15}	Below 5^{*15}	Below 2^{*15}	Below 2^{*15}	Below 0.3^{*15}	Below 0.3^{*15}	Below 0.2^{*15}	Below 0.2^{*15}

* 9: It is recommended to keep the feedwater pH in the higher range in a system that the feedwater preheater is made of carbon steel.

*10: Keep below 0.02 mg Fe/l if possible.

*11: Keep below 0.01 mg Fe/l if possible.

*12: Analyze after treating a sample water by passing through a H-form strong acid cation exchange resin bed.

*13: In case of waste heat recovery boilers, it is recommended to keep the pH and phosphate ion concentration in the range of 9.0 to 10.5 and 2 to 20 mg PO_4^{3-}/l respectively.

*14: When boiler water is contaminated with calcium, magnesium and substances reducing pH, because of the leakage of seawater and so on from steam condensers, add a required concentration of phosphate for minimizing the bad influence of the contaminants as an emergency measure.

*15: Keep silica concentration in steam below 0.02 mg SiO_2/l.

A34.3 Feedwater qualities for once-through boilers (JIS B8223-1989)

Division	Maximum operating pressure (MPa) [kgf/cm^2]	Above 7.5 to 10 [Above 75 to 100]		Above 10 to 15 [Above 100 to 150]		Above 15 to 20 [Above 150 to 200]		Above 20 [Above 200]	
	Kind of treatment	Volatile	Oxygen	Volatile	Oxygen	Volatile	Oxygen	Volatile	Oxygen
Feedwater	pH (25° C)[*16]	8.5–9.6[*9]	6.5–9.0[*17]	8.5–9.6[*9]	6.5–9.0[*17]	8.5–9.6[*9]	6.5–9.0[*17]	8.5–9.6[*9]	6.5–9.0[*17]
	Electrical conductivity (μS/cm) (25° C)[*12]	Below 0.3	Below 0.2	Below 0.3	Below 0.2	Below 0.3	Below 0.2	Below 0.25	Below 0.2
	Dissolved oxygen (mg O/*l*)	Below 0.007	0.02–0.2[*18]	Below 0.007	0.02–0.2[*18]	Below 0.007	0.02–0.2[*18]	Below 0.007	0.02–0.2[*18]
	Iron (mg Fe/*l*)	Below 0.03[*10]	Below 0.02	Below 0.02	Below 0.01	Below 0.02[*11]	Below 0.01	Below 0.01	Below 0.01
	Copper (mg Cu/*l*)	Below 0.01	Below 0.01	Below 0.005	Below 0.01	Below 0.003	Below 0.005[*19]	Below 0.002	Below 0.002
	Hydrazine (mg N_2H_4/*l*)	Above 0.01	—	Above 0.01	—	Above 0.01	—	Above 0.01	—
	Silica (mg SiO_2/*l*)	Below 0.04[*20] Below 0.02[*21]	Below 0.02	Below 0.03[*20] Below 0.02[*21]	Below 0.02	Below 0.02	Below 0.02	Below 0.02	Below 0.02

*16: Use ammonia or volatile amines for the pH control of feedwater.

*17: It is recommended to keep the pH in the range of 8.0–8.5 for a system including copper and copper alloys.

*18: Select an appropriate minimum dissolved oxygen concentration among this range for minimizing the amount of corrosion product.

*19: Keep below 0.003 mg Cu/*l*, if possible.

*20: Apply for a boiler equipped with a mist separator.

*21: Apply for a boiler without mist separator.

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