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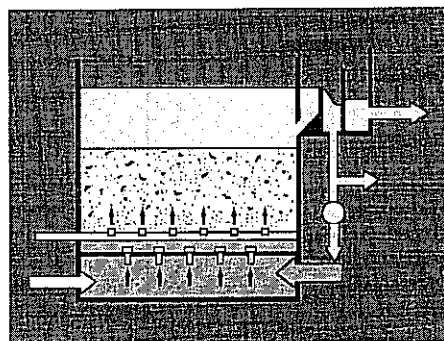
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INSTITUT FRANÇAIS DU PÉTROLE PUBLICATIONS

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INDUSTRIAL WATER TREATMENT

**Refining
Petrochemicals
and Gas Processing
Techniques**



GULF PUBLISHING COMPANY ÉDITIONS TECHNIP

Refining, Petrochemicals
and Gas Processing Techniques

**INDUSTRIAL
WATER
TREATMENT**

Foreword

This book is part of the teaching course material in the Post-Graduate Study Centre for Refining, Petrochemicals, Gas at the Ecole Nationale Supérieure du Pétrole et des Moteurs of the Institut Français du Pétrole.

It is a fact that the treatment of industrial waste water and cooling water has become an ever-present concern for managers in industry. This is particularly true for managers of oil refineries and petrochemical facilities.

Pollution control and constant efforts to curb consumption of increasingly scarce water are fundamental problems for industry. As a result, treatment facilities are getting as much care and attention as production plants.

This book provides an assessment of the sources of pollution and a summary of the latest techniques used in pollution control and cooling systems. It will remain a reference work for engineers in our industry.

M. Verwaerde

Table of contents

Foreword	V
Abbreviations and Acronyms	1

Chapter 1

Chemistry of natural water and industrial waste water

1.1 Mineral composition of water	3
1.1.1 Mineralization of water	3
1.1.2 Parameters specific to the chemistry of water	5
1.1.2.1 Hardness and M alkalinity	5
1.1.2.2 M alk and carbonic eq A) and alkaline ion content	7
1.1.2.4 Silica	7
1.1.2.5 CO ₂	8
1.1.3 Ion balances	8
1.1.4 Other useful parameters	10
1.2 Impurities in natural water	11
1.2.1 Suspended solids (SS)	11
1.2.2 Colloidal material	12
1.2.3 Dissolved organic matter (dissolved OM)	12
1.3 Characterizing open cooling system water	13
1.4 Characterizing oil industry waste water	14
1.4.1 General parameters in common with MWW (municipal waste water)	14
1.4.1.1 SS	14
1.4.1.2 Biochemical oxygen demand (BOD ₅)	15
1.4.1.3 Chemical oxygen demand (COD)	16
1.4.1.4 Nitrogen compounds	19
1.4.2 Parameters specific to the oil industry	20
1.4.2.1 Hydrocarbons (HC)	21
A. Solubility	21
B. COD and BOD ₅ equivalence for hydrocarbons	22

C.	Measuring HC	22
D.	Polyaromatic hydrocarbons (PAH)	28
E.	Chlorinated solvents	28
F.	Humic acids	29
1.4.2.2	Phenols	30
1.4.2.3	Sulfides and sulfur compounds	30
A.	Sulfides and mercaptans	32
B.	Thiosulfates and tetrathionates	32
C.	Analysis of sulfur compounds	33
1.4.2.4	M alk in waste water	34
1.4.2.5	Naphthenic acids	34
1.5	Interpreting water analyses	34
1.5.1	Industrial water	34
1.5.1.1	Sampling	34
1.5.1.2	Ion balance	35
1.5.1.3	Examples of analyses of natural water	35
1.5.2	Refinery waste water	35
1.5.2.1	Representative sampling	36
1.5.2.2	Preserving samples	36
1.5.2.3	Pollution assessments	37
1.6	Main reactions during chemical treatments	37
1.6.1	Precipitation reactions	37
1.6.1.1	Precipitation of Al and Fe metallic hydroxides	37
1.6.1.2	Precipitation of iron sulfide	38
1.6.1.3	Precipitation of M alk during bicarbonate removal from water by lime or caustic	38
1.6.2	Oxidation-reduction reactions (redox)	38
1.6.2.1	Examples of redox reactions in make up water treatment	39
1.6.2.2	Oxidation reactions specific to IWW	39
A.	Oxidation of sulfur compounds	42
B.	Choice of oxidizing agents	42

Chapter 2

Refinery effluents and primary treatment

2.1	Sources of WW in refining and steam cracking	43
2.1.1	Desalter water	44
2.1.2	Process condensates	45
2.1.2.1	Distillation condensates	45
2.1.2.2	Sour FCC and hydrocracking condensates	45
2.1.2.3	Production and composition of refinery process condensates	48
2.1.2.4	Product heating condensates	48
2.1.3	Particular process effluents	48
2.1.3.1	Bitumen blowing WW	48
2.1.3.2	Catalytic alkylation WW	48
2.1.3.3	Lube oil plant WW	48

2.1.4	Oily water	49
2.1.4.1	Normally oily water	50
2.1.4.2	Accidentally oily water	50
2.1.5	Nonoily waste water	51
2.1.6	Transportation waste water	51
2.1.6.1	Deballasting water	51
2.1.6.2	Tanker cleaning water	52
2.1.7	Spent caustic	52
2.1.8	Steam cracking condensates	52
2.2	Legislation	52
2.2.1	Standards for discharge and monitoring of hydrocarbons in France	52
2.2.2	Belgian regulations	55
2.2.3	Canadian regulations	56
2.3	Definition and layout of treatments	56
2.3.1	Need to separate sewer systems	56
2.3.2	Stages in treating the general effluent	57
2.3.2.1	Preliminary oil removal	57
2.3.2.2	Physicochemical purification	58
2.3.2.3	Biological purification	58
2.3.2.4	"Tertiary" purification	58
2.3.3	Planning sewer networks (surge tanks, lagoons)	59
2.4	Pretreatment of sour condensates	62
2.4.1	Stripping	62
2.4.1.1	Preacidification	62
2.4.1.2	Steam stripping	63
2.4.1.3	Air stripping	64
2.4.2	Air oxidation of sour condensates	64
2.5	Preliminary oil separation	66
2.5.1	Principles of preliminary oil separation	66
2.5.1.1	Objectives	66
2.5.1.2	Processes	67
2.5.1.3	Rising velocity of oil droplets	68
2.5.2	Construction of gravity oil separators	70
2.5.2.1	Longitudinal API separators	70
A.	Design	70
B.	API separator feed	72
C.	Outlet weir	72
D.	Disposal of bottom sludge	72
E.	Disposal of oil and floating matter	73
F.	Example of design	74
2.5.2.2	Circular oil separators	75
A.	Principle	75
B.	Implementation	76
2.5.2.3	Lamella oil separators	76
A.	Principle	76
B.	Implementation	77
C.	Efficiency	79

2.5.3	Choosing oil gravity separators	79
2.5.4	Oil collectors and skimmers	79
2.5.4.1	Static collectors	79
2.5.4.2	Oil collectors	80
2.5.4.3	Dynamic stationary separators	80
2.5.4.4	Dewatering surface slops	80
2.6	Physicochemical purification of effluents	
	from preliminary oil separators	80
2.6.1	Aims of physicochemical purification	81
2.6.2	Notes on coagulation and flocculation	82
2.6.2.1	Conventional flocculation	82
2.6.2.2	Flocculation by organic cationic coagulant	82
2.6.2.3	Specific features of organic coagulants	83
2.6.2.4	Limits of organic coagulants	84
2.6.2.5	Desulfurization by precipitation of FeS	84
2.6.3	Floc separation by settling-sedimentation	86
2.6.4	Separation by dissolved air flotation (DAF)	86
2.6.5	Separation by filtration (downflow on granular material)	89
2.6.6	Separation by coalescence	92
2.6.7	Choosing separation processes	93
2.6.8	Induced air flotation (IAF) or mechanical flotation	94

Chapter 3

Aerobic biological purification and tertiary treatments for refinery and petrochemical plant effluents

3.1	Aerobic biological purification systems	95
3.1.1	Activated sludge	96
3.1.1.1	Removing carbonaceous pollution	97
3.1.1.2	Removing nitrogen biologically	98
3.1.2	Trickling filters	99
3.1.2.1	Principle	99
3.1.2.2	Operating the trickling filter with refinery WW	100
3.1.3	Attached growth on granular beds-biofilters	101
3.1.3.1	Pressurized oxygen saturation filters	101
3.1.3.2	Water and air upflow biofilters (Biofor, for example)	102
3.2	Implementation of biological purification	
	by activated sludge (ASP)	103
3.2.1	Sizing activated sludge aerobic biological purification facilities	103
3.2.2	Means of aerating activated sludge tanks	105
3.2.2.1	Surface aerators	105
3.2.2.2	Blowered air	106
3.2.2.3	Example of medium load activated sludge sizing	106
3.2.3	Biological treatability of refining and steam cracking effluents	107
3.2.3.1	Composition of effluents and importance of BOD ₅	107
3.2.3.2	Removing aromatic hydrocarbons	108

3.2.3.3	Causes of upsets in biological purification	109
3.2.3.4	Operating difficulties	110
A.	Poor settleability of activated sludge	110
B.	Foaming	111
3.2.3.5	Monitoring biological purification	111
3.2.4	Areas where aerobic purification is used in refineries and petrochemical plants	112
3.2.4.1	Purification by activated sludge	112
3.2.4.2	Trickling filters	113
3.2.4.3	Biofilters	114
3.2.4.4	Recent changes	114
3.3	Tertiary treatments	114
3.3.1	Eliminating SS	115
3.3.2	Eliminating the COD or TOC	116
3.4	Recycling	116
3.4.1	High concentration ratios in atmospheric cooling	117
3.4.2	Recycling MWW in cooling	118
3.4.3	Recycling process water in cooling	118
3.4.4	Reusing WW with reverse osmosis (RO) desalting	120
3.4.5	Heating condensates	120
3.4.5.1	Oil separation by coalescence	120
3.4.5.2	Polishing oil separation	121
3.4.5.3	Thermal degassing	121
3.4.5.4	Total demineralization	121

Chapter 4

Treatment of spent caustic

4.1	Origin and composition of spent caustic	124
4.1.1	Nonregenerative desulfurization processes	124
4.1.2	Composition of spent caustic	128
4.1.2.1	Physical composition of spent caustic	129
A.	SS	129
B.	HC	129
C.	Gums or "polymers"	129
4.1.2.2	Chemical composition of spent caustic	130
A.	Free caustic and total alkalinity	130
B.	Chlorides and cyanides	130
C.	Phenolic compounds	130
D.	Sulfur compounds	132
E.	Examples of spent caustic analyses	133
4.2	Desulfurization of spent caustic	133
4.2.1	Acid hydrolysis and stripping	134
4.2.1.1	Prewashing of steam cracking spent caustic	134
4.2.1.2	Acidification	135
A.	Choosing the reactor	135
B.	Choosing the acid	135

C.	Precipitation of Na_2SO_4	137
D.	Using spent acids	137
E.	Carrying out laboratory tests	138
F.	Consumption of sulfuric acid and changes in specific gravity	138
4.2.1.3	Stripping acidified spent caustic	139
4.2.2	Oxidation of spent caustic	141
4.2.2.1	Oxidation reactions	141
4.2.2.2	Impact of the reactions on the COD and the general chemical balance	142
4.2.2.3	Pressurized reactors (oxidizers)	143
A.	With air	143
B.	With oxygen	144
4.2.2.4	Atmospheric pressure reactors	145
4.3	Removing phenols from spent caustic	145
4.3.1	Solvent extraction	145
4.3.1.1	Principle	146
4.3.1.2	Choosing the solvent	147
4.3.1.3	Impact of pH and temperature	147
4.3.1.4	Implementation	148
A.	Mixer-settlers	148
B.	Pulsed columns	149
C.	Extractors with electric fields	152
D.	Centrifuge extractors	152
4.3.2	Aerobic biological purification	152

Chapter 5

Treatment of petrochemical plant effluents

5.1	Original features of petrochemical plant effluents	155
5.2	The concept of "toxic pollutants"	156
5.3	Influence of salinity and of certain compounds	157
5.4	Particular treatments	158
5.4.1	Use of strong oxidizing agents	158
5.4.2	Adsorption on granular activated carbon (GAC)	159
5.4.2.1	Pretreatment before filtration on GAC	159
5.4.2.2	Scope of adsorption	159
5.4.2.3	Implementation	159
5.4.2.4	Regenerating GAC	160
5.5	Styrene production	160
5.5.1	Conventional process	160
5.5.2	Main discharges	160
5.5.3	Pollution	160
5.5.4	Treatments	161
5.6	Propylene oxide production	162
5.6.1	Lime and epichlorhydrin process	162
5.6.2	Discharges and pollutants	162
5.6.3	Treatment	162

5.7 Polypropylene production	163
5.7.1 Aqueous dispersion process	163
5.7.2 Discharges and pollution	163
5.7.3 Treatment	163
5.8 Polystyrene production	164
5.8.1 Process	164
5.8.2 Discharges and pollutants	164
5.8.3 Treatment	164
5.9 Nylon-6 production	165
5.9.1 Process	165
5.9.2 Discharges and pollutants	165
5.9.3 Treatment	165

Chapter 6

Treatment case studies Purification monitoring and sludge disposal

6.1 French Mobil Oil Gravenchon refinery	168
6.1.1 Treatment of waste water	168
6.1.1.1 Deballasting water	168
6.1.1.2 Oily water	170
6.1.1.3 Heating condensates	170
6.1.2 Eliminating purification sludge	170
6.1.3 Cooling systems	170
6.2 Elf Grandpuits refinery	171
6.2.1 Particular treatments	171
6.2.1.1 Process condensates	172
6.2.1.2 Spent caustic	172
6.2.2 Treatment of general waste water stream	172
6.2.2.1 Process water system	172
6.2.2.2 Oily water system	174
6.2.2.3 Eliminating purification sludge	174
6.2.2.4 Cooling systems	174
6.3 Shell Oil Company Petit-Couronne refinery	175
6.3.1 Effluent and pretreatment set up	176
6.3.2 General treatment of effluents	176
6.3.3 Eliminating purification sludge	178
6.4 Esso-SAF: Port-Jerome	178
6.4.1 Treatment of waste water	178
6.4.1.1 Process water	181
6.4.1.2 Oily water	181
6.4.1.3 Treatment of "clear" water	181
6.4.2 Eliminating purification sludge	181
6.4.3 Cooling systems	181

6.5	Shell complex in Berre	182
6.5.1	Effluent and pretreatment set up	182
6.5.2	General biological treatment	184
6.5.3	Sludge treatment	186
6.5.4	Cooling systems	186
6.6	Disposal of sludge	187
6.6.1	Categories of sludge	187
6.6.2	Amounts discharged	188
6.6.3	Ultimate sludge disposal	189
6.6.4	Dewatering equipment	189
6.6.4.1	Dynamic thickening by dissolved air flotation	189
6.6.4.2	Continuous centrifuges	189
6.6.4.3	Filter presses	190
6.6.4.4	Gravity-fed belt filters	191
6.6.4.5	Producing less sludge	191
6.7	Monitoring purification plants	192
6.7.1	Measuring hydrocarbons	192
6.7.2	Measuring organic matter	193
6.7.3	pH-meters	193
6.7.4	Miscellaneous devices	194

Chapter 7

Conditioning of cooling system water

7.1	Systems different types of systems	195
7.1.1	Once-through system	195
7.1.2	Closed recirculating system	195
7.1.3	Open recirculating system	196
7.2	Main characteristics of an open recirculating system with a cooling tower	197
7.3	Problems and their causes	199
7.3.1	Fouling and biological growth	199
7.3.2	Scale build up	202
7.3.3	Corrosion of steel	204
7.3.3.1	Note on electrochemical corrosion in water	204
7.3.3.2	Main influencing parameters	204
7.3.3.3	Main types of corrosion and causes	207
7.4	Protection against fouling and biological growth	208
7.4.1	Action taken on make up water	208
7.4.2	Action on the system	208
7.4.2.1	Side-stream filtration possibly with in-line coagulation	208
7.4.2.2	Using organic dispersing agents	208
7.4.2.3	Using surfactants	209
7.4.2.4	Using chlorination and brominated compounds	209
7.4.2.5	Using biocides	210

A.	Biocide action	210
B.	Choosing a biocide	210
C.	Implementation	211
7.4.2.6	Special case of hydrocarbon pollution	211
7.5	Protection against scale and corrosion	211
7.5.1	Note on calcium carbonate equilibrium and the Ryznar index	211
7.5.2	"Natural equilibrium" process	214
7.5.3	Scale-inhibitor or stabilization process	214
7.5.3.1	Advantages and limitations of processes to delay precipitation	215
7.5.4	Corrosion inhibitor processes (with controlled pH)	216
7.5.4.1	Principle	216
7.5.4.2	Main categories of corrosion inhibitors	216
7.5.4.3	Obtaining the optimum pH	217
A.	Adding acid	217
B.	Softening (carbonate removal) on carboxylic resin for all or part of the make up as shown in the principal reactions	218
C.	Lime softening	218
7.5.5	Determining the optimum concentration rate	218
7.5.6	Discharges	220
7.5.7	Choosing processes: how to design a cooling system	220
7.5.7.1	Controlling parameters	220
7.5.7.2	Guidelines	221
7.5.7.3	Operating balance sheets	221
7.5.8	Comments on stainless steel corrosion	221
7.5.9	Comments on degradation of concrete	222
7.6	Saving water	223
7.6.1	Purification of make up water	223
7.6.2	Side-stream purification	223
7.6.3	Reusing industrial waste water	224
7.7	Implementing protection	224
7.7.1	Preparing the system	224
7.7.2	Maintaining protection	225
7.7.3	Precautions required when systems are shut down	225
7.8	Monitoring and effectiveness	226
7.8.1	Monitoring water and reagent consumption	226
7.8.2	Monitoring purification and metering stations	226
7.8.3	Analytical monitoring	226
7.8.4	Monitoring and measuring corrosion	227
7.8.4.1	Measuring the corrosion current: corrosion meters	227
7.8.4.2	Measuring by test samples	227
7.8.4.3	Examining system materials	231
7.8.5	Heat exchange quality	231
7.8.5.1	Monitoring a reference exchanger in the system	231
7.8.5.2	Measuring scale deposits: the scale meter	232
7.8.6	Remote monitoring	232

7.9 Once-through systems	234
7.9.1 Protecting against fouling and biological growth	234
7.9.2 Protecting against scale and corrosion	234
7.9.2.1 If the water is close to stability or scale-forming when cold	234
7.9.2.2 Special case of strongly mineral water from deep wells	234
7.9.2.3 If the water is corrosive	234
7.10 Closed recirculating systems	235
7.10.1 Controlling fouling and scale formation	235
7.10.2 Controlling corrosion	235
7.10.2.1 Corrosion inhibiting processes	235
7.10.2.2 Oxygen reducer processes	236
7.10.3 Comments on so-called "closed" systems	237
7.11 Seawater systems	237
7.11.1 Seawater and brackish water	237
7.11.2 Organic fouling	239
7.11.3 Scale formation	239
7.11.4 Corrosivity of sea water	239
7.11.5 Choosing materials	240
7.11.6 Once-through cooling systems	240
A. Protecting against organic fouling	240
B. Protection against scale formation	240
C. Protecting against corrosion	240
7.11.7 Open recirculating systems with cooling towers	241
7.12 Conclusion	241
References	243
Index	245

Abbreviations and acronyms

1 Refining processes

FCC	Fluid catalytic cracking
HDS	Hydrodesulfurization
LCO	Light cycle oil
LOP	Lube oil plant

PS	Polystyrene
SC	Steam cracking
TC	Thermal cracking
VB	Viscosity breaking

2 Associations and organizations

AFNOR	Association Française de Normalisation, (French Standards Committee)
API	American Petroleum Institute
ASTM	American Society for Testing Materials
CONCAWE	Oil Companies International Study Group for Conservation of Clean Air and Water
EPA	Environmental Protection Agency (USA)
IFP	Institut Français du Pétrole (French Petroleum Institute)
UNEP	United Nations Environmental Protection

3 Water treatment

AS	Activated sludge	MWW	Municipal waste water
DAF	Dissolved air flotation	NTU	Nephelometric turbidity unit
GAC	Granular activated carbon	PAC	Powdered activated carbon
IE _x	Ion exchange	RO	Reverse osmosis
LAF	Induced air flotation	SC	Spent caustic
IR	Infrared	TF	Trickling filter
IWW	Industrial waste water	UV	Ultraviolet

4 Water chemistry

BOD ₅	Biological oxygen demand, 5 days	PAH	Polyaromatic hydrocarbons
BOD ₂₀	Ultimate BOD, or 20 days	P alk	Phenolphthalein alkalinity
COD	Chemical oxygen demand	PV	Permanganate Value
COD _{AD}	Chemical oxygen demand after settling for 2 hours	SS	Suspended solids
DAAP	Diaminoantipyrine	SSA	Salts of strong acids
DEA	Diethanolamine	SVI	Sludge volume index
DO	Dissolved oxygen	TA	Alkaline concentration
DS	Dry solids	TAC	Total alkalinity
HC	Hydrocarbons	TDS	Total dissolved solids
M alk	Methyl orange alkalinity	TH	Total hardness
MEA	Monoethanolamine	ThOD	
MEK	Methylethylketone	or TOD	Theoretical oxygen demand
MIBK	Methylisobutylketone	TKN	Total Kjeldahl nitrogen
MU	Make up	TOC	Total organic carbon
NMP	N-methyl 2 pyrrolidone	VOC	Volatile organic carbon
OM	Organic matter (consumed MnO ₄ K as O ₂)	VS	Volatile solids

Chemistry of natural water and industrial waste water

Chapter

1

1.1 Mineral composition of water

1.1.1 Mineralization of water

Pure natural water is defined as containing no suspended solids (SS), colloids, or dissolved organic matter (this is true for mineral waters and many types of well water). It therefore contains only dissolved mineral salts dissociated into cations and anions.

The main ions in water can be classified in decreasing order of frequency.

Cations	Atomic mass	Anions	Atomic mass
Ca^{2+} calcium	40	HCO_3^- bicarbonate	61
Mg^{2+} magnesium	24	Cl^- chloride	35.5
Na^+ sodium	23	SO_4^{2-} sulfate	96
K^+ potassium	39	NO_3^- nitrate	62
NH_4^+ ammonium	18	F^- fluoride	19
Fe^{2+} ferrous iron	56	PO_4^{3-} phosphate	95

However, PO_4^{3-} , NH_4^+ and NO_3^- are not often present in water and may indicate pollution when they are.

After undergoing chemical treatment, water may also contain CO_3^{2-} or OH^- ions (alkaline water) or H^+ ions (acid water).

All the ions present come from solubilization and ionization of salts that were directly washed down by the water (NaCl , CaCl_2 , Na_2SO_4 , NH_4NO_3 , etc.). They can also come from salts formed in the water by carbon dioxide, dissolved CO_2 , acting on calcareous or magnesian materials. This is termed **carbonic attack** and causes calcium bicarbonate $\text{Ca}(\text{HCO}_3)_2$ or magnesium bicarbonate $\text{Mg}(\text{HCO}_3)_2$ to form. The CO_2 comes mainly from biological activity in the soil.

After dissolution, the initial salts lose their individuality. Only cations and anions subsist in the water in equilibrium with each other according to the rule of overall electric neutrality of the solution.

In order to define the composition of such a solution, the concentrations of the different ions must be measured in a unit that takes into account both their molecular weight and electric charge.

This unit is the **gram-equivalent per liter of solution** ($\text{eq}\cdot\text{l}^{-1}$). This is the quotient of the quantity unit of matter, the mole, and the number of charges of the same sign carried by the ions (i.e. valence).

For example, a gram-equivalent of Na_2SO_4 , which releases two positive charges and two negative charges in solution, is equal to half of the mass of a mole of Na_2SO_4 , i.e. $71\text{ g}\cdot\text{l}^{-1}$.

The gram-equivalents of the two ions, Na^+ and SO_4^{2-} , released in the solution are 23 and $48\text{ g}\cdot\text{l}^{-1}$ respectively.

A solution of an ion is termed **normal (N)** when it contains a gram-equivalent of this ion per liter.

In water treatment, much smaller units than the gram-equivalent are commonly used to take into account the order of magnitude of concentrations. These units are:

- The **milliequivalent**, or $\text{meq}\cdot\text{l}^{-1}$, which is one one-thousandth of a gram-equivalent.
- The **French degree**, $^\circ\text{F}$, which corresponds to the concentration of a N/5000 solution and is therefore equal to one-fifth of a $\text{meq}\cdot\text{l}^{-1}$.

These units allow the establishment of ion balances that are characteristic of a given water. The balances are indispensable in understanding and measuring the changing status of the water when it is treated or used. Though the expression in $\text{meq}\cdot\text{l}^{-1}$ is the most rational, in industry the most commonly-used units are:

- The French degree in Europe.
- The ppm CaCO_3 in the English-speaking world, which corresponds to $0.02\text{ meq}\cdot\text{l}^{-1}$ or 0.1 degree.

Therefore a French degree is equivalent to 10 ppm CaCO_3 .

Table 1 summarizes the different expressions of these units for the main ions in $\text{mg}\cdot\text{l}^{-1}$.

In Germany, the German degree (1.78 of a French degree) is now being phased out and replaced by the $\text{meq}\cdot\text{l}^{-1}$ for hardness or alkalinity values.

Table 1

$\text{mg}\cdot\text{l}^{-1}$ versus other units of concentration for the main ions

Cation	$\text{meq}\cdot\text{l}^{-1}$	French degree	ppm CaCO_3	Anion	$\text{meq}\cdot\text{l}^{-1}$	French degree	ppm CaCO_3
Ca^{2+}	20	4	0.4	HCO_3^-	61	12.2	1.2
Mg^{2+}	12.1	2.43	0.24	Cl^-	35.5	7.1	0.71
Na^+	23	4.6	0.46	SO_4^{2-}	48	9.6	0.96
K^+	39	7.8	0.78	NO_3^-	62	12.4	1.24
NH_4^+	18	3.6	0.36	F^-	18.5	3.7	0.37
Fe^{2+}	27	5.4	0.54	PO_4^{2-}	31.6	6.3	0.63
Al^{3+}	9	1.8	0.18	CO_3^{2-}	30	6	0.6

1.1.2 Parameters specific to the chemistry of water

In the past a great deal of importance was given to controlling water hardness and to the various related chemical softening operations. This led to particular expressions of titration related to the hardness of water and its alkalinity: the titration for hardness (TH), the methyl orange alkalinity, M alk, and the phenolphthalein alkalinity, P alk. In demineralization by ion exchange, the measurement of salts of strong acids (SSA) is also used.

1.1.2.1 Hardness and M alkalinity

Water hardness, TH:

Hardness is measured by the sum of Ca^{2+} and Mg^{2+} concentrations in degrees and is expressed by TH. It can be divided up into the calcium content and the Mg content:

$$\text{Ca content} + \text{Mg content} = \text{TH}.$$

TH was formerly measured with a soap solution, but is now determined by complexometric titration with EDTA (complexone) in the presence of Eriochrome T Black at a pH of 10. The calcium content by itself can be determined with EDTA but at a pH of 12 and in the presence of calcein.

When demineralized waters are monitored (Na, Si, etc.), more sophisticated measurements are made by using a number of spectrophotometric techniques (flame emission, atomic absorption, colorimetric methods, etc.).

Water alkalinity, M alk and P alk:

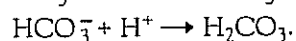
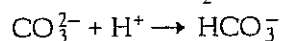
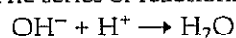
Alkalinity is measured by the sum of alkaline (Na, K) or alkaline-earth (Ca, Mg) bicarbonate, carbonate and hydroxide anions. It is expressed by the M alk, or total alk (TAC).

When the pH is lower than 8.3, the M alk is measured by acidification of the medium until methyl orange changes color. The M alk then expresses the bicarbonate concentration.

When the pH is greater than 8.3, there may be a simultaneous presence of carbonates and even alkaline hydroxides. Two measurements are then made in succession:

- Acid titration with phenolphthalein which changes to colorless below pH 8.3 and thereby measures the alkaline concentration or P alk (TA).
- After addition of methyl orange, titration is continued until the color changes to orange, which measures the M alk for all of the acid added.

The series of reactions is usually:



Depending on the relationship between P alk and M alk/2, the fractions of the three anions involved are given in Table 2.

Table 2
Significance of P alk and M alk

If	TA = 0	TA < TAC/2	TA = TAC/2	TA > TAC/2
HCO_3^-	TAC	TAC - 2TA	0	0
CO_3^{2-}	0	2TA	TAC	2(TAC - TA)
OH^-	0	0	0	2TA - TAC

Therefore:

- The P alk represents the hydroxide content and half of the carbonate content.
- P alk = M alk/2 means that carbonates alone are present.
- P alk = M alk means that only strong OH^- bases are present.

Some examples, in $\text{meq}\cdot\text{l}^{-1}$:

	Standard seawater	Typical city water	
		raw	lime softened
Hardness	130	5	1.8
M alk	3	4	0.8
P alk	0	0	0.4

For waste water, care must be taken since:

- Color changes are often not visible and potentiometric titration must be done with a pH meter.
- Other anions are measured by the P alk and M alk, in particular acids (organic acids, e.g. H_3PO_4 , HCN , etc.) and sulfur compounds (see 1.4.2.4).

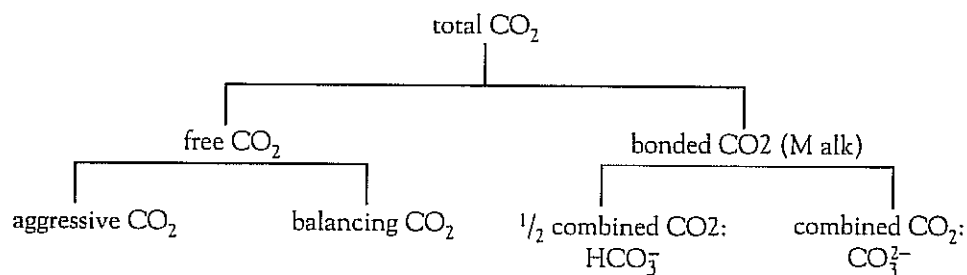
1.1.2.2 M alk and carbonic equilibrium

a. When the difference $\text{TH} - \text{M alk}$ is positive in natural water, it is said to represent the **permanent hardness** (i.e. related to strong acid salts). The M alk itself is called **temporary hardness**. The water is said to be **calcium bicarbonated** and:

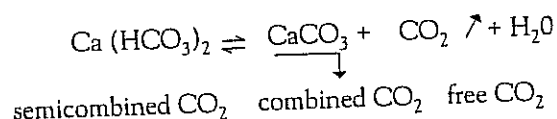
$$\begin{aligned} \text{Total hardness} &= \text{permanent hardness} + \text{temporary hardness} \\ \text{TH} &= (\text{TH} - \text{M alk}) + \text{M alk.} \end{aligned}$$

M alk is said to be temporary because it is only made up of the bicarbonates, ions that can be precipitated out either by lime in the form of CaCO_3 , or by a considerable rise in temperature.

In natural water, the M alk, the CO_2 content, the pH and the TH are the basic parameters (among others) that define the **carbonic equilibrium** or **aggressivity** of the water. The aggressivity is related to limestone or "marble" (CaCO_3) which is the major component in the natural protective layer laid down in piping that carries nonaggressive water. The equilibrium depends on the following balance:



Calcium bicarbonate (hydrogen carbonate) exists in water in an unstable state. If well water that is saturated in CO_2 is brought to atmospheric pressure or heated, it tends to lose its balancing CO_2 and precipitate limestone. It causes scaling up:



High M alk may exist and remain stable in hard well water due to CO₂ partial pressures as long as the pressure is maintained and there is no escape of carbon dioxide.

Surface water is in extensive contact with the atmosphere, which in comparison is very poor in CO₂, and so it is often in equilibrium.

Carbonic aggressivity for water is defined based on the five parameters below. It is indispensable to know them to make a proper assessment.

Calcium content	Temperature
M alk	Dissolved salts
pH or free CO ₂	

In fact, the way natural or purified water behaves toward piping and exchangers, i.e. toward steel, also depends greatly on the dissolved O₂ content. This is what governs the corrosivity of the water, along with carbonic aggressivity (see Chapter 5).

b. When M alk is higher than the TH, it no longer represents temporary hardness, but only the alkaline bicarbonates that may be bonded to:

- Sodium and potassium: this is true for some well water and a good deal of saline waters in oil and geothermal reservoirs.
- Ammonium: this is true for waste water (condensate, gas scrubbing, etc.), but not for natural water.

In the second case, the added presence of organic acids does not allow the interpretation mentioned above. In refinery wastes these acids can be naphthenic or acetic acids.

1.1.2.3 Salts of strong acids (SSA) and alkaline ion content

The SSA represents the sum of existing strong acid anions, and also those such as Cl⁻ and SO₄²⁻ in natural water and NO₃⁻ and F⁻ in polluted water.

Measurement is made directly after percolating water in a column loaded with strong cation exchangers in H⁺ form. Neutralization is then performed by means of a titrated caustic solution until the methyl orange color change at pH 4.3.

It can also be calculated indirectly by adding strong anions when they are known and are measurable individually.

The alkaline ion content expresses the Na⁺ + K⁺ sum and can be measured by flame emission spectrometry.

1.1.2.4 Silica

In river water silica is present in the form of barely ionized silicic acid, H₂SiO₃, in concentrations of 5 to 30 mg·l⁻¹ depending on the soil. The amount can be determined by flame emission spectrophotometry or by ammonium molybdate colorimetry.

During ion exchange on resins, silica is fixed in its monovalent form and a degree represents 15.4 mg·l⁻¹ of HSiO₃⁻ or 12 mg·l⁻¹ of SiO₃²⁻.

In some rivers or even some boreholes, a fraction of the silica is colloidal rather than dis-

solved and is extremely finely dispersed. It can remain intact after flocculation and migrate through the ion exchangers. Fractions greater than 1 to 2 $\text{mg}\cdot\text{l}^{-1}$ are very rare, however.

1.1.2.5 CO_2

Carbon dioxide dissolved in water in the form of H_2CO_3 is likely to dissociate into HCO_3^- and H^+ or CO_3^{2-} and 2 H^+ . It is therefore evaluated in degrees in two possible ways:

- By ion exchange which fixes the HCO_3^- ion with the degree equivalence of $8.8 \text{ mg}\cdot\text{l}^{-1}$.
- By neutralization or precipitation by lime, where the CO_3^{2-} ion reacts, with the degree equivalence of $4.4 \text{ mg}\cdot\text{l}^{-1}$.

Free CO_2 concentrations in natural water vary between a few milligrams and several dozen milligrams per liter. The first figure corresponds to river waters in equilibrium with the atmosphere and the second to deep well water that is subjected to high CO_2 partial pressures and can be very aggressive.

The CO_2 measurement must always be given in correlation with the temperature and the pH. This means that care must be taken when taking well water samples under pressure.

1.1.3 Ion balances

Based on the measurement of ions present (they can generally be identified in natural water but not in waste water), the water can be characterized by an ion balance. The balance is set up on the basis of the sum of cation degrees being equal to the sum of anion degrees.

When the content of some ions can be calculated only by difference this balance is often approximate. For instance, in water with a limited ion diversity:

SO_4^{2-} is deduced from $\text{SSA} - \text{Cl}^-$

Mg^{2+} , Ca^{2+} content is deduced from $\text{TH} - \text{Ca}^{2+}$ content

Na^+ is deduced from the sum of cations - TH.

The most simplified expression of a balance is:

$$\text{M alk} + \text{SSA} = \text{TH} + \text{alkaline ion content.}$$

In natural water balances, silica and carbon dioxide often appear separately from the anion column.

Several examples of balances can be given to represent the different families of natural water that are available for industrial uses (Table 3). The families may be:

- Surface water (rivers and lakes). The physical composition depends on the river regime while the chemical composition is governed by the vagaries of urban or industrial discharges.
- Well water taken from the water table of a river. It generally has comparable, though better, chemical characteristics than the river. It is generally oxygenated and physically clean.
- Deep well water (10 to 50 m), which is deoxygenated, mineralized (SO_4^{2-}), and often ferruginous and aggressive.
- Very deep well water whose temperature and mineralization are high. Beyond a salinity of 0.8 to $1 \text{ g}\cdot\text{l}^{-1}$, it can be termed brackish (oligobrackish up to $5 \text{ g}\cdot\text{l}^{-1}$).

In contrast, in what is termed soft water, salinity (TDS) is less than 75 to $120 \text{ mg}\cdot\text{l}^{-1}$ and may be wholly due to Ca and Mg salts.

Water softening is a process that removes part or all of these two cations by:

- Chemical precipitation with lime, which only removes temporary hardness.
- Na cycle ion exchange or Na_2CO_3 treatment, which removes all or almost all of the hardness.

In both cases, the resulting water, said to have been softened, may still be brackish. Only double exchange of cations then anions can achieve cold demineralization (with the exception of reverse osmosis).

Table 3

Examples of ion balances for natural water (in °F)

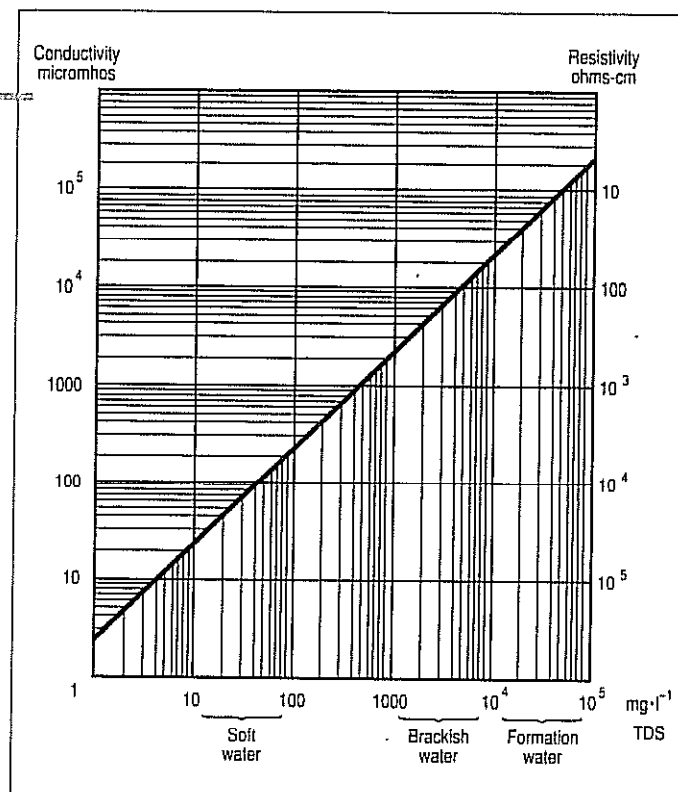
No.	TH	TCa	Na^+K^+	M alk	Cl^-	SO_4^{2-}	TDS	Comments
1	5.5	2.5	2	5.5	1	1	7.5	Soft water
2	22	19	1	19	3	1	23	} Mean mineralization
3	29.5	19	2	29	1	1.5	31.5	
4	37		3	12	24	4	40	} Hard water
5	52		3	34	1	20	55	
6	62	42.5	44	16	40	50	106	Brackish water
7	7		4	9	1	1	11	
8	270		1180	25.5	1340	85	1450	Geothermal water

- Analysis No. 1: characterizes a soft water (total dissolved salinity TDS $<10^\circ$) that is found on granitic terrains (Vosges, Armorican basin, Auvergne). Volvic mineral water is an example.
- Analysis No. 2: characterizes water with mean mineralization, not too hard, found in the Paris basin. Evian mineral water is a comparative example.
- Analysis No. 3: water which is less soft.
- Analysis No. 4: characterizes a river water that has been subjected to a massive discharge of CaCl_2 which leaves its initial alkalinity (M alk) unchanged. However, the hardness and mineralization have been increased considerably making it unfit for human consumption and costly to demineralize.
- Analysis No. 6: characterizes water from a deep well in the Middle East with high coexisting chloride and sulfate content. It is brackish water whose TDS is in excess of 100° (or 1000 ppm as CaCO_3).
- Analysis No. 7: characterizes soft well water that can be termed "soda bicarbonated" since its M alk is higher than its TH.
- Analysis No. 8: of a Dogger-age geothermal water indicates a considerable salinity level. This can also be found in formation water in oil- and gas-bearing reservoirs, i.e. in crude oil at the desalter inlet.

1.1.4 Other useful parameters

It is also necessary to know the dissolved oxygen, and useful to assess the total salinity for industrial uses of natural or recycled water.

Fig. 1
Resistivity/conductivity and
dissolved salt (NaCl) content
equivalence at 20°C



The dissolved oxygen content can be nil in wells or exhibit a certain supersaturation in a piping network (sometimes after ozonization). The oxygen content governs the water's corrosivity in piping systems.

Total salinity, TDS, can be assessed in three ways with a satisfactory degree of reliability:

- Weighing the dry extract of a previously filtered sample. However, in this measurement the CO_2 of the bicarbonates has come off and a correction must add the bonded CO_2 to the initial M alk.
- Adding concentrations in milligrams per liter of the different titrated ions. However, important ions may have been omitted or hidden.
- Measuring the conductivity of the water at a given temperature. It is roughly proportional to the concentration in a given salt, up to a few dozen grams per liter. There are a large number of correlation graphs depending on the ion and the amount of concentration. The equivalence is poor for natural low-salt water of varied compositions. For brackish water or brines where CaCl_2 or NaCl prevail, the equivalence becomes feasible (see Fig. 1).

1.2 Impurities in natural water

Impurities are suspended solids and colloids, which show as turbidity, and dissolved organic matter which gives coloring (sometimes in conjunction with Fe^{2+}).

1.2.1 Suspended solids (SS)

Suspended solids are of heterogeneous shape and varied origin in surface water. In well water, they include fine-grained sand, oxidized iron and sometimes filamentous algae.

In river water, a distinction must be made between:

- Bulky material which often floats or can not be settled out (twigs, leaves, paper) and is removed by mechanical means (brush screening to 2 mm, gravity-flow sieves to 250 μm).
- Fine-grained material (silts, sands, clays, plant and animal debris) which remains in suspension in the water either indefinitely (for the colloidal fraction) or eventually settles out very slowly. In both cases the material can be properly removed only after coagulation and flocculation.

The water of the River Seine contains 40 to 60 $\text{mg}\cdot\text{l}^{-1}$ SS and even more during periods of high water. Mountain streams may contain only 10 to 30 $\text{mg}\cdot\text{l}^{-1}$ in winter, but over 1 $\text{g}\cdot\text{l}^{-1}$ during stormy weather or spring thaws.

The SS must be determined in conjunction with precise information on the sample-taking conditions (date, place, climate, presence of a nearby upstream industrial facility or sewer).

Measuring the SS

The SS are impurities that are not dissolved in the water. Their content is measured by weighing a cake formed by filtering a given volume of water on a specified filtering membrane and drying the resulting solids in an oven. For water that has a low solids load or is highly colloidal, the result of measurement depends how fine the filter paper is.

French standard AFNOR T 90-105 defines a protocol based on the use of Millipore AP 20, Sartorius 13 400, and Whatman GF/C discs (among other specifications). These discs provide a given pore diameter (a few micrometers).

Besides this standard, industrial operators can use finer pore diameter filters, such as Millipore 0.45 and 0.20 micrometer.

These filters enable better removal of colloidal particles. In contrast, there are faster filter papers (for example Durieux, black stripe) that have less capture capability than standard discs.

Whereas it is imperative to comply with the standard for discharged waste water, the three types of filters mentioned earlier may be used in monitoring make up water clarification or defining treatment. The results of these filtering operations may differ widely.

Supplementary rinsing operations must be added when the water is very salty.

The SS are an overall parameter which does not express the treatability of a turbid water either in make up water clarification or in waste water treatment. Treatability, settleability or filterability depend on the nature, texture and specific gravity of the SS:

- Clays, silts, hydroxides and sulfides are colloidal and hard to filter out.

- Sands, catalysts and corrosion products on the other hand can be readily settled out.
- Fibers and greases may float or form unsettleable aggregates with the products mentioned above.

Since these components are highly variable in natural water, both in nature and in proportions, a number of laboratory, or preferably in situ, tests must be run in order to define treatability.

1.2.2 Colloidal material

Suspended particles, whose size ranges from 0.1 to 1 to 2 micrometers, have a considerable specific area that is electronegatively charged in almost all cases. Accordingly, the particles are subjected to electrostatic repulsion forces which keep them in suspension indefinitely (zeta potential from -5 to -20 mV). In order to precipitate or filter them out, inorganic coagulants, Al or Fe salts, must be used. When the coagulants are dissolved in water, electropositive charges are released that can neutralize the negative charges of the colloids and cancel out the zeta potential. The extent of the colloidal state can be estimated in an initial approximation by the turbidity if not by the color of the water.

Turbidity

Turbidity defines water opalescence, due much more to colloidal particles in suspension and to "dissolved" organic matter than to the SS as such.

Conventionally, it is measured by comparison with reference solutions in a nephelometer with the units below:

- I.U. international units, with a formazine-base reference solution.
- Silica units, with a kieselguhr reference solution.
- Mastic drops mainly used to characterize clarified water.

There is no straightforward correspondence among these units. As an indication of the orders of magnitude involved, the turbidity of water from the River Seine is:

- Before treatment, from 5 to 10 I.U.
- After flocculation-settling, from 1 to 2 I.U.
- After filtration, from 0.1 to 0.5 I.U. or 5 drops of mastic.

Color

Color is measured by comparison with a platinum-cobalt solution. For example, water from the River Seine can have coloring of from 10 to 15 $\text{mg}\cdot\text{l}^{-1}$ Pt, rising to 60-70 in the rainy season.

It is due to dissolved organic matter, to ferritic iron precipitated out in a colloidal hydroxide form, to ferrous iron bonded to organic complexes and to a number of colloids.

1.2.3 Dissolved organic matter (dissolved OM)

In natural water, dissolved OM comprises several families of compounds, e.g. humic acids, carboxylic acids and carbohydrates. It is characterized as a general rule by permanganate oxidizability or total organic carbon (TOC).

Permanganate oxidizability (PV Permanganate Value)

This is the consumption of oxygen from hot MnO_4K in milligrams per liter in 10 minutes in an acid range: 3.8 mg of MnO_4K are equivalent to 1 mg of O_2 (AFNOR T 90-050).

In an alkaline range, plant-origin OM is measured primarily, while animal-origin OM should show up in an acid range.

The river waters of the Paris basin exhibit consumptions ranging from 1 to 3 mg·l⁻¹ of O₂. Of this, 30 to 45% can be eliminated during clarification by flocculation with the traces of organic micropollutants that the waters may contain.

Nonpolluted well water seldom exhibits consumptions greater than the sensitivity threshold (0.4 mg·l⁻¹), except in formations rich in humic acids. Here the high demand is more the cause of stable coloring than a sign of harmful effects (except for anionic resins).

In some countries the PV is the parameter that replaces the BOD₅, with higher values in raw municipal waste water and lower ones in treated municipal waste water.

Total organic carbon (TOC)

This is the measurement of the carbon bonded to the OM. It is obtained by burning the OM and reading the CO₂ that is produced (AFNOR T 90-102).

Since TOC meters are now reliable, the measurement can be generalized to clarified or filtered water preferably and treatment steps can be monitored. Additionally, some countries sometimes impose TOC standards rather than COD standards when industrial waste water is disposed of.

1.3 Characterizing open cooling system water

Water in an open recirculating cooling system is characterized in comparison to make up water by the changes in some parameters due to several processes:

- Concentration in salts due to evaporation. It is defined by the concentration factor (number of cycles) measured in turn by the ratio:

$$\frac{(\text{Cl}^- \text{ in system})}{(\text{Cl}^- \text{ in make up})} \text{ or estimated by the ratio: } \frac{\text{make up flow rate}}{\text{blowdown flow rate}} . \text{ This ratio varies from}$$

1.1 to 4, less often from 5 to 8.

- Precipitation of bicarbonates: slight but significant of the quality of the antiscaling treatment. It is measured by the M alk whose increase does not match the rise in chlorides.
- Dissolution of gases from the air: increments in SO₂ or SO₃ are sometimes possible. The increase in (SO₄²⁻) can then be greater than the increase in (Cl⁻). The presence of atmospheric pollution is deduced from it.
- Appearance of NO₃⁻ due to biological nitrification of ammonia. This often leads to a drop in M alk by acidification in thermal power plant cooling systems.
- Development of a variety of bacteria, whose mass is monitored by measuring the fouling volume and by bacteria counts.

Fouling volume

The volume filtered in 15 min on a 47 mm diameter, 0.45 μm Millipore membrane is measured at a vacuum pressure of 0.5 bar. The volume can vary from 1 to 5 liters. The most important factor to monitor is the way it changes with time in the system and downstream from bypass filtration whose efficiency can thereby be estimated.

Bacteria counts

Several counting operations can be performed, especially the first one mentioned below:

- Concentration in total bacterial germs per milliliter measured at 37°C or at 25°C.
- Concentration in revivable bacteria measured in a liquid medium (soybean tryptone diluted to 1/10) at 37°C for 7 days (or 20°C).
- Total coliform bacteria per 100 ml.

It is advisable that counts should not exceed 10^4 total germs per milliliter in an open recirculating system and $5 \cdot 10^2$ in make up water.

Table 4 shows the levels found in the open recirculating system of a thermal power plant fed by highly infected river water (before carbonate removal) undergoing effective antialgae chlorination treatment.

Table 4

Example of bacterial population development in an open recirculating cooling system

Medium	Total germs $\cdot \text{ml}^{-1}$		Total coliform bacteria/100 ml	Fecal streptococci /100 ml
	37°C	20°C		
River	$5.7 \cdot 10^3$	$3.0 \cdot 10^4$	$1.5 \cdot 10^4$	$4.0 \cdot 10^0$
Make up	<100	<100		0
System	$6.0 \cdot 10^2$	$1.0 \cdot 10^3$	$9.3 \cdot 10^1$	$9.3 \cdot 10^1$

Preventing a nitrification process also requires monitoring NH_4 , NO_2 and NO_3 concentrations, or Kjeldahl nitrogen (organic N + $\text{N} \cdot \text{NH}_4$).

1.4 Characterizing oil industry waste water

The parameters that characterize potential pollution in refinery and petrochemical plant WW include general parameters in common with MWW on the one hand, and parameters specific to the oil industry (hydrocarbons, sulfur compounds, etc.), on the other.

1.4.1 General parameters in common with MWW (municipal waste water)

This category includes SS, biochemical oxygen demand (BOD_5), chemical oxygen demand (COD) and ammonium nitrogen ($\text{N} \cdot \text{NH}_4$).

1.4.1.1 SS

As stated earlier (Chapter 1, Section 1.2), the presence of colloids makes the result of membrane filtration highly dependent on the quality of the membrane and the volume filtered, especially for water that is biologically treated. As a result, some European countries have arbitrarily limited the minimum applicable standard to $3 \text{ mg} \cdot \text{l}^{-1}$ for discharges.

French legislation on MWW as well as IWW sets a maximum content of $30 \text{ mg}\cdot\text{l}^{-1}$ of SS measured according to standard AFNOR T 90-105 for discharges into the environment (levels IV and V) or $20 \text{ mg}\cdot\text{l}^{-1}$ (level VI, after tertiary treatment). In some Scandinavian countries, discharge standards of 5 or $10 \text{ mg}\cdot\text{l}^{-1}$ of SS are often enforced for lakes.

In IWW, such as from a refinery, two points are critical when SS are measured:

- Some oil industry water is very saline (petrochemical plants, deballasting). It may be necessary either to dilute the sample or to rinse the cake more generously with distilled or demineralized water.
- The oils, hydrocarbons and greases present in the water are for the most part included in the weighing operation which then gives total SS. These oils can be dissolved by a solvent prior to weighing to determine SS alone.

1.4.1.2 Biochemical oxygen demand (BOD_5)

BOD_5 is measured by the oxygen consumption of a preseeded sample at 20°C in darkness over an incubation period of five days. This period allows biological oxidation of a fraction of carbon-bearing OM. Some countries (Sweden, Germany) measure a BOD_7 for reasons of practical convenience. Complete aerobic biological treatment of water would actually require 21 days (BOD_{21} , or ultimate demand) or 28 days (BOD_{28}). The 21-day duration is necessary for biodegradable nitrogen compounds (proteins and ammonium salts) to be oxidized.

A 28-day, or even 35-day, duration is sometimes considered. This is the time required for certain families of hydrocarbons to be broken down.

The curves in Fig. 2 show changing oxygen consumption versus time, with different rates specific to different types of water.

MWW naturally contains the germs needed for aerobic fermentation. This is not true for all IWW, particularly not for process condensates.

They must be preseeded with MWW sludge when BOD is measured.

Curve (1) shows a change in slope when five to seven days have elapsed for MWW that naturally contains organic or ammonia nitrogen. This indicates the transition to protide breakdown.

Curve (2) shows a steady breakdown of carbohydrates or oxygenated compounds for nitrogen-free IWW.

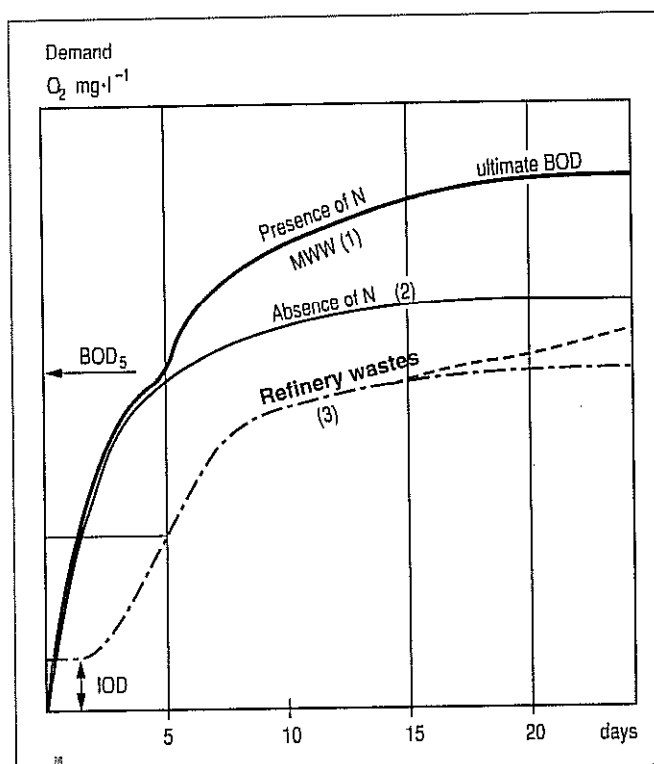


Fig. 2 Changes in the oxygen consumed by waste water

Curve (3) for refining IWW indicates several phases of development in the oxygen demand:

- The initial stage corresponds to an immediate oxygen demand (IOD) that shows the consumption due to reducing inorganic compounds such as sulfides or ferrous salts. It is fulfilled in a nonstandardized time frame, which may be two hours.
- The part involving the BOD_5 .
- The part involving ultimate BOD.
- Possibly one further part shown in a broken line that involves the gradual start of a breakdown in soluble (especially aromatic) hydrocarbons. Depending on the author, the developed time requires from 28 to 35 days.

In refinery and petrochemical plant IWW, the BOD components other than carbohydrates and protides exhibit biodegradation kinetics that are slower or subjected to particular inhibitions. For aromatic hydrocarbons or arylsulfonates, biodegradation may be very slow. They of course require preseeded with biological refinery sludge that already performs this type of function, or else with particular slops.

Industrially the chances of successful biodegradation of these stubborn compounds (with no predominant atmospheric stripping) depends on tight control of the biological purification unit. Among other parameters, sludge of sufficient age must be maintained (see Chapter 3).

In France, the BOD_5 is governed by the standard AFNOR T 90-103 method.

In France, BOD_5 standards in urban discharge are:

- For MWW undergoing normal treatment (level IV), mean BOD_5 over 24 hours less than or equal to $30 \text{ mg} \cdot \text{l}^{-1}$, or over 2 hours less than or equal to $40 \text{ mg} \cdot \text{l}^{-1}$.
- For refinery WW, mean BOD_5 less than or equal to $30 \text{ mg} \cdot \text{l}^{-1}$ for a hydroskimming plant, or less than or equal to $40 \text{ mg} \cdot \text{l}^{-1}$ for a complex refinery.

1.4.1.3 Chemical oxygen demand (COD)

COD is measured by the oxygen consumption of a hot refluxing potassium dichromate solution in two hours. It represents most of the organic compounds present and the oxidizable mineral salts such as a number of sulfur compounds. In MWW, the COD/ BOD_5 ratio is around 2 to 2.6.

After the sample has settled for two hours and the settled SS have been separated out, the COD measurement of the water decanted for two hours is called COD_{AD} and corresponds to the COD of the dissolved and colloidal material alone (COD_{AD}/BOD_5 ratio is around 1.46 in MWW).

Some nitrogen compounds (mainly ammonium salts and urea) are not covered by this measurement.

In France, the COD is set out in the standardized AFNOR T 90-101 method.

COD standards for discharge in France are:

- For MWW undergoing normal treatment (level IV), mean COD less than or equal to $90 \text{ mg} \cdot \text{l}^{-1}$, and over two hours less than or equal to $120 \text{ mg} \cdot \text{l}^{-1}$.
- For refinery WW, COD less than or equal to $120 \text{ mg} \cdot \text{l}^{-1}$ for a hydroskimming plant or $150 \text{ mg} \cdot \text{l}^{-1}$ for a complex refinery or one that has a catalytic cracker.

When water is discharged into protected lakes or rivers, some countries may require a maximum COD of $60 \text{ mg} \cdot \text{l}^{-1}$, which is very hard to comply with using routine processes.

The COD measurement sensitivity is approximately from 10 to 15 $\text{mg}\cdot\text{l}^{-1}$, but over 50 $\text{mg}\cdot\text{l}^{-1}$, there is only about a 10% accuracy rate.

Chlorides, oxidizable into chlorites, must first be precipitated by mercury sulfate as soon as their concentration rises above 2 $\text{g}\cdot\text{l}^{-1}$. A number of precautions must be taken in handling.

COD/reducing agent equivalences

In the same way as the specific BOD_5 of a number of different organic compounds is established (see Table 6), the COD equivalence of reducing inorganic compounds can be measured (see Table 5). These tables should be considered as mere guidelines due to possible vagaries in sampling and actual procedure conditions.

These COD correspond fairly well to the calculated theoretical oxygen demand (TOD), except for urea (2.4), the SCN^- (2.2) and the cyanides (2.9).

The TOD of a compound stands for the theoretical O_2 consumption required to oxidize it into CO_2 , H_2O , SO_4 , PO_4 and NO_3 .

Table 5
COD equivalence of inorganic
reducers

Compound	Ion	COD ($\text{mg O}_2\cdot\text{mg}^{-1}$)
Sulfide	S^{2-}	2
Sulfur	S_0	1.5
Thiosulfate	$\text{S}_2\text{O}_3^{2-}$	0.57
Tetrathionate	$\text{S}_4\text{O}_6^{2-}$	0.5
Sulfite	SO_3^{2-}	0.2
Thiocyanate (sulfocyanide)	SCN^-	0.6-1.5
Cyanide	CN^-	1-2.9

Table 6

TOD, COD and BOD₅ equivalence of oxygenated compounds (mg O₂ per mg of compound)

Compound	TOD	COD	BOD ₅	TOC (mg C · mg ⁻¹)
Acids				
Formic acid	0.35	0.35	0.25	0.26
Acetic acid	1.06	1.0	0.8	0.4
Benzene-sulfonic acid	1.62	1.5	0.05	0.45
Aldehydes				
Formaldehyde	1.07	1.06	0.6-0.8	0.4
Acetaldehyde	1.82	1.8	1.3	0.54
Benzaldehyde	2.42	1.9	1.5	0.79
Furfural	1.66	1.6	0.3-0.8	0.62
Alcohols				
TBA	2.59	2.2	—	0.64
Isopropanol	2.4	2.2	1.2	0.6
Methanol	1.5	1.4	0.9	0.37
Ethyleneglycol	1.3	1.29	0.8	0.39
Amines				
MEA (monoethanolamine)	2.49	1.3-2	0.8-1	0.39
DEA (diethanolamine)	2.13	1.6	0.2-0.4	0.46
Phenols				
Phenol	2.4	2.3	1.8	0.76
Cresols	2.52	2.4	1.6-1.8	0.78
Miscellaneous				
MEK	2.44	2.3	1.5-1.8	0.66
Acrylonitrile	3.17	1.4	0.7	0.68
Caprolactame	2.1	0.6	0.4	0.64
Ethylene oxide	1.82	1.74	0.1	0.54
Propylene oxide	2.21	1.8	0.2	0.62
Isopropylether	2.8	1.5-1.7	0.2	0.7
MTBE	2.72	2.5	—	0.68

The COD in refinery WW

The COD varies depending on the nature of the effluent and obviously according to the treatment stage.

In spent caustic soda, the COD mainly comes from sulfides, mercaptans and phenols, with hydrocarbons (HC) as secondary coexisting components. After an air or O₂ oxidation treatment, most of the residual COD is due to the thiosulfates formed or to slightly oxidized phenols.

In deballasting water, the COD is chiefly due to HC but measurement is made more difficult by the strong presence of Cl^- .

In a FCC condensate, the COD is due to sulfides and phenols, whereas in a steam cracking condensate, it can be due mainly to aldehydes and acetic acid.

The aryl or alkyl sulfonates are also sources of COD in complex refineries.

In order to define how this COD can be reduced, it is necessary to know the relationship between a number of families of reducing compounds and a fraction of the total COD. In this connection, the TOD (theoretical demand), COD and BOD_5 equivalence tables for some common compounds can be used.

Table 6 for oxygenated compounds and Tables 7 and 11 for hydrocarbons can be used with Table 5 for sulfur compounds.

Table 7

TOD and COD equivalence for some hydrocarbons (mg O_2 per mg HC)

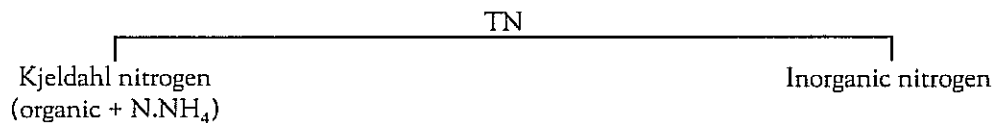
Hydrocarbon	TOD	COD
n-hexane	3.5	<0.2
n-heptane	3.52	<0.2
d-decane	3.36	<0.8
n-hexadecane	3.46	2-2.2
Cyclohexane	3.42	1.8-2
Benzene	3.07	2-2.8
Styrene	3.07	2.6-2.8
Toluene	3.12	1.4-1.8
Xylene	3.12	2.5-2.9

The HC particularly involve COD equivalences that are fairly dependent on handling conditions and BOD_5 equivalences that are even more difficult to pin down (see paragraph 1.4.2.1).

As hydrocarbons increase in reactivity with H_2SO_4 , the COD obviously increase accordingly. Thus, the paraffinic hydrocarbons C_4 to C_{10} , which are relatively nonreactive and volatile, exhibit very low COD. They are lower than the BOD_{30-35} (see Table 11) or the TOD of these compounds.

1.4.1.4 Nitrogen compounds

This parameter is becoming increasingly important. The total content in WW, termed TN, covers all possible forms:



The Kjeldahl nitrogen content in MWW discharged into the environment is limited in France to $40 \text{ mg}\cdot\text{l}^{-1}$ over 24 hours or $50 \text{ mg}\cdot\text{l}^{-1}$ over two hours at the normal NK1 level. However, because nitrates are increasingly present in surface waters, there is a tendency to enforce tougher levels, such as the NK2 level, of $10 \text{ mg}\cdot\text{l}^{-1}$ N over 24 hours.

There are specific requirements for refinery WW. They involve the NH_4 ion and vary from 10 to $100 \text{ mg}\cdot\text{l}^{-1}$ depending on the regulations.

The standardized measurement in France is the AFNOR T 90-015 method (acidimetry after distillation applicable to concentrations of over $4 \text{ mg}\cdot\text{l}^{-1}$ of $\text{N}\cdot\text{NH}_4$).

In refinery WW, the NH_4^+ ion is the most common nitrogen compound. Other nitrogenated forms occur in lower concentrations (SCN^- , CN^- and amines).

Depending on the type of production in petrochemical plants there can also be high urea concentrations which exhibit zero COD.

NH_4^+ has two major origins in refining:

- Injection of NH_3 at the top of the fractionating column to neutralize potential H_2S . It forms HSNH_4 .
- Hydrogenation of organic nitrogen when the crude is refined. It initially forms NH_4OH .

The most NH_4 -rich effluents are FCC condensates. The volatility of weak acid salts, HCO_3^{2-} and HS^- , facilitates preprocessing of the condensates by steam or flue gas stripping.

1.4.2 Parameters specific to the oil industry

Table 8 lists the main pollutants involved in oil industry WW. It is necessary to know a number of chemical and physical properties of three main families of these pollutants (HC, sulfur compounds and phenols) as well as the methods for measuring them so that treatment can be understood.

Table 8

Oil industry pollutants

Insoluble	Dissolved
Aliphatic HC	Aromatic HC
	Sulfides
	RSH
	Oxygenated compounds
	Phenols
	Acids
	Aldehydes
	Nitrogen compounds
	NH_4
	Amines
	Urea
Clays	
Sands	
CaCO_3	
	Salts, alkalinity
	NaCl
	$\text{S}_2\text{O}_3^{2-}$
	F^-

1.4.2.1 Hydrocarbons (HC)

These C_nH_m compounds have a number of properties. They are apolar or relatively apolar and have variable solubility in water. Furthermore they can react to a greater or lesser degree with sulfuric acid and are therefore COD titrated to a greater or lesser extent. Their biodegradability is also variable and still not very well understood. The volatility of some of them affects the COD measurement. The way they behave in water can be summed up by the PNOA classification shown in Table 9.

Table 9

Hydrocarbon behavior

		H_2SO_4 reactivity	Solubility in water
P	Paraffinic $C_n H_{2n+2}$ - CH_3	Not very reactive	Insoluble
N	Cycloparaffinic $C_n H_{2n}$ - CH_2	Fairly unreactive	Relatively insoluble
O	Olefinic Cycloolefinic - CH_2	Reactive	Not very soluble
A	Aromatic - CH	Very reactive	Very soluble

A. Solubility

Table 10 shows the almost zero solubility of paraffinic HC and the considerable solubility of aromatic HC. These are maximum solubilities under cold conditions and after energetic stirring (see work by Clayton McAuliffe). In the warm and highly aerated effluents in catch drains, the maximum existing values are much lower.

Table 10

Solubility of some hydrocarbons of various molecular weights and types

	Solubility in $mg \cdot l^{-1}$		Solubility in $mg \cdot l^{-1}$
Paraffins		Olefins	
Isopentane	48	Ethene	131
n-hexane	9.5	Propene	200
Trimethylpentane -2,2,4	2.5	Hexene-1	50
n-octane	0.7	Aromatics	
Cycloparaffins		Benzene	1780
Cyclopentane	156	Toluene	515
Cyclohexane	55	o-xylene	175
Cyclooctane	7.9	Ethylbenzene	152

B. COD and BOD₅ equivalence for hydrocarbons

The difficulty in measuring these two general parameters in oily water has been pointed out. They were studied by Zobell (1964) and Baker. BOD measurements carried out over 35 and five day periods show how slow biodegradation is. However, specific seeding and increased age of biological sludge can help control the process.

Table 11

Physical characteristics and TOD, COD and BOD₃₀ (mg per mg) equivalences for some hydrocarbons

Hydrocarbons	Boiling pt (°C)	sp-gr. (20°C)	TOD	COD	BOD ₃₀₋₃₅
Paraffinic					
Ethane			3.73		2.4
n-hexane	68	0.67	3.5	<0.2	2.5
n-heptane	98	0.69	3.52	<0.2	2-2.5
n-hexadecane	285	0.78	3.46	2-2.2	2.8
Cycloparaffinic					
Cyclohexane	80	0.79	3.42		2.3
Aromatic					
Benzene	80	0.88	3.07	2-2.8	1.2-1.9
Ethylbenzene	136	0.87	3.16		
Styrene	145	0.9	3.07	2.6-2.8	
Toluene	110	0.87	3.12	1.4-1.8	1.5
Xylene	140	0.9	3.12	2.5-2.9	
Naphthalene	217	1.1	2.99	2-2.4	1.92

C. Measuring HC

Measuring HC is difficult for several reasons:

- Sampling is hard to control, especially when the water sample is not taken from pressurized piping or when it is conveying a heavy oil load.
- There are a large number of standard or standardized methods with their own operating procedures. Some procedures are chosen for application under given regulations and can be ill-suited for monitoring industrial facilities.
- There is interference by polar compounds when infrared methods are used and by miscellaneous organic matter when extraction and gravimetry methods are used.

Table 12 shows the three kinds of method which are the most common. The last two in particular are widespread in the refining and petrochemical industry and as such should be granted special attention.

Table 12

Quantitative analysis of hydrocarbons

Determination by direct extraction

(used for measuring many types of organic matter besides hydrocarbons)

	Solvent
API 731 53	Benzene
ASTM XII	Petroleum ether
H17-18 No. 1	Petroleum ether

Determination by indirect extraction

AFNOR T 90-202	Aluminum sulfate/hexane
DIN 17 118 No. 1	Aluminum sulfate/petroleum ether
HMSO	Magnesia/petroleum ether
API 732-53	
EPA	Diatoms - Hexane

Determination by infrared

	Wavelength (μm)	Florisil	Threshold
AFNOR T 90-203	- 3.42	yes	
CONCAWE	- 3.38 and 3.42	yes	$0.1 \text{ mg}\cdot\text{l}^{-1}$
API 733-58	- 3.42 and 3.5	no	$1 \text{ mg}\cdot\text{l}^{-1}$
DEV H 17/18 No.4	- 3.29, 3.38 and 3.42	yes	
AFNOR T 90 -114	- dito and 3.5	yes	$0.5 \text{ mg}\cdot\text{l}^{-1}$

Methods by indirect extraction

The principle is that they absorb insoluble HC on a massive metallic hydroxide floc or on diatoms. The HC are then extracted by a solvent and once the solvent has been evaporated, a gravimetric measurement is made.

This method reproduces a physicochemical HC treatment process with redundancy and is accordingly suited to monitoring this type of process. When the treatment process is efficiently run, it should leave only a few milligrams per liter of HC in the floated or filtered water.

In fact depending on the country, requirements of $5 \text{ mg}\cdot\text{l}^{-1}$ (from 3 to 10) can be related to these methods.

The drawback can be the measurement of organic matter that in some cases leads to overestimating the HC in raw nonfloculated clarified water.

In contrast, in some official standards the oven drying time is not specified and leads to underestimating the HC that may be volatilized or oxidized.

Methods by infrared spectrophotometry

The principle is to extract the HC directly by a solvent, CCl_4 or more recently freon. Then any polar OM that was extracted at the same time may be separated out. Concentrations corresponding to distinguishable wavelength absorptions are then read by spectrophotometry (see Fig. 3):

- CH groups 2850 cm^{-1} or $3.5 \mu\text{m}$
- CH_2 groups 2920 cm^{-1} or $3.42 \mu\text{m}$
- CH_3 groups 2960 cm^{-1} or $3.38 \mu\text{m}$
- CH aromatic groups 3040 cm^{-1} or $3.30 \mu\text{m}$.

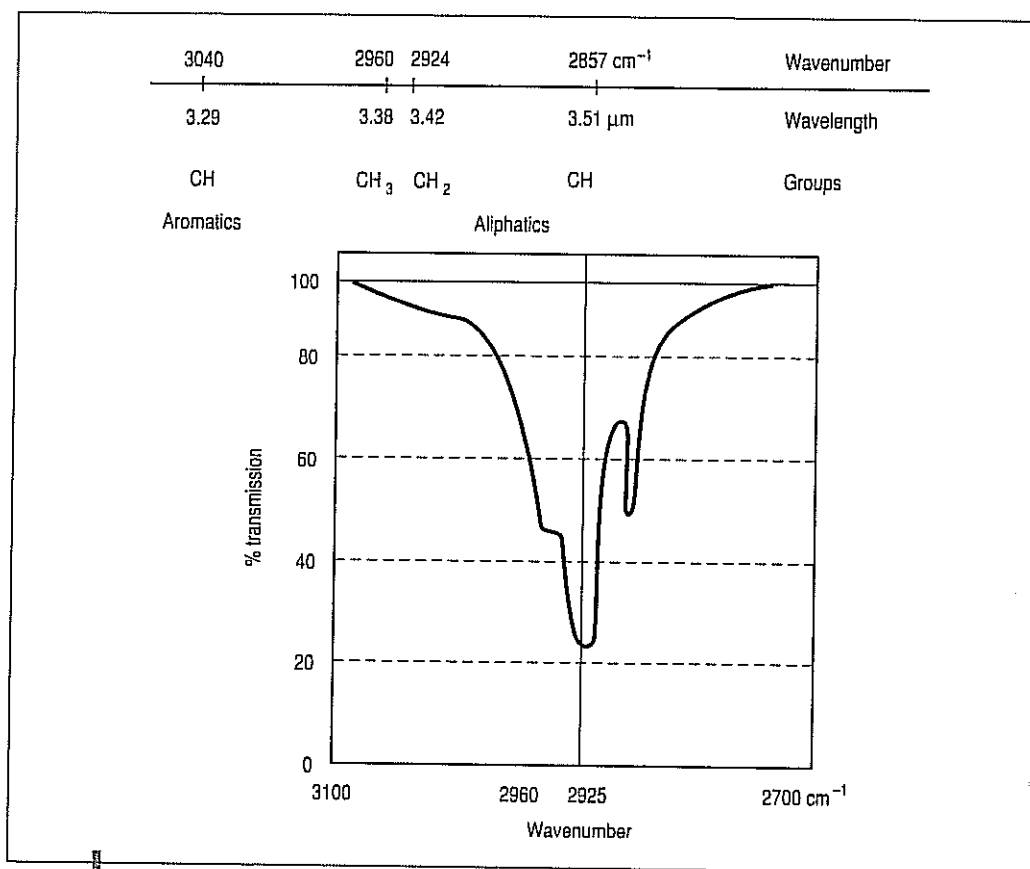


Fig. 3 IR Quantification of hydrocarbons

Percolating the solvent in a Florisil or diatom adsorbent column generally eliminates from 10 to 30% of the polar compounds. At the same time it can also remove a fraction of the HC. Fig. 4 shows two exceptional examples (with the standard Florisil load quadrupled).

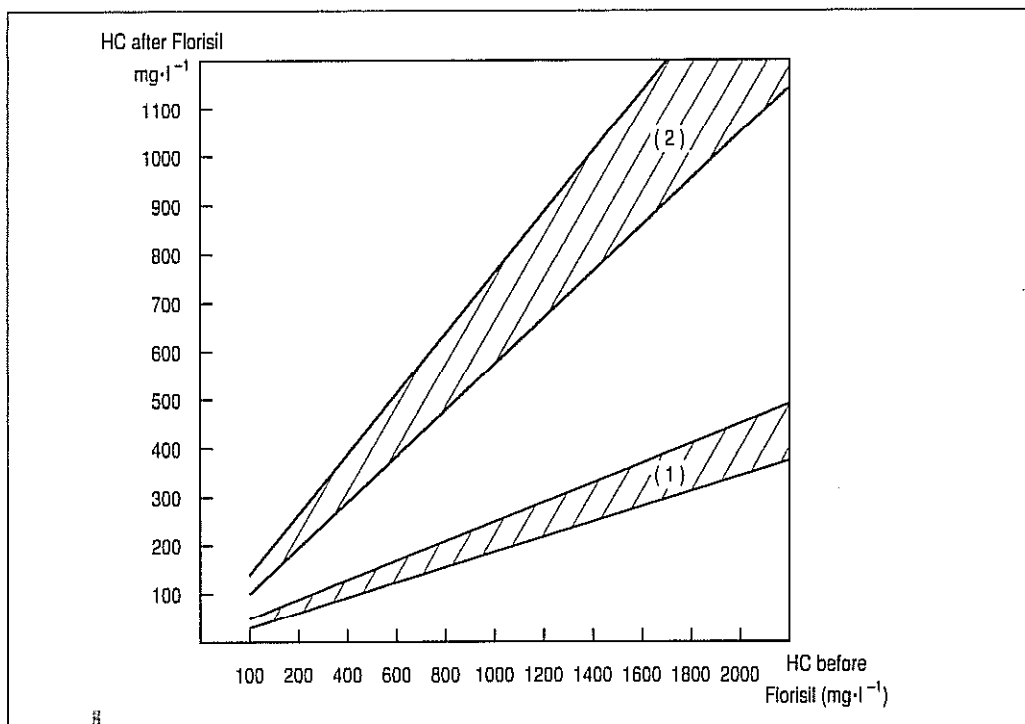


Fig. 4 Lower IR HC readings after Florisil for emulsions of two naphthenic crudes

Numerous methods are used around the world and are published in an exhaustive list by CONCAWE. ("Determination of hydrocarbons in aqueous effluents from the oil industry"). However, the methods:

- Do not all specify removal of polar compounds prior to reading results.
- May call for reading only one or two peaks and as a result express only part of the HC that are present.
- Perform calibration based either on slopes or on standard solutions that are widely different as to their aromatics content.

The end result is that any statement of HC content in a publication should always define the measurement method that was used.

The choice of methods to be used is in fact clear:

- The method for monitoring discharges is determined by legislation, whose severity can decrease in accordance with the scope of the method. For example, in France the AFNOR T 90-203 method which reads a CH_2 peak at $3.42 \mu\text{m}$, corresponds to a standard of $20 \text{ mg}\cdot\text{l}^{-1}$ of HC. Meanwhile, the AFNOR 90-202, whose scope is limited to insoluble HC, requires a standard of $5 \text{ mg}\cdot\text{l}^{-1}$.
- For monitoring the different steps in treatment alone, it may be of interest to know how the different fractions of HC vary. In this instance, the following methods can be used:
 - In physicochemical treatment, the second main type of methods (e.g. AFNOR T 90-202).
 - In biological purification, where the HC are chiefly dissolved, a spectrophotometric method specifying a reading of all the peaks (e.g. AFNOR T 90-114).
 - If the only point is to know dissolved aliphatic HC, the AFNOR T 90-203 is indicated as an initial approach.

Test reference	(t1)	(t2)	(t3)	(t4)	(t5)
Method	API Method 733-58	DEV H 17/18 1971	CONCAWE	Unichim 1975	NBN T91502 (1977)
Matter revealed	hydrocarbons, hydrocarbon derivatives, all substances with CH, CH ₂ , CH ₃ groups	hydrocarbons	hydrocarbons, or hydrocarbon derivatives of any kind	mineral oils	hydrocarbons
Minimum Determinability (ppm)	1	0.1	0.1	0.5	0.2
Sample volume (l)	3	1	3	variable	1
pH Adjusted to	5		5	5	5
Extraction Solvent	CCl ₄	CCl ₄	CCl ₄	CCl ₄	CCl ₄
Boiling point (°C)	77	77	77	77	77
Volume (ml)	100 + 100	25	50	50	50
Extraction in	original container	original container	original container	original container	original container
By means of	shaking machine 100 strokes/min. ampl: 3.8 cm	mechanical stirrer	shaking machine 100 strokes/min. ampl: 3.8 cm	hand or shaking machine 100 strokes/min.	magnetic stirrer (4 cm long)
For	15 min	30 sec	15 min	15 min	15 min
Chromatographic Adsorbent		Florisil added	Florisil added	Florisil added	Florisil
Column diam (cm)					1
Height of filling (cm)					5 - 6
Quantity (g)		1	5	5	
Matter removed		non-hydrocarbons	most of the non-hydrocarbons	non-hydrocarbon-aceous polar organic compounds	polar components
Wavelength (µm)	3.42 3.50	3.30 3.38 3.42	3.38 3.42	3.38 3.42	3.30 3.38 3.42
Groups detected	CH ₂ CH ₂	CH CH ₃ CH ₂	CH ₃ CH ₂	CH ₃ CH ₂	CH CH ₃ CH ₂
Calibration	known oil or reference oil (37.5%) iso-octane 37.5% cetane 25% benzene)	typical spec. absorptivities for CH, CH ₃ , CH ₂ bands	known oil or typical absorptivities (one normal, one for gasoline)	known oil or typical absorptivities (one normal) one for gasolines)	typical absorptivities for CH, CH ₃ , CH ₂
Accuracy	about ± 10% known oil; ± 20% ref. oil; essentially undetected benzene, xylene, cumene	not suitable for highly aromatic products, such as tar oil and aromatic extract	in the case of gasolines less accurate values are to be expected		less suitable for highly aromatic hydrocarbons

st: overall (total) standard deviation

so: single operator standard deviation

a) The information contained in this table has been reported as stated in the texts of the individual methods.

No attempt has been made to amend it, if it appears inconsistent in some cases.

Summary of IR measurements for HC in water.

(CONCAWE, The Hague, March 1984)
Report 1.84

Test reference	(t5)	(t6)	(t7)	(t8)	(t9)
Method	EPA 1978 418.1	IMCO 1978	AFNOR T 90-203/79	Paris Commission 1979	Swedish Standard SS028145 (1979)
Matter revealed	petroleum hydrocarbons inclusive of light fuels	oil, inclusive of most light oil fractions	total hydrocarbons	oils, including most light fractions	most components in mineral oil, some org. solvents petr. based part of greases, petr. based waxes
Minimum Determinability (ppm)	≤1	0.1		0.1	0.1
Sample volume (l)	1	1	0.9	1	1 - 2
pH Adjusted to	<2	≤2	5	<2	<2
Extraction Solvent	Freon 113	CCl ₄ (other)	CCl ₄	CCl ₄ / Freon 113	CCl ₄
Boiling point (°C)	48	77	77	77 / 48	77
Volume (ml)	30 + 30 + 30	50 + 50	50	50 + 50	50
Extraction in	separatory funnel	separatory funnel	original container	separatory funnel	separatory funnel
By means of	hand	hand	magnetic stirrer (4 cm long)	hand	shaking
For	2 min	2 min	15 min	2 min	60 min
Chromatographic Adsorbent	silica gel added		Florisil		Al ₂ O ₃
Column diam (cm)				1	1
Height of filling (cm)					10
Quantity (g)	3		5		
Matter removed	animal greases and vegetable oils		other organic non-hydrocarbon matter		separate detmn. humic substance; high molecular aromatics; deter- gents, veg. fats, fatty oils; saponifiable grease; lactic fat, glycols, alco- hols, ketones
Wavelength (µm)	3.41	3.41	3.42	3.41	3.38 3.42
Groups detected	CH ₂	CH ₂	CH ₂	CH ₂	CH ₃ CH ₂
Calibration	known oil or reference oil (37.5% iso- octane 37.5% cetane 25% chloro-benzene)	known oil	known oil	known oil	known oil or reference oil (37.5% iso- octane 37.5% cetane 25% benzene)
Accuracy	loss of about half of any gasoline present can be expected	some loss of volatile components will occur		some loss of volatile components will occur	± 5-10% if hydrocarbon mixture is used; ± 30-40% in extreme cases

(CONCAWE, The Hague, March 1984)
Report 1.84

Methods by ultraviolet quantification

These methods are not common in Europe but some are nevertheless being developed (automated systems). Some knowledge of the methods is recommended, especially since there is a risk of confusing two very different analytic techniques, UV fluorescence and UV absorption.

The method by fluorescence measures the fluorescent light reemitted by fluorescent particles at a 90° angle. Detected HC may be in a solution or in an emulsion. The main substances measured are heavy HC ($C > 6$) that can be present in heating condensates, but also OM. According to this principle, automated systems can monitor condensates and cutting oils at concentrations between 0.1 and 500 $\text{mg}\cdot\text{l}^{-1}$ of HC that do not fall into the category of light fractions (see Chapter 6).

In contrast, UV absorption at 254 nm measures light aliphatic or aromatic HC from C_3 to C_6 at concentrations between 0.3 and 20 to 30 $\text{mg}\cdot\text{l}^{-1}$ maximum. Dissolved OM and SS can also interfere.

The areas where these two UV methods can be used are therefore relatively restricted.

D. Polyaromatic hydrocarbons (PAH)

Some national legislations limit the PAH content in industrial discharges as these compounds are highly carcinogenic. Since there are too many PAH compounds, a list of six as indicated below is considered representative of the potential total PAH:

- Fluoranthene ($C_{16}H_{10}$).
- 3,4 benzofluoranthene ($C_{20}H_{12}$).
- 11,12 benzofluoranthene ($C_{20}H_{12}$).
- 3,4 benzopyrene ($C_{20}H_{12}$).
- 1,2 benzopyrene ($C_{22}H_{12}$).
- 1,2,3 indenopyrene ($C_{22}H_{12}$).

They are extracted by a nonpolar solvent and concentrated by adsorption on a capillary column eluted by a polar solvent. Then their concentration is measured by high-pressure liquid chromatography

Measurement sensitivity varies from 3 to 30 nanograms per liter depending on the compound.

In biologically purified coking plant effluents, which are monitored particularly closely, the commonly detected sum of the six PAH is less than 0.1 $\text{mg}\cdot\text{l}^{-1}$ (but also 0.1 to 0.2 $\text{mg}\cdot\text{l}^{-1}$ of naphthalene).

E. Chlorinated solvents

These solvents chiefly include trichlorethylene and perchlorethylene. After isooctane extraction, measurement is based on the formation of AgCl , which is reduced under UV rays to colloidal Ag measured by photometry.

F. Humic acids

These compounds are very stable and soluble. They are present in some surface water and a few $\text{mg}\cdot\text{l}^{-1}$ can subsist in biologically treated effluents where they give rise to a residual TOC.

After alkaline hydrolysis for 48 hours, acid-amy alcohol process separation and redissolution, their concentration is measured by colorimeter.

1.4.2.2 Phenols

Phenols and their derivatives indicate industrial WW discharge when they occur in surface water. They are harmful because they form stable addition compounds during chlorination, i.e. chlorophenols. Tiny traces of chlorophenols ($0.1 \mu\text{g}\cdot\text{l}^{-1}$) give treated water a characteristic taste.

In refineries, phenols can be present in massive amounts in spent caustic and, to a lesser extent, in delayed coking effluents. Detailed characteristics of the different phenol compounds are listed in the chapter on spent caustic (see Chapter 4, paragraph 4.1.2.2.C).

Analytically speaking, the following can be distinguished:

- **Phenols that can be carried off by steam**, wrongly termed volatile phenols. They are made up of monohydric or dihydric phenols. They can be titrated by the AFNOR T 90-204 method chosen by French legislation to be applied to refineries (aminoantipyrine colorimetry and extraction in presence of K ferricyanide).
- **Total phenols** which also include heavy compounds that can not be carried off by steam. They can be titrated by bromination when effluents are concentrated enough and have undergone efficient filtration to remove interference-causing oils.

Legislation usually concerns only the phenols in the first category, for which quite low limits are required, i.e. 0.2 to $2 \text{ mg}\cdot\text{l}^{-1}$ (in France 0.5 for hydroskimming refineries and 1 for complex refineries).

Phenol biodegradation

The biodegradability of phenols was still considered debatable in the 1960s. In actual fact, it is good and well controlled in aerobic biological purification as long as the compounds are fed in at a relatively constant rate and there are no coexisting inhibiting agents such as S^{2-} in overly strong concentrations.

In coking plants, ammonia process water containing up to $2.5 \text{ g}\cdot\text{l}^{-1}$ of phenols can be treated directly in this way. The removal efficiency is over 99.5%.

The biodegradation process is thought to be as follows:

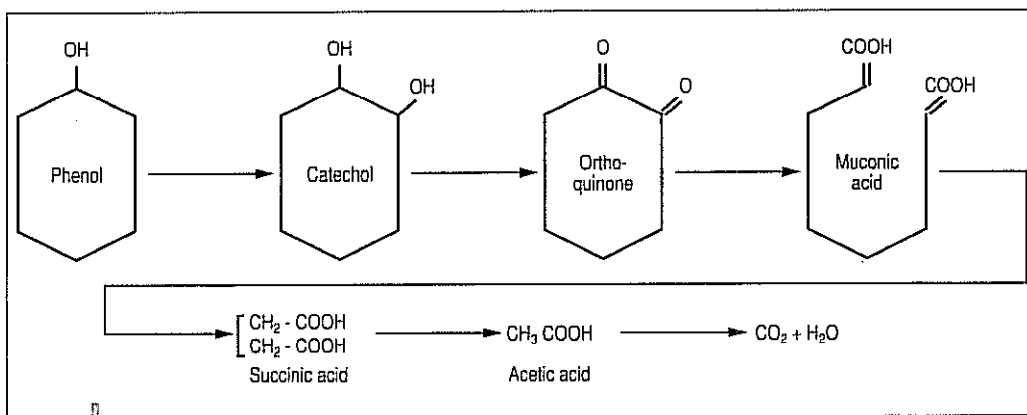


Fig. 5 Aerobic biodegradation of phenols

Anaerobic biodegradation of phenols is possible and is now the subject of development studies. They do not seem applicable to refining and petrochemical plant effluents because concentrations are too low.

1.4.2.3 Sulfides and sulfur compounds

A. Sulfides and mercaptans

Hydrogen sulfide has a strong characteristic smell. It is deleterious because of its corrosivity and toxicity for fish and many bacteria, among other organisms.

When it is released in sewers it indicates putrid anaerobic fermentation that can be monitored by smell or by the methylene blue putrescibility test.

It is present in refinery WW in two forms which come from two sources:

- NH_4HS in FCC condensates.
- Na_2S in spent caustic.

The treatability is different for these two compounds due to the volatility of the first and the high solubility of the second.

Mercaptans, R-SH , are associated with sulfides and present in spent caustic and FCC condensates. These compounds are increasingly volatile in inverse proportion to their molecular weight. They are malodorous in tiny concentrations in the air.

Table 13

Characteristics of some mercaptans

Compound	Boiling Pt.(°C)	Solub. 25°C (g·l ⁻¹)	K _D
CH_3SH methylmercaptan	7	—	—
$\text{C}_2\text{H}_5\text{SH}$ ethylmercaptan	35	15	$4 \cdot 10^{-11}$
$\text{C}_3\text{H}_7\text{SH}$ propylmercaptan	68	2	$3.6 \cdot 10^{-11}$
$\text{C}_4\text{H}_9\text{SH}$ n-butylmercaptan	97	0.1-0.4	$3.5 \cdot 10^{-11}$

Dissociation of sulfides

H_2S is a weak diacid which is solubilized in water in the three forms H_2S , HS^- and S^{2-} :

$$\text{S}_t = (\text{H}_2\text{S}) + (\text{HS}^-) + (\text{S}^{2-})$$

Their hydrolysis is characterized by the two dissociation constants K_D at 25°C:

$$K_1 = \frac{(\text{HS}^-)(\text{H}^+)}{(\text{H}_2\text{S})} = 10^{-7}$$

$$K_2 = \frac{(\text{S}^{2-})(\text{H}^+)}{(\text{HS}^-)} = 10^{-14}$$

The diagram in Fig. 6 shows the equilibria versus the pH. It can be seen that:

- The pH of a solution of H_2S is around 5.
- The pH of a solution of HNaS ranges from 8.8 to 9.8.
- The pH of a solution of Na_2S is about 11.

Mercaptan dissociation is low and corresponds to a dissociation constant of around 10^{-11} . In FCC condensates, the major sulfur component is NH_4HS along with small concentrations of H_2S . In spent caustic, the main components are sodium mercaptides, RSNa , along with the Na_2S sulfide.

Fig. 6 shows the dissociation of methylmercaptan which precedes that of HS^- . It can be seen that a large fraction of CH_3SH is not dissociated at pH values near 11, which are the values for air oxidation treatment. CH_3SH can be carried off by stripping.

Fig. 7 shows an order of magnitude of the relationship between the concentrations of pure solutions of H_2S , NH_4HS , Na_2S and the pH.

Fig. 6
Dissociation of H_2S , HS^-
and CH_3SH at 25°C

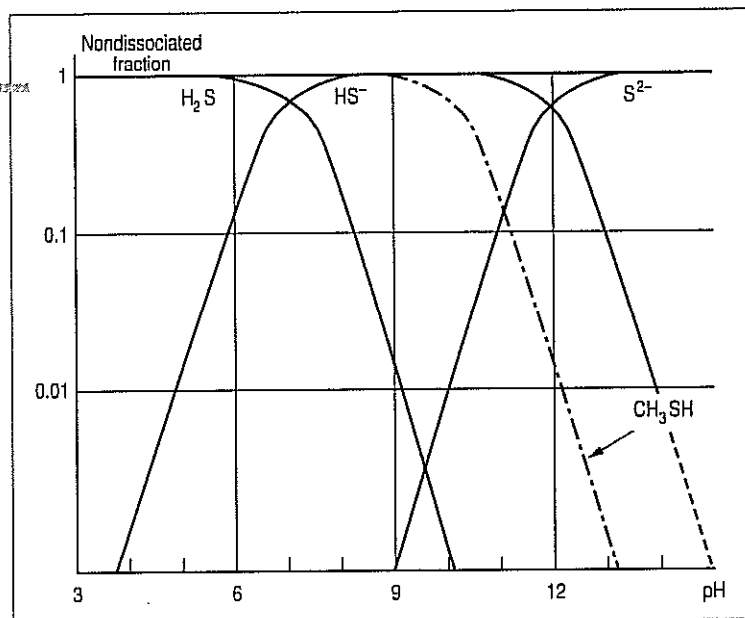
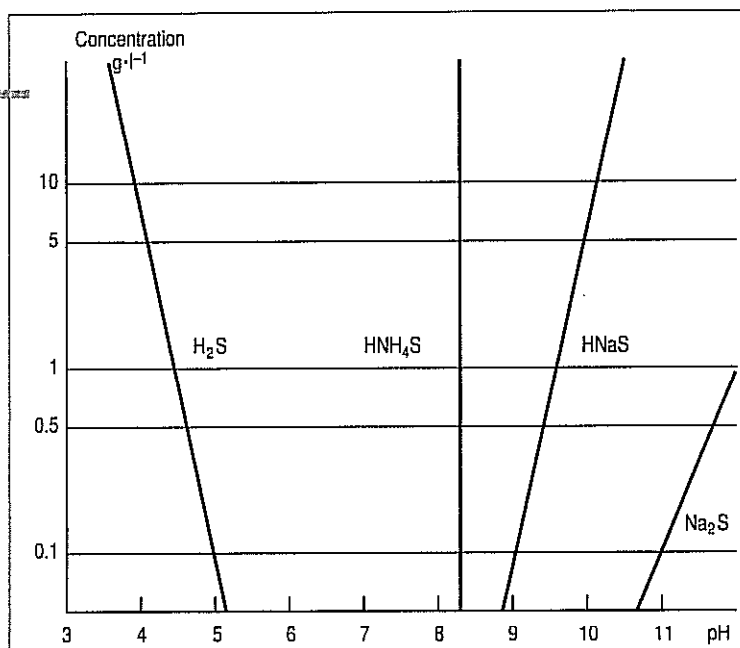


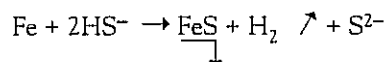
Fig. 7
Relationship between pH
and concentrations of
some sulfides



H₂S corrosion

H₂S can also impact systems of sour condensates and be promoted by the presence of CN⁻ in water phase reflux accumulators.

The corrosion process is due to HS⁻ and, depending on variable coexisting NH₄Cl, can be at a maximum at pH values of 7 to 8:



i.e. in areas where the HS⁻ concentration is high.

The pH must therefore be kept relatively low in these areas, between 5.5 and 6.5, with or without a corrosion inhibitor. FeS, which is hardly soluble in water at all, forms a protective layer whose thickness and stability rise with increasing pH. The layer can be broken down by formation of Prussian blue, Fe(CN₆)⁴⁻, which is soluble in the presence of CN⁻.

B. Thiosulfates and tetrathionates

The oxidation of sulfur compounds is not very well understood due to its complexity (formation of intermediate polysulfides). It is also difficult to analyze the intermediate oxidation products in an industrial facility at least. Some of them should be known:

Thiosulfates (S₂O₃²⁻)

These products, with an oxidation number of 2, can be present:

- Initially in raw spent caustic or in sour condensates in considerable contact with air.
- As a final product of spent caustic oxidation by air, or by oxygen in most industrial facilities which can not provide the residence time, the pressure or the temperature required to get to the SO₄²⁻ stage.

Tetrathionates (S₄O₆²⁻)

These products, with an oxidation number of 2.5, are presented in the literature as the final oxidation stage of thiosulfates in aerobic biological purification where enzymes act to achieve more complete oxidation (autotrophic microorganisms of the thiobacillus thiooxidans type).

C. Analysis of sulfur compounds

Sulfides

Potentiometric method with silver electrode probe and titration of sulfides at a -700 mV level and of mercaptans at a -200 mV level (Fig. 8).

Ways of analyzing other sulfur compounds:

- Conductimetry with barium chloride (conductivity lowered as a function of BaSO₄ precipitation): SO₄²⁻ (in the absence of SO₃²⁻).
- Ion-exclusion chromatography: SO₄²⁻ + SO₃²⁻ and S₂O₃²⁻.
- Iodometry: S²⁻ and after fixing of S²⁻, S₂O₃²⁻ + SO₃²⁻.
- Precipitation with BaCl₂ (turbidimetric measurement): SO₃²⁻ + SO₄²⁻, roughly.

The drawback of several of these methods applied to complex solutions is the risk of interference due to oxidation-reduction reactions occurring at the same time as titration.

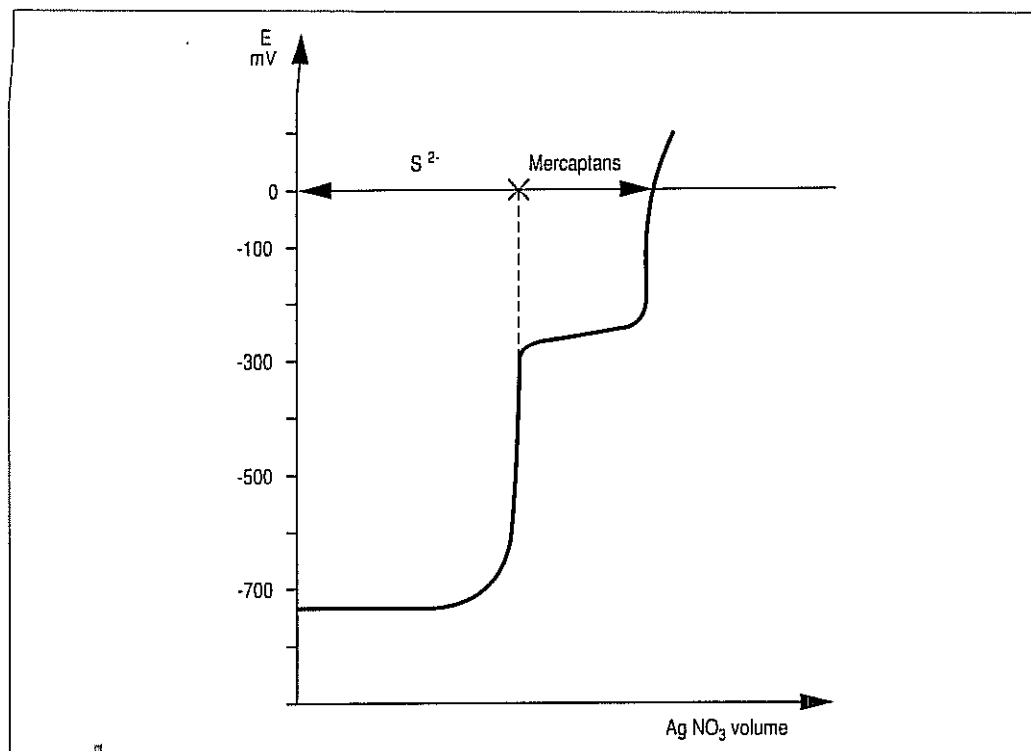


Fig. 8 Potentiometric titration of sulfides and mercaptans

1.4.2.4 M alk in waste water

On the one hand, the methyl orange color change is often hard to see in IWW because of the color or turbidity of the water and must therefore be replaced by potentiometric measurement. On the other hand, titration may involve many other ions besides HCO_3^- or CO_3^{2-} . Among others, there are:

- Sulfur compounds with a reminder of their pK:

$\text{H}_2\text{S} / \text{HS}^-$	7
$\text{HS}^- / \text{S}^{2-}$	13
$\text{H}_2\text{SO}_3 / \text{HSO}_3^-$	1.8
$\text{HSO}_3^- / \text{SO}_3^{2-}$	7.2

- Organic acids, including volatile fatty acids. Their presence interferes partially with M alk measurement. They are themselves measured after hot hydrolysis at pH 3, followed by back titration according to a method specific to volatile fatty acids. Acetic (pK 4.8) and hydrocyanic (pK 9.1) acids are also to be considered, as well as phosphorous and NH_4 compounds.

In FCC condensates and spent caustic, the M alk and P alk have the following meaning:

$$\begin{aligned} \text{M alk} &= \text{HCO}_3^- + \text{CO}_3^{2-} + \text{OH}^- + \text{HS}^- + \text{S}^{2-} \\ \text{P alk} &= \frac{1}{2}\text{CO}_3^{2-} + \text{OH}^- + 0.5\text{S}^{2-} + 0.1\text{HS}^- \end{aligned}$$

Acerates occur in steam cracking condensates and in some formation water.

Bisulfites can be present after flue gas stripping.

1.4.2.5 Naphthenic acids

Naphthenic acid value

Crude oils may contain naphthenic acids which confer an "organic acidity" of greater or lesser degree depending on their origin. This acid number or value is expressed in milligrams of KOH per gram of crude (ASTM D 974 method). The acidity is neutralized at the desalter outlet by injection of caustic.

Some crude oils are known for their high acid number which corresponds to a low API degree:

	mg KOH·g ⁻¹	% asphaltene
• Nigeria	0.5	0.21
• Bachaquero	3.13 (13°API)	8.8
• Tijuana	3.9 (12°API)	7.5
• Marienbronn	2.8 (11.8°API)	5.6

These acids solubilized in the form of sodium salts cause two problems in WW:

1. They interfere with HC quantitative analysis

Because of their -CH₂ groups, they are almost totally read in IR spectrophotometry. Removing them as polar compounds in the specially designed Florisil column is highly dependent on the column height (see Fig. 5).

2. They are difficult to eliminate

Naphthenates, titrating in COD if not in HC, can be removed physicochemically. The process requires acidification to pH5 if not 4 and therefore considerable acid consumption (production WW may titrate a "naphthenic" M alk of 16 to 20 meq·l⁻¹!).

1.5 Interpreting water analyses

1.5.1 Industrial water

1.5.1.1 Sampling

No study can be planned and no make up facility can be monitored on the basis of only one analysis result sheet without knowing the sample-taking conditions, especially for surface water. It is necessary to know:

- The circumstances in which the sample was taken (date, day of the week, dry or rainy season, distance from the river bank and depth).
- The potential sources of pollution upstream (MWW or IWW discharge).
- The river's regime.

Samples of well water need to be taken under pressure to keep the excess CO₂ from escaping as this would throw off the pH. The in situ temperature and pH must be recorded.

1.5.1.2 Ion balance

In addition to the approximations already mentioned in 1.1.3, other approximations or deductions can sometimes not be avoided for industrial water that has been polluted to a certain extent and concentrated by evaporation in cooling towers:

(Na⁺ + K⁺) deduced from the "sum of cations minus TH".
 (HCO₃⁻), (CO₃²⁻) and (OH⁻) deduced from M alk and P alk.

If the presence of NH_4 is suspected, the cation which interferes greatly with treatment must be quantified.

1.5.1.3 Examples of analyses of natural water

The three analyses given below with their ion balances represent the titer changes for raw river water containing some NH_4^+ . After bicarbonate removal, natural concentration occurs in a cooling system which can undergo partial biological nitrification.

	Raw water		Lime softened		Open recirculating (number of cycles 2.5)	
pH	7.3	to 7.9	8.9	to 9.6	6.6	4.0
Conductivity ($\mu\text{S}\cdot\text{cm}^{-1}$)	500	to 2000	500	to 2000	1000	to 3000
OM ($\text{mg}\cdot\text{l}^{-1}\text{ O}_2$)	20	to 50	16	to 40	—	—
P alk	0	0	6	to 9	0	0
Anions						
M alk	15°	28.5°	10°	15°	5.5°	0
Cl^-	12°	100°	12°	100°	35°	250°
SO_4^{2-}	10°	26°	12°	28°	30°	70°
NO_3^-	0	0.5°	0	0.5°	7.5°	21.25°
Cations						
Ca content	24°	100°	11°	93°	28°	232.5°
Mg content	4°	5°	4°	0.5°	10°	1.25°
$\text{Na}^+ + \text{K}^+$	6°	30°	16°	30°	40°	75°
NH_4^+	3°	20°	3°	20°	0	30°
H^+	—	—	—	—	0	2.5°
TDS	37°	155°	34°	143.5°	78°	341.25°

In practice, secondary reactions develop and actual changes are a little different. There is a more marked acidification with nitrification, while in alkaline pH there is possible precipitation of CaCO_3 which slows down the rising M alk.

1.5.2 Refinery waste water

Three problems arise:

- Getting representative samples.
- Preserving samples.
- Assessing pollution.

1.5.2.1 Representative sampling

■ Free HC

The free floating HC phase gets to the sewers intermittently depending on hydraulic surges (slugs) and malfunctions. An estimate of free HC can be established only a posteriori and incompletely by weekly or daily reports on volumes of oil removed from gravity separators (water-in-oil emulsions) minus the water content (+5 to 50%). The HC remaining after the separators, considered to be in chemical emulsion, can reliably be estimated based on mean daily samples which then become representative.

■ Accidental discharge of soluble pollutants

Although refinery processes are continuous, some production streams give rise to accidental and irregular discharges sometimes during the night. They may escape detection by continuous or spot sampling when they occur too far upstream from the drainage system. Sample-taking over a 24-hour period may not be indicative of the maximum accidental pollution levels much farther upstream. Subsequent dilution and mixing with other pollutants then make it difficult to identify and quantify the accident rapidly and the officer in charge can not react. Wherever these risks exist, it is advisable to provide surge tanks immediately downstream or perform separate hourly sampling closer to the critical area.

1.5.2.2 Preserving samples

This problem mainly affects petrochemical effluents. A large proportion of refinery WW is relatively sterile and takes a long time to seed because of its high pH (spent caustic) or its origin (condensates). In some particular units (lubricating oils) or in petrochemical plants (urea, acetic acid, aldehydes), anaerobic or aerobic fermentation can develop. As a result, strict conditions must be enforced for preserving samples between sample-taking and analysis.

1.5.2.3 Pollution assessments

Ion balances are obviously seldom feasible in refinery WW since many pollutants are of organic origin and not ionized much if at all. It is still necessary to proceed to an overall evaluation of pollutant families. This can be done for HC, for sulfur compounds and for the COD.

Hydrocarbons:

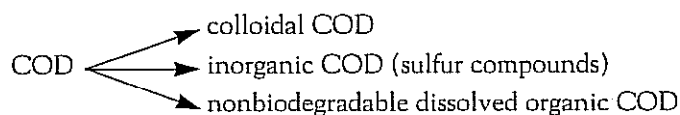
$$\begin{aligned} & \text{Total hydrocarbons (AFNOR T 90-114)} \\ & = \text{insoluble HC (AFNOR T 90-203) + soluble HC} \end{aligned}$$

Sulfur compounds (see paragraph 1.4.2.3.C):

$$S_{\text{total}} \cong \text{SO}_4^{2-} + \text{S}_2\text{O}_3^{2-} + \text{S}^{2-} + \text{HS}^- + \text{H}_2\text{S}$$

COD:

In order to lower the COD to standards that may go down to $50 \text{ mg} \cdot \text{l}^{-1}$, (often a difficult job) its nature must first be understood. After physicochemical and biological treatment of WW, the COD can be broken down into three categories:



Colloidal COD corresponds to flocculable OM and colloids remaining after biological sludge has undergone secondary settling. This settling process is often of poor quality, especially in petrochemical plants. Colloidal COD can be measured by the decrease in COD achieved after massive coagulation by an inorganic coagulant (Al^{3+} or Fe^{3+}) (for example with 50% FeCl_3 , from 100 to $500 \text{ mg} \cdot \text{l}^{-1}$), and after the resulting floc has settled out. In petrochemical plants, decreases of 40 to $60 \text{ mg} \cdot \text{l}^{-1}$ of COD can be achieved in this way, thereby justifying a tertiary treatment.

Nonbiodegradable dissolved organic COD corresponds to macromolecular OM that is unaffected by biological purification (e.g. sulfonates and naphthenates). It can be measured by slow percolation (space velocity of 2) on granular activated carbon (GAC).

Inorganic COD of sulfur compounds that may have withstood biological purification ($S_2O_3^{2-}$, $S_4O_6^{2-}$) should represent residual COD after filtration on granular activated carbon. It can be titrated by ion-exclusion chromatography.

1.6 Main reactions during chemical treatments

1.6.1 Precipitation reactions

These are reactions that form a compound that is insoluble in water. The most common are precipitation of Mg and Ca bicarbonates (carbonate removal by lime), of di- and trivalent metals in the form of hydroxides and of sulfides. Precipitation of $CaSO_4$ or $CaFe_2$ are uncommon in refineries, but possible in petrochemical plants.

1.6.1.1 Precipitation of Al and Fe metallic hydroxides

Precipitation occurs simultaneously with the use of inorganic coagulants (iron and aluminum salts) during clarification of surface water and physicochemical treatment of oily water.

The dispensed coagulant is dissociated and ionized into metals that instantly precipitate as hydroxides if the water has the required alkalinity, whether natural (1) or added (2):

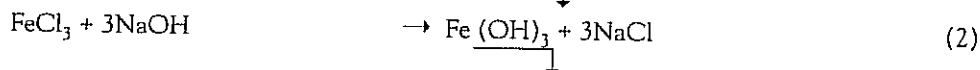
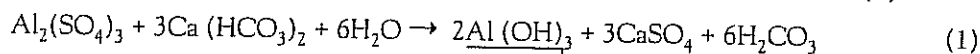


Table 14

Mass of inorganic coagulant and of precipitated hydroxide when 1° of m^{n+} is added

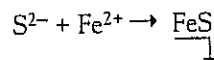
Inorganic coagulant	mg·l ⁻¹	Crystalline form	Mass of coagulant (mg·l ⁻¹)	Mass of precipitated hydroxide (mg·l ⁻¹)	Optimum pH
Al ³⁺	1.8	18H ₂ O	21.7	2.7	6-7.5
Fe ³⁺	5.6	6H ₂ O	26.5	10.1	>5
Fe ²⁺	3.7	7H ₂ O	18.3	5.9	<8.5

Table 14 shows the impact of adding one degree of coagulant metal on the production of hydroxide sludge.

In surface water clarification, the added $FeCl_3$, $6H_2O$ can be 25 to 50 mg·l⁻¹. Doses two to three times greater are involved in flocculating oily emulsions. From 1 to 6° of alkalinity can be "consumed" in this case and the pH must be kept neutral.

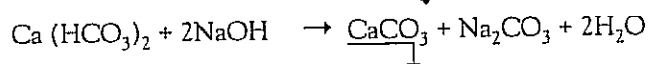
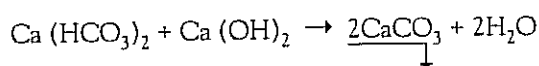
Hydroxides are relatively insoluble and in their optimum range dissolved residual traces of the Fe and Al metals may remain lower than 1 mg·l⁻¹.

1.6.1.2 Precipitation of iron sulfide



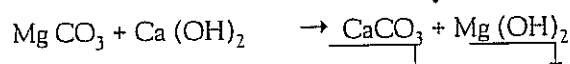
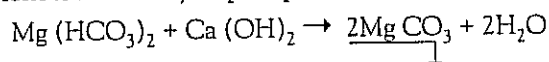
FeS is a black colloidal precipitate that can not readily be settled out. It is difficult to flocculate and generally requires coprecipitation of an analogous mass of metallic hydroxide by addition of an iron or aluminum salt

1.6.1.3 Precipitation of M alk during bicarbonate removal from water by lime or caustic



CaCO₃ is a precipitate made up of elementary crystals a few micrometers in size, but crystallization develops very quickly and heterogeneously. Though the whole of the precipitate agglomerates and settles out very fast, a fraction of the crystals remain in suspension and must be flocculated by the addition of an inorganic coagulant (a few milligrams of the metal per liter). The settling velocity of the whole precipitate then accelerates.

The magnesium content is also likely to precipitate out during bicarbonate removal:



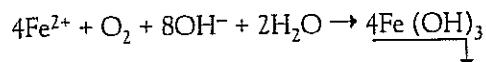
Mg carbonate is in fact relatively soluble (about 65 mg·l⁻¹). The precipitated magnesia, Mg(OH)₂ itself behaves like a coagulant. When carbonates are removed from magnesium-rich water, it is often unnecessary to add a metallic coagulant.

1.6.2 Oxidation-reduction reactions (redox)

These reactions are between the oxidized or reduced form of an ion and the reduced or oxidized form of an opposed ion. The opposed ion is added during treatment to turn the first one into a nontoxic or precipitable product.

1.6.2.1 Examples of redox reactions in make up water treatment

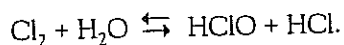
■ Iron removal: oxidation of Fe²⁺ into Fe³⁺ by the oxygen contained in air:



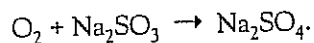
The reaction consumes alkalinity which is generally provided in sufficient amounts by the M alk of the water.

The treatment is usually purely chemical, but under particular conditions (0.2 to 0.5 mg·l⁻¹ of dissolved O₂, pH of 6.3 to 7.5, rH > 14), a biological process catalyzes it with the double advantage of faster kinetics and production of a denser, readily dehydratable ferric hydroxide.

■ **Chlorine disinfection of water:** Cl_2 is a powerful oxidizing agent which can have a dual biocide and coagulation action on OM by breaking it down. It acts in the form of hypochlorous acid produced between pH 5 and 10:



■ **Removal of dissolved oxygen by sodium sulfite:**



This reaction may be used in:

- Deoxygenation of closed system cooling system make up water.
- Degassing of boiler or injection water.

1.6.2.2 Oxidation reactions specific to IWW

Reducing refining effluent COD requires the implementation of numerous oxidation reactions. The main agent is generally the oxygen in the air. The reactions may be:

- Purely chemical, with or without a catalyst, if they are used with sulfur compounds.
- Associated with biological action, if they are used with organic compounds (phenols, aldehydes, acids, etc.).

Occasionally, other oxidizing agents may be used:

- pure oxygen.
- Cl_2 , ClO_2 .
- $\text{H}_2\text{O}_2 + \text{Fe}^{2+}$ (Fenton's reagent), $\text{H}_2\text{S}_2\text{O}_5$ (persulfuric acid).
- ozone.

The advantages of these agents depend on the nature of the compound to be oxidized, on their cost and on the final oxidation stage targeted.

A. Oxidation of sulfur compounds

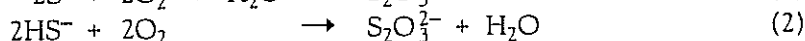
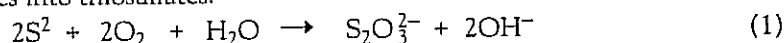
Table 15

Oxidation of sulfur compounds by oxygen

Oxidation number	Ion	pK	pH ≤ 7.5 (bio)	pH 7.5 to 8.5 (cat)	pH 11 to 12
-2	$\text{H}_2\text{S} / \text{HS}^-$ $\text{HS}^- / \text{S}^{2-}$ RS^-	7.1 14 -	↓		Air
0	S_0	-	↑		
2	$\text{S}_2\text{O}_3^{2-}$	1.7	↓	↓	Air/O ₂
2.5	$\text{S}_4\text{O}_6^{2-}$		↓		+ pressure and temperature
4	HSO_3^- SO_3^{2-}	1.8 7.2		↓	
6	H_2SO_4 HSO_4^-	<0 1.9		↓	↓

The major reactions are (see Table 15):

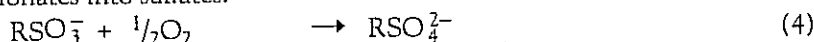
- Oxidation of sulfides into thiosulfates:



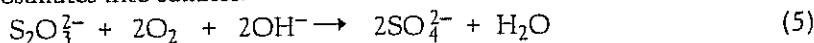
- Oxidation of mercaptans into disulfides:



- Oxidation of sulfonates into sulfates:



- Oxidation of thiosulfates into sulfates:



- Oxidation of sulfites:

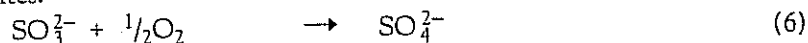


Figure 9 shows the different ways oxidation or acidification reactions can proceed.

Under atmospheric pressure and temperature, reactions (1) and (2) are limited to the $S_2O_3^{2-}$ stage and are fairly slow. Reaction (5) oxidizing $S_2O_3^{2-}$ into SO_4^{2-} is even slower and is mainly developed in reactors or oxidizers at high temperatures (70 to 90°C) and pressures (5 to 10 bar) which make it more expensive. The presence of catalysts (Fe^{3+} , Fe^{2+} , Mn^{2+} , Ni^{2+} , Co^{2+}) accelerates reactions (1) and (2) considerably. These catalysts are already present in spent caustic (oxides) or added into process condensates, especially if the condensates have undergone physicochemical treatment.

The nature of the cations linked to the sulfur compounds also has an influence on the treatment due to the occurrence of reactions parallel to oxidation:

- If the cations are basically made up of NH_4^+ , several sulfur compounds are then volatile and likely to be carried off in successive stages in substantial amounts by the oxidation air (e.g. FCC condensates).
- If the cations are basically made up of Na^+ , the corresponding sulfides and thiosulfates are very stable and nonvolatile (e.g. spent caustic).

In aerobic biological purification, the contact with a mass of bacteria can also have a considerable "catalytic" effect related to enzyme action. This time the advantage per se would not be a reduction in oxidation time (oxidation time is governed by the oxidation of OM) but the final SO_4^{2-} stage which would be prohibitive by chemical means.

According to some authors however, the final product of the oxidation of $S_2O_3^{2-}$ by autotrophic bacteria is $S_4O_6^{2-}$. This product is limited to the oxidation number 2.5 and its formation goes hand in hand with considerable acidification of the effluent.

Reaction (4) which is used for effluents of sulfonation processes can be developed by biological means. However, the degradability of benzo-sulfonic acids, like that of aromatic hydrocarbons, is very slow and requires very small loading masses. Satisfactory efficiency can be achieved in two-staged serial biological purification.

All these reactions occur in steps and in sequences where the accumulation of intermediate products can modify the kinetics of the main reactions or develop side reactions (see treatment of FCC condensates and spent caustic).

It is difficult to analyze the concentrations in intermediate products in these complex and often saline solutions in an industrial context. This explains the divergence in the theories

that have been put forward on the reactions involved. It should be recalled that what is at stake is the maximum reduction in COD while preventing a transfer of pollution from the water to the air.

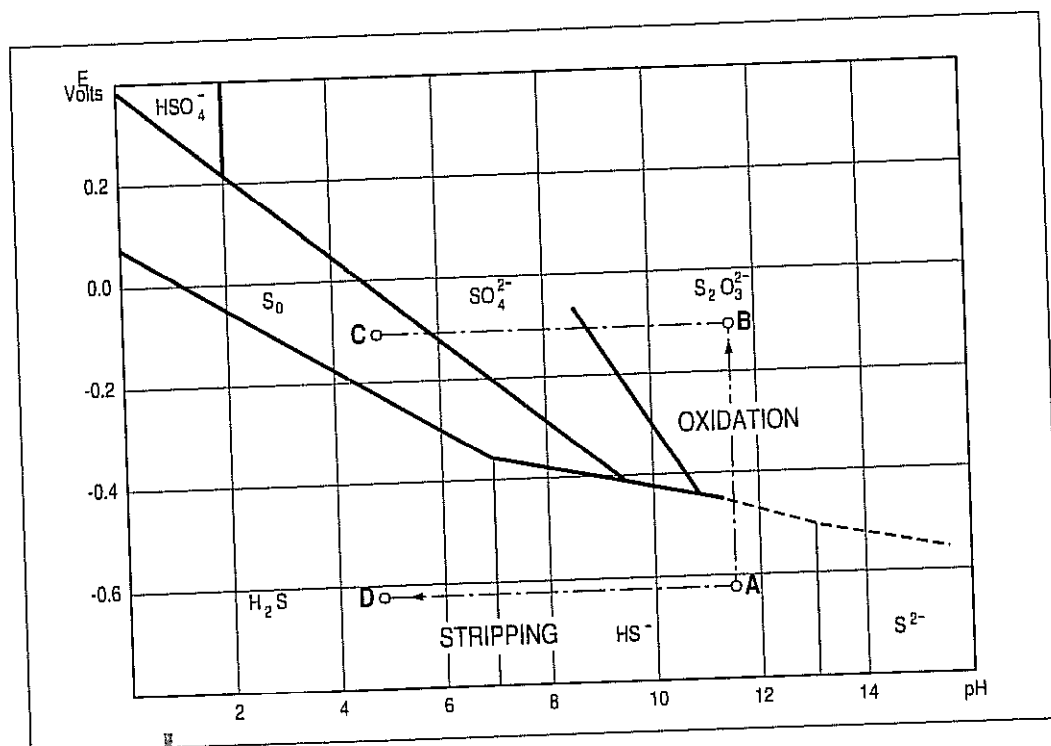


Fig. 9a Stages in oxidation of sulfur compounds

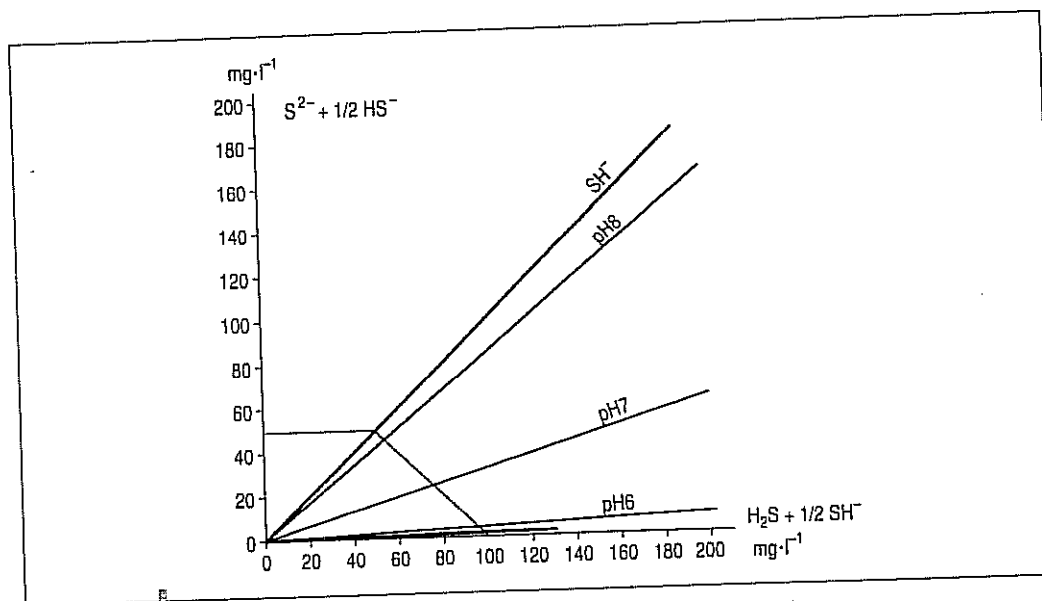


Fig. 9b Dissociation of $\text{HNaS} - \text{H}_2\text{S}$

B. Choice of oxidizing agents

The refining industry uses:

- Atmospheric O_2 , usually under pressure.
- Liquid oxygen if there is an economically attractive oxygen pipeline nearby.
- Make up chemical oxidizing agents very occasionally and only for detoxication or polishing treatments (traces of a few milligrams per liter of CN^- or phenols). Consumption is never limited to the harmful compound alone, other copollutants' O_2 demand can increase the stoichiometry five or ten fold (see Chapter 5).

Under these hypotheses in an industrial context, most processes resort to chlorine dioxide or Fenton's reagent ($H_2O_2 + Fe^{2+}$). Table 16 shows the possible reactivity areas for the different oxidizing agents.

Table 16

Areas of action for the major oxidizing agents

	Air/atmospheric O_2	O_2 pressure + temperature	Air/activated sludge	$H_2O_2 + Fe^{2+}$	Cl_2/ClO_2	O_3
Phenols	W	P	T	T	T*	T
S^{2-}	P	P	—	T	T	T
$S_2O_3^{2-}$	W	P	P	T	T	T
NH_4^+	W	W	T**	W	P*	W
RSO_3^-	W	P	P	W	W	P
CN^-	W	W	P	T	T	T

T: total reaction

P: partial reaction

W: worthless reaction

* But addition compounds are formed.

** If no inhibitors and sufficient acclimatization time.

The use of atmospheric air in an open oxidation or activated sludge basin may, however, promote a certain degree of stripping of volatile compounds. They must not be allowed to pollute the surrounding atmosphere.

Refinery effluents and primary treatment

Chapter

2

Before designing general treatments for refinery and petrochemical plant WW, it is necessary to know where the different polluted discharges come from, the levels of pollution and whether they can be classified into segregated sewers each equipped with its own pretreatment if need be. Pretreatment is designed either to allow a certain degree of recycling in situ or to control costs and sizes that would increase if an overly diluted pollutant were treated.

The main effluent itself, oily and accidentally oily water, undergoes the now routine series of three basic purifications which constitute the three stages of general treatment:

- Preliminary oil removal.
- Physicochemical oil removal.
- Biological or secondary purification.

It may have had particular effluents added after their pretreatment or nonoily effluents inserted before the second or third stage.

Lastly, a fourth stage, often called tertiary treatment, has become increasingly common. It is designed either to meet tougher standards (nitrogen, especially) or to recycle make up water to atmospheric cooling systems.

2.1 Sources of WW in refining and steam cracking

As an introductory step to designing treatments and systems, it is first necessary to be able to characterize a refinery according to production features and a number of qualitative points:

Production features

- Yearly or daily refining throughput and breakdown between topping and vacuum distillation.
- Feed for thermal process units (visbreaking and coking) and catalytic units (fluid catalytic cracking and hydrocracking).
- Throughput of lube oil plants.
- Throughput of edible oil dewaxing units.

Qualitative features

- General characterization of the crudes that are processed: API degree, content in sulfur, paraffins, naphthenic acids (acid value) and asphaltenes.
- Solvents used (NMP, furfural, MEK, MIBK).

2.1.1 Desalter water

Generally speaking, the desalter is designed to provide the refinery with desalted crude containing from 0.1 to 0.2% water and less than 1 to 10 mg of salt per liter (0.3 to 3 p.t.b.).

When it comes into the refinery, the crude itself should exhibit the following maximum values: from 0.1 to 0.2% water and 100 mg equivalent of NaCl per liter. Actually however, common figures are respectively from 0.3 to 0.5% by volume, and 150 to 350 mg per liter of salts (20 mg·l⁻¹ is required for some visbreaker feed).

The water comes only for a very small part from the crude (30 ppm), and has two main sources:

- During production, the crude may be mixed with formation water, which may be NaCl-saturated brine, or with waterflood water.
- During transportation, the crude becomes mixed with ballast water, which is often oxygenated seawater.

The salinity of the water that is emulsified with the crude varies from 4 to 250 g·l⁻¹ (NaCl, MgCl₂, CaCl₂).

The water used for crude desalting is ideally low in mineralization, neutral and soft if possible:

- pH 6 to 7.3
- Cl⁻ < 50 mg·l⁻¹
- S²⁻ < 20 to 50 mg·l⁻¹
- Deoxygenated.

The volume of washing water added depends on the viscosity of the crude and the desalting temperature. The following figures give an idea of the amounts required:

- 3 to 5% of the feed for API° 40
- 5 to 8% of the feed for API° from 30 to 40
- 8 to 10% of the feed for API° 30.

The crude washing water can be supplied by:

- Industrial water.
- Partial recycling of distillation condensates, stripped FCC condensates, or better yet by steam cracking condensates that contain fewer salts.

Composition of the desalting effluent

At the desalter outlet, the desalting blowdown water may exhibit the following characteristics:

- Temperature: 40 to 60°C.
- High chloride salinity: 2 to 15 g·l⁻¹.
- Low S²⁻ (10 mg·l⁻¹) and phenol (5 to 20 mg·l⁻¹) content.
- pH: 7 to 8.
- COD: 100 to 300 mg·l⁻¹.
- Emulsified HC: 100 to 200 mg·l⁻¹.
- Black color due to colloidal corrosion FeS.
- Miscellaneous sediments containing vanadium and aluminum salts.

N.B.: The low S²⁻ and phenol content comes from the fact that the desalter performs a liquid-liquid extraction from the condensates to the crude (K_D coefficient of phenols is 1.3).

Effluent volume

The desalting system blowdown represents from 5 to 6% of the volume of crude processed.

Example of salt discharge by draining the washing water system of a desalter:

- Desalter capacity: $12,000 \text{ m}^3 \text{ day}^{-1}$ (75,500 barrels $\cdot \text{day}^{-1}$)
- Salt in the crude: $300 \text{ mg} \cdot \text{l}^{-1}$ (104 pounds per 1000 barrels)
- Salt from the desalted crude: $10 \text{ mg} \cdot \text{l}^{-1}$ (3.5 pounds per 1000 barrels)
- Initial water in the crude: 0.4%
- Desalting water: 6%
- Residual water in the crude: 0.2%
- Salt removed per day: $290 \times 12,000 = 3480 \text{ kg}$
- Volume of water blowdown per day: $(0.06 + 0.002) \times 12,000 = 744 \text{ m}^3$
- Salinity drained out: $4.67 \text{ g} \cdot \text{l}^{-1}$.

2.1.2 Process condensates

These condensates come from the condensation of steam that has been in contact with petroleum products and can be broken down into three categories:

- Distillation condensates.
- Sour condensates.
- Product heating condensates.

2.1.2.1 Distillation condensates

Topping

The condensates come from the distilled product carrier steam and are collected at the top of the column. They represent 2.5 to 3.5% of the feed throughput rate.

Vacuum distillation

The condensates come from distilled product carrier or dilution steam, and from power steam (ejectors and barometric condenser). They represent 3 to 4% of the feed (see Fig. 10a).

Pollution is low in these condensates (see Table 17) and would warrant pumping them back to crude washing.

2.1.2.2 Sour FCC and hydrocracking condensates

These condensates come from thermal or hydrogen cracking operations where carrier steam is used in injection or aeration. The heavy viscous products processed are rich in sulfur which is hydrogenated and carried off by the steam. Demineralized water may also be added upstream from the FCC to decrease the H_2S and NH_3 partial pressures in the steam and carry off these gases by dissolving them (Fig. 10b).

NH_3 comes from the hydrogenation of nitrogen compounds and phenols from a reaction between the steam and cyclic HC.

These condensates are termed sour because of their high H_2S content along with considerable phenol compound content (see Table 17).

They represent approximately 6 to 12% of the feed.

They can not be recycled to the desalter or discharged into the general sewer system without first undergoing desulfurization by stripping. Given the nature of cracked products, these condensates can quite often form a stable chemical emulsion.

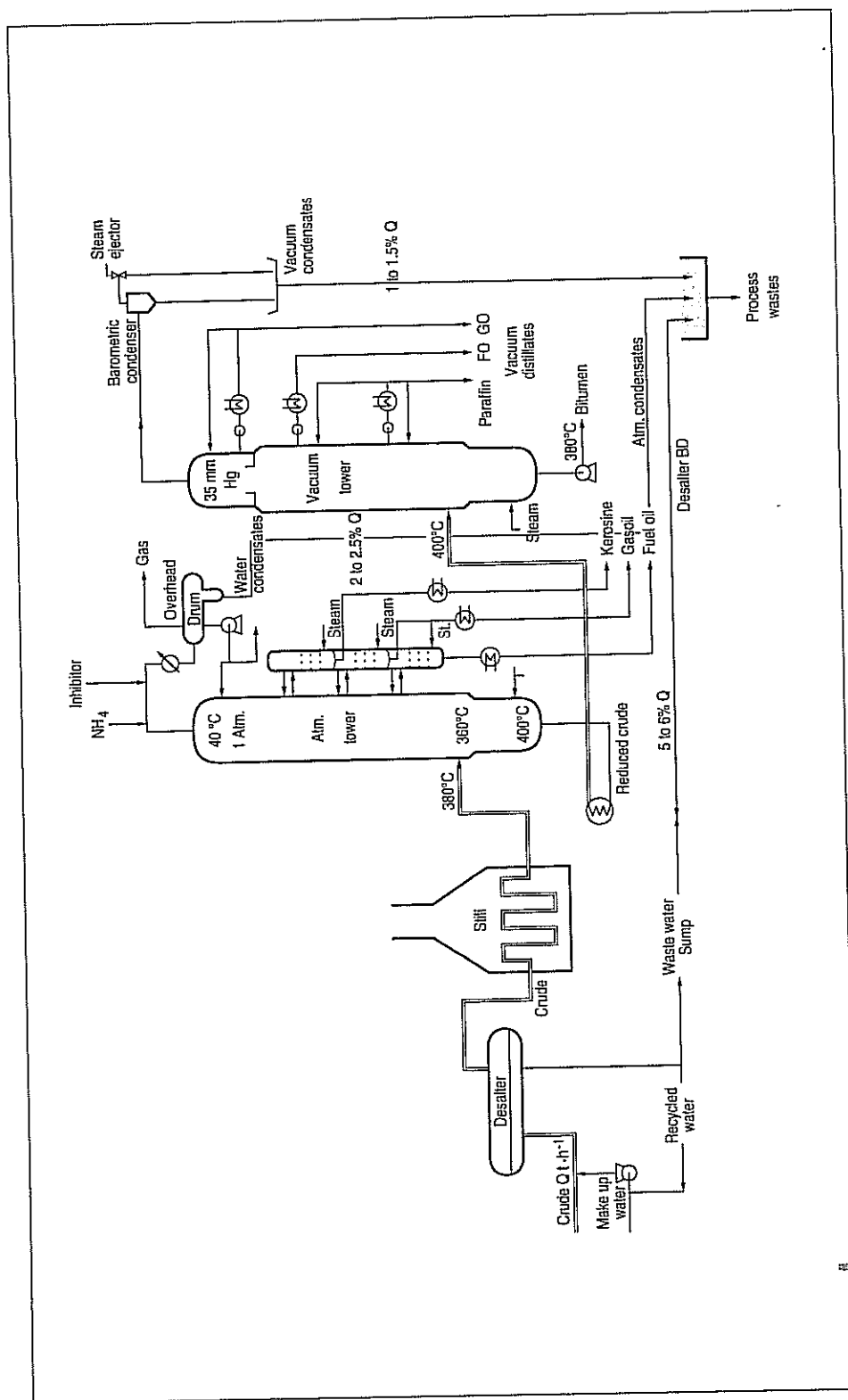


Fig. 10a Distillation condensates and effluents

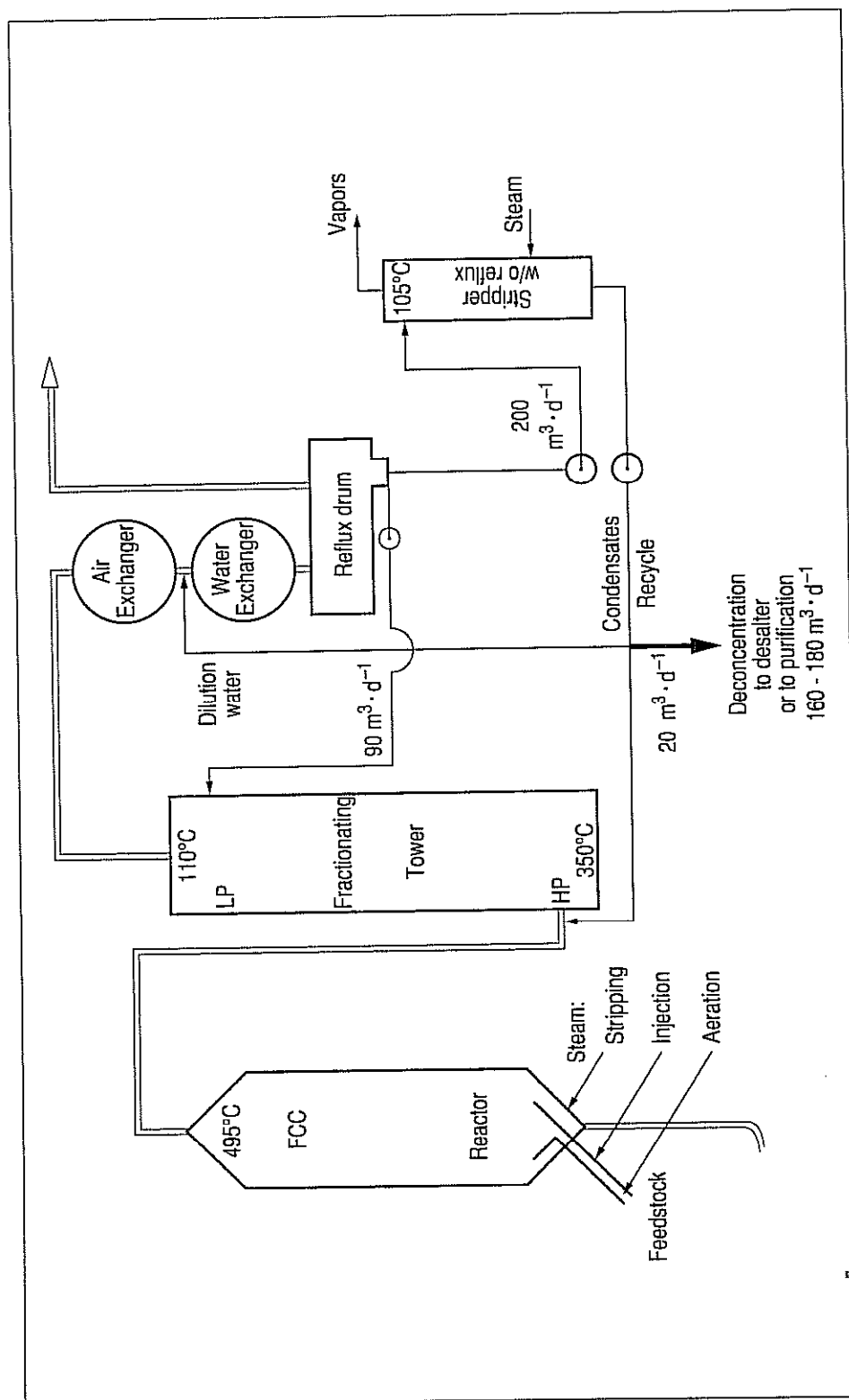


Fig. 10b Recycling condensates from a 1800 ton/day FCC

2.1.2.3 Production and composition of refinery process condensates

Table 17

Example of composition in milligrams per liter of process condensates

	Topping	VD	FCC	GO HDS	Steam cracker
% feed	2.5-3.5	3-4	6-12	3-6	15-35
pH	6-7	6-7	8-9.5	5-6	6-8.5
HS ⁻ , RSH	20-200	10-50	500-3000	3000-5000	10-20
Cl ⁻	5-100	5-50	10-50	10-30	10-30
CN ⁻	—	—	5-200	5-10	—
NH ₄	10-60	5-30	300-3000	1500-3000	Traces
Phenols	10-30	5-10	80-300	10-20	20-30
HC	30-60	5-20	5-60	5-20	30-50
CH ₃ CO ₂ H					50-100
CH ₃ CHO					

2.1.2.4 Product heating condensates

These condensates are hot and since they have only accidentally been in contact with hydrocarbon-bearing products, they do not contain much dissolved pollution. The low paraffinic HC content must be eliminated before they can be recycled to LP boilers (see Chapter 4, Section 4.5). This type of recycling is increasingly advantageous.

2.1.3 Particular process effluents

2.1.3.1 Bitumen blowing WW

Bitumen blowing is an oxidation operation by the O₂ in the air. It is designed to increase asphaltene dispersion in bitumen. The gases are scrubbed in a hot soft water countercurrent and the resulting water constitutes a remarkably stable chemical emulsion (2000 to 8000 mg·l⁻¹) which can be broken only by severe coagulation or by acidification.

2.1.3.2 Catalytic alkylation WW

Alkylation catalysis is generally performed by H₂SO₄ and may produce discharges rich in sulfonic acids as mentioned earlier. Any use of HF may create problems of eliminating fluorides that are more or less easy to precipitate depending on whether NaF or NH₄F is involved (F⁻ precipitation as CaF₂).

2.1.3.3 Lube oil plant WW

The feedstock here is topping distillates or, after deasphalting, vacuum residues. The oils are produced from isoparaffins between C₂₂ and C₄₀, extracted in two steps from the preceding cuts:

2.1.4.1 Normally oily water

This includes:

- **Drainage** from crude oil or refined product storage facilities. It can contain up to a few grams per liter of HC associated with 1 to 10 $\text{mg}\cdot\text{l}^{-1}$ of phenols according to the nature of the stored product.
- **Rainwater** that has fallen on the units, pumping stations and loading stations, paved areas that can cover up to 10 ha.
- **Water used to wash the ground.**

2.1.4.2 Accidentally oily water

■ **Atmospheric cooling system blowdown** when exchangers have leaked (products heavier than C_5). The relative amounts of condensate and atmospheric cooling system purge discharges for different units can be noted as published by R. Chevallier in "Technique de l'eau et de l'assainissement" (February 1979 no. 386):

Production in % of feed	Top.	VD	FCC	Reform.	Lube oil plant
WW	3.3	4.7	10.7	0.24	23.8
Cooling blowdown	0.2	3.3	2.8	0.24	81

Overall blowdown is very different depending on the relative size of atmospheric cooling. The CONCAWE 5/77 report forecast cooling system water flow rates in 1980 for a typical 10 Mt/year refinery at 2500 to 10 500 $\text{m}^3\cdot\text{h}^{-1}$, i.e. 2 to 8.4 $\text{m}^3\cdot\text{t}^{-1}$ of crude, depending on the complexity of the plant. Relatively old refineries (see Chapter 6) circulate from 10 to 24 $\text{m}^3\cdot\text{t}^{-1}$. Here deconcentration blowdown varies from 50 to 500 $\text{l}\cdot\text{t}^{-1}$ and can make up a considerable proportion of their discharge, ranging from 0.2 to 1 $\text{m}^3\cdot\text{t}^{-1}$ excluding rainwater.

These figures should be compared to French requirements (see Section 2.1) on discharge volumes (excluding rainwater and deballasting water).

■ **Rainwater** that has fallen on the refinery outside of the paved areas. Considerable flows can be involved:

- Continuous and related to rainy seasons (Brazil, Colombia).
- Short and related to relatively severe storms.

In both cases, the amount of rainfall and the areas involved (12 to 24 acres) need to be known.

In France, depending on the location, the volume of rain falling for 12 to 30 min on a refinery can vary between 2000 and 8000 m^3 . Rainfall can amount to around 5 to 20 mm in 15 min.

During storms, the first water to fall washes the ground and is the most polluted. The flow may be from 500 to 3000 $\text{m}^3\cdot\text{h}^{-1}$. Since it is not feasible to treat this amount at its instantaneous flow rate, the water must be stored in a storm basin designed on the basis of historical meteorological statistics.

2.1.5 Nonoily waste water

This category includes:

- Sanitation waste water (showers and toilets) from the site. It can amount to 80 to 200 l for three shifts and the BOD₅ load is much higher if mess kitchens are located in the plant. BOD₅ discharges amount to 45 to 75 g per day: sewage water 15 g per shift, mess with prior grease extraction 30 g per meal.
- Laboratory water.
- Boiler blowdown, if PO₄³⁻ conditioning.
- Ion exchanger regeneration eluates, with prior neutralization.
- Sludge from make up water lime softeners or settlers and filter washing water.

These effluents must be sent to the sewers that are the most suitable for treatment (see Section 2.3).

In conclusion:

- Discharge of nonoily water is fairly constant and adds low-level dissolved organic pollution.
- Accidentally oily water is much more variable and accounts for the main HC input in sewers. In a refinery with 8 to 10 Mt/year throughput, HC losses of 20 to 100, even 200 m³ per day may occur depending on the number of accidents and how well it is managed. Of this amount, 80 to 95% is reclaimed in gravity separators, a fact which justifies good separator design and operation.
- Process water is sometimes separated from oily water and includes sour condensates and desalter blowdown.

2.1.6 Transportation waste water

2.1.6.1 Deballasting water

Depending on the size of the oil tanker, deballasting water accounts for 25 to 33% of the vessel's effective capacity. It is estimated that the amount of HC contained represents about 0.4% of the transported product, i.e. a potential concentration of 1% of HC in the water.

If the water is drawn off and the oil gathered in the buffer tank with the right planning and execution in the terminal, the water for treatment after the storage tank has the following characteristics:

- High salinity usually (brackish or seawater).
- A HC content of 50 to 100 mg·l⁻¹, with an emulsion of a mechanical nature generally, except if the oil layer of the tank has been sucked up inadvertently.
- A SS content of less than 50 mg·l⁻¹.
- Very seldom S²⁻ and phenol pollution (except when gas oil is transported).

2.1.6.2 Tanker cleaning water

Cleaning tankers before periodical maintenance involves the use of powerful hydraulic jets to scour off thick crusts of viscous bitumen- or asphaltic-base slops. Sometimes massive amounts of detergents (0.1 to 3 g·l⁻¹) must be used and sometimes the water must be heated or alkalinized.

The emulsions that are produced on these occasions are very stable and concentrated. SS are present in large amounts at the same time. The water remains treatable after neutralization as long as the detergent content does not exceed 60 to $100 \text{ mg}\cdot\text{l}^{-1}$. Above this figure, a frothing pretreatment is possible upstream from physicochemical purification with an organic or inorganic coagulant.

2.1.7 Spent caustic

This effluent involves very small volumes (0.2 to $4 \text{ m}^3\cdot\text{h}^{-1}$), but it is very rich in Na salts, in phenols and in S^{2-} . This precludes dilution and necessitates independent treatments which are discussed in Chapter 4.

2.1.8 Steam cracking condensates

A steam cracker circulates a considerable amount of steam to dilute gases and lower their partial pressure (1 to 2 tons per ton of feed). A fraction of the steam condensed at 90° is drawn off and coalesced to treat the HC emulsion. It is then stripped of the gasoline carried over before being recycled to the LP process steam producer and pumped to preheat the feed.

The blowdown of the closed system, called quenching water, often amounts to 15 to 30% of the feed throughput (Fig. 11).

This water is slightly alkaline ($\text{pH } 8$ to 9) and contains phenols (20 to $30 \text{ mg}\cdot\text{l}^{-1}$). In addition, there is the blowdown water from the boiler itself which is very alkaline (concentration of conditioning products) and saline, but several times smaller in volume than the condensates.

No incorrectly or incompletely treated spent caustic must be reintroduced in the system as this would cause mineralization of the water and a rise in the mineral COD.

2.2 Legislation

2.2.1 Standards for discharge and monitoring of hydrocarbons in France

For crude oil processing plants the standards are laid down in the decree of 12 September, 1973. Two articles are summarized below:

Article 47: Amount of water discharged

Except for rainwater and deballasting water, the amount must be lower than:

- 0.4 m^3 per ton of crude oil for a hydroskimming refinery (distillation, reforming, desulfurization) without catalytic cracking.
- 0.8 m^3 per ton of crude oil for a simple refinery with catalytic cracking.
- 1.2 m^3 per ton of crude oil for a complex refinery.

It is prohibited to cool products by using nonrecycled water.

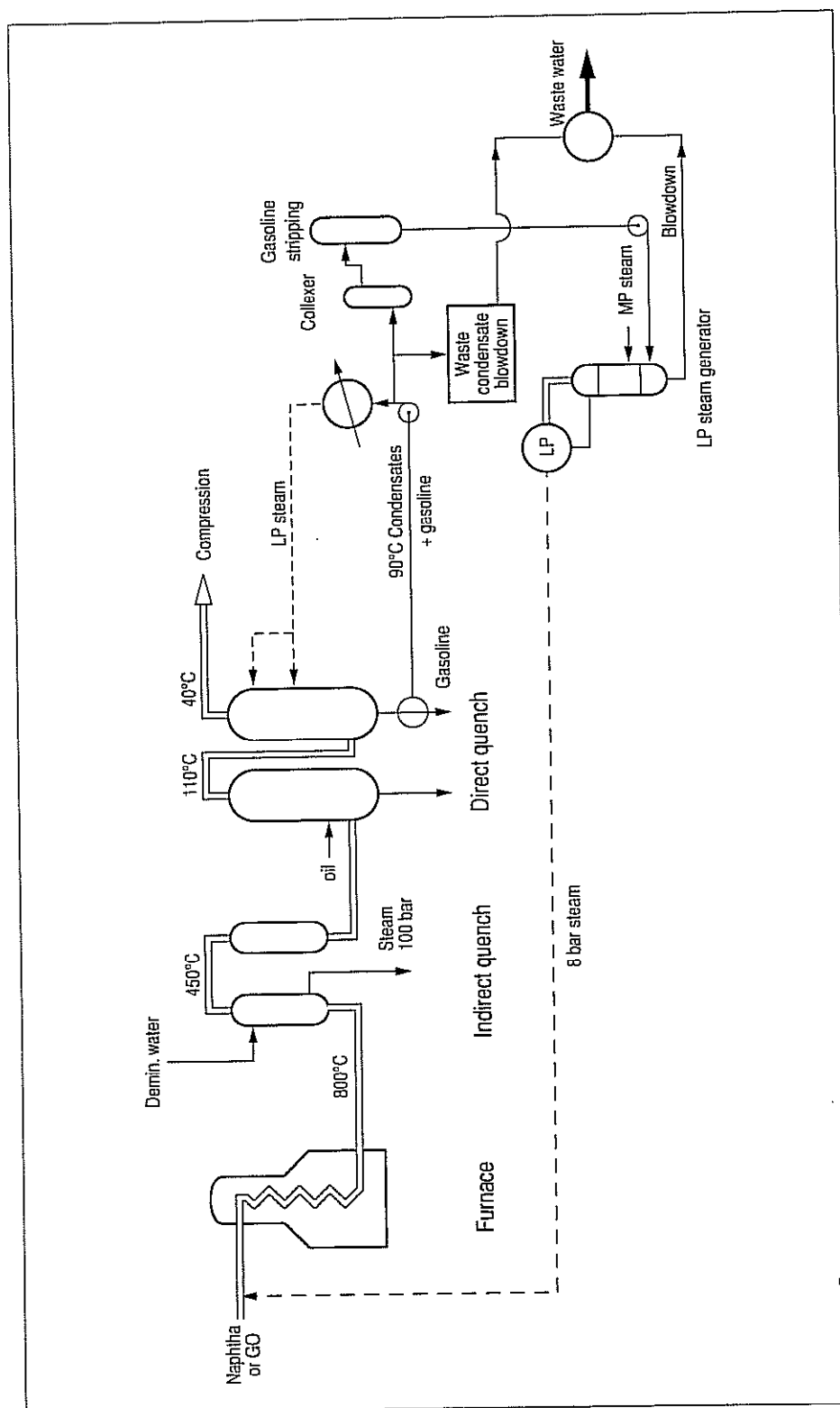


Fig. 11 Example of steam cracking systems

Article 48: Quality of discharged effluents

1. Measurement provisions will include:

- Continuous measurement and recording of the water flow rate through the treatment station and of the total flow discharged by the refinery.
- Automatic sampling as per standard AFNOR T 90-201.

2. Monitoring samples as per standard AFNOR T 90-201.

3. Maximum characteristics of discharged water represented by a daily sample:

	Hydroskimming refinery	Simple refinery with cracking or complex refinery
pH	5.5 to 8.5	5.5 to 8.5
Phenols ($\text{mg}\cdot\text{l}^{-1}$)	0.5	1
SS ($\text{mg}\cdot\text{l}^{-1}$)	30	30
BOD ₅ ($\text{mg}\cdot\text{l}^{-1}$)	30	40
COD ($\text{mg}\cdot\text{l}^{-1}$)	120	150

Moreover, for all refineries:

- Hydrocarbons $< 5 \text{ mg}\cdot\text{l}^{-1}$ as per standard AFNOR T 90-202 (indirect hexane extraction).
- Hydrocarbons $< 20 \text{ mg}\cdot\text{l}^{-1}$ as per standard AFNOR T 90-203 (CCl_4 extraction and IR reading).
- Pb content $< 0.1 \text{ mg}\cdot\text{l}^{-1}$.
- Hexavalent chromium content $< 0.05 \text{ mg}\cdot\text{l}^{-1}$.
- Temperature lower than or equal to 30°C .

Two examples of non-French regulations show the diversity of situations and the eventuality of standards on nitrogen (which, in fact, may be covered by local decrees in France).

In fact, a regulation has recently been enacted in France for new refineries. It specifies weight limits for pollutant discharges expressed in $\text{g}\cdot\text{t}^{-1}$ of crude. An excerpt is given below:

	Hydroskimming + Cat. Reform.	Same + CC + SC or lube oil plant
COD	$10 \text{ g}\cdot\text{t}^{-1}$	$30 \text{ g}\cdot\text{t}^{-1}$
BOD ₅	5	10
SS	2	10
HC	0.1	0.5
Total N	5	10
Water	$0.1 \text{ m}^3\cdot\text{t}^{-1}$	$0.4 \text{ m}^3\cdot\text{t}^{-1}$

2.2.2 Belgian regulations

According to royal decree of 3 February, 1988, a distinction is made among three types of refineries:

- Subsector I: Hydroskimming refineries.
- Subsector II: Complex refineries, with one or more of the following processes:
 - Group A: catalytic cracking, hydrocracking, visbreaking, alkylation, etc.
 - Group B: isomerization, polymerization, naphthenic acid, bitumen and asphalt, etc. production.
- Subsector III: Secondary production units (lube oils and grease) that are not integrated in a refinery.

Along with the basic conditions governing discharge of MWW in rivers or sewers, there are the following additional conditions:

1. For the three subsectors:

$$\text{Total Cr} < 0.5 \text{ mg} \cdot \text{l}^{-1}$$

$$\text{Cr}^{6+} < 0.05 \text{ mg} \cdot \text{l}^{-1}$$

$$\text{Total Pb} < 0.05 \text{ mg} \cdot \text{l}^{-1}$$

$$\text{S}^{2-} < 1 \text{ mg} \cdot \text{l}^{-1}$$

$$\text{Total P} < 2 \text{ mg} \cdot \text{l}^{-1}$$

2. According to subsector, in milligrams per liter:

	I	II	II
TOC	200	250	350
COD	200	250	350
Kjeldahl N	10	30	20
Phenols	0.5	1	1

3. Notwithstanding the general regulations on WW:

	I	II	II
BOD ₅	35	35	70
Nonpolar HC	20	20	30

These conditions are set according to the following specific reference volumes:

1. Subsector I: 0.5 m³ of effluent per ton of processed crude oil, + 0.1 m³ per ton of processed product.
2. Subsector II: 0.5 m³ per ton of crude oil + 0.1 for each additional operation listed in group A or 0.03 m³ for each additional operation listed in group B (the total is to remain lower than 1.2 m³).

2.2.3 Canadian regulations

Federal regulations are enforced in conjunction with provincial regulations whose specifications may be more stringent.

The Ontario province guidelines for the refining industry particularly involve the five parameters listed below and are considered as representative:

- Oils and greases (extracted by solvent): $<15 \text{ mg} \cdot \text{l}^{-1}$
- Phenols: $<0.02 \text{ mg} \cdot \text{l}^{-1}$
- SS: $<15 \text{ mg} \cdot \text{l}^{-1}$
- NH_3 , in N: $<10 \text{ mg} \cdot \text{l}^{-1}$
- COD: $<200 \text{ mg} \cdot \text{l}^{-1}$
- Metals (Cr^{6+} , Cu^{2+} , Pb^{2+} , Zn^{2+} , Ni^{2+}): $<1 \text{ mg} \cdot \text{l}^{-1}$ each.

Compliance with the above concentrations must go hand in hand with compliance on corresponding specific refinery pollutant loads expressed in kilograms per day to prevent dilution.

2.3 Definition and layout of treatments

2.3.1 Need to separate sewer systems

As mentioned before, the different sources of WW include:

- Particular effluents, FCC condensates and spent caustic, whose high pollution level (S^{2-} , phenols) requires a specific pretreatment sequence. Sending them into the general WW would throw off treatment or make it much more expensive.
- Process condensates that are low in salinity and recyclable.
- General oily and accidentally oily effluents, whose pollution is mainly due to HC in different states and to a generally low BOD_5 (hydroskimming refineries). They warrant purification in two or three stages: physical, physicochemical and biological.
- Non-oily effluents, small in volume but quite saline and thereby poor candidates for recycling. They can warrant a fairly simple treatment (neutralization of resin regeneration eluates or settling of make up water clarification sludge).

Planning the treatment setup first of all entails the separation of sewer systems. In this way each treatment can be adapted to each level of pollution. As a result, treatment can be made both more effective and less expensive to build and to run.

A second point of concern is to promote water recycling (to the desalter, to the cooling system, etc.) by clear-cut separation of:

- Saline water to be excluded: deballasting, spent caustic, cooler blowdown, sour condensates, etc.
- Softer recyclable water: topping condensates, accidentally oily and non-oily water, HP boiler blowdown.

In addition to the salinity criterion, two other parameters influence separation: S^{2-} content and the nature of the emulsion.

Sulfides have a certain inhibiting effect on biological purification, or can at least limit the development of some strains of bacteria and delay the breakdown of some BOD_5 components (phenols, SCN^-).

By precipitation in the form of colloidal S or FeS, they can also make physicochemical purification flocculation more problematical and more sludge-producing.

The risk of atmospheric pollution due to their volatility or toxicity in the form of H_2S means they can not be directly introduced in the sequence of general effluent treatments.

HC are present in many different states that are difficult to characterize analytically. The four forms below warrant attention if treatment is to be understood:

- Free HC.
 - Mechanical emulsions.
 - Chemical emulsions.
 - HC in solution.
- a. Free HC floating in slicks in catch drains or carried along in slugs in piping.
 - b. HC in what is termed primary mechanical emulsion with a droplet size of some few dozen micrometers. Their stability when at rest is limited to a few hours.
 - c. HC in what is termed secondary mechanical emulsion which is indefinitely stable due to the submicrometric size of the particles, similar to colloids.
 - d. HC in chemical emulsion where either a third polluting agent (soap, caustic, Na, detergents), or the nature of the HC (asphaltenic compounds) modifies the surface tension and chemically stabilizes dispersion.
 - e. Molecularly dissolved HC such as aromatics.
 - f. HC solubilized by their particular origin (naphthenic acids related to the crude's organic acidity).

Insoluble HC that form a film coating coarse SS should also be mentioned. They can considerably modify the settling or floating capability of the solids by forming unseparable aggregates.

Since it is impossible to classify HC simply in a laboratory, they are separated into three main categories industrially. Each one can be treated by a specific purification process:

- **Preliminary oil removal** which eliminates free HC and the coarsest fraction of the mechanical emulsion.
- **Physicochemical purification** which eliminates the residual fraction of the mechanical emulsion or all of the HC in chemical emulsion.
- **Biological purification** which removes the biodegradable fraction of dissolved or solubilized HC.

Soluble nonbiodegradable HC such as aromatics make up a fourth category which rarely but nevertheless effectively undergoes treatment such as steam stripping for high concentrations and percolation on granular activated carbon (GAC) for low concentrations.

2.3.2 Stages in treating the general effluent

It is possible to go into the general area of activity of the three stages in more detail. Theoretically, they were designed for HC alone (and for soluble BOD in the third stage) and are now made more complete by the addition of a fourth stage.

2.3.2.1 Preliminary oil removal

Elimination of pollution in suspension:

- Granular SS (sands, clays, fine gravel).
- Free HC, in layers, in droplets of 100 to 200 micrometers.

2.3.2.2 Physicochemical purification

Elimination of colloidal pollution:

- Fine SS (silts, corrosion products).
- HC in mechanical or chemical emulsion.

This stage is called physicochemical because it combines the use of a coagulating agent and gravity separation of flocculated SS or HC.

2.3.2.3 Biological purification

Elimination of dissolved biodegradable BOD₅ pollution:

- Oxygenated compounds (acids, aldehydes, phenols, solvents).
- Sulfur compounds such as $S_2O_3^{2-}$ (enzyme effect).
- Aromatic HC, partly.
- NH_4 (nitrification/denitrification).

2.3.2.4 "Tertiary" purification

This stage is given its name by analogy with the MWW purification step which follows what is termed secondary biological purification. Here, one of the aims is to enhance P removal. In both refining and petrochemicals, this increasingly common stage may aim either to meet tougher discharge standards (TOC, SS, COD, $N-NH_4$) or to recycle the water.

Tertiary purification often proceeds as follows:

- Improvement in clarification and phosphate removal.
- Improvement in phenol removal (biological filters).
- Reduction in aromatics and COD (GAC).

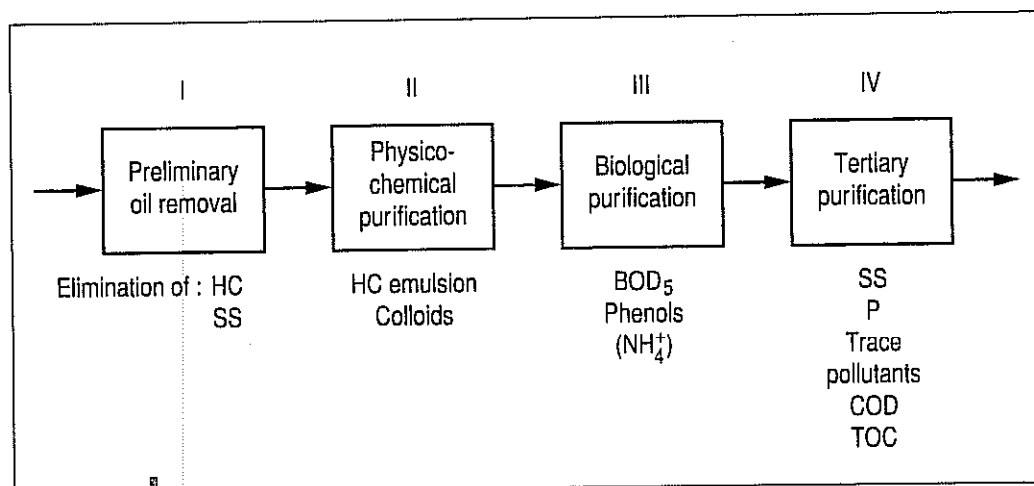


Fig. 12 The stages in purifying refinery WW

2.3.3 Planning sewer networks (surge tanks, lagoons)

In principle, two main systems need to be set up:

- The oily water sewer that also accommodates process condensates after desired pretreatment.
- The accidentally oily water sewer which is characterized by the addition of a storm basin.
- A third sewer to segregate saline water if recycling is required.

Figure 13 shows a fairly common setup for coastal refineries.

Figure 14, based on the same three-way separation principle, shows greater complexity in systems due to the numerous purification techniques in use.

Basins, surge tanks and lagoons

These facilities can have very distinct functions:

- Buffer storage tank for high but sporadic flow rates, such as from storms or oil tanker deballasting. If no economically feasible facility can be built to deal with them directly, they must be stored in closed (deballasting) or open gravity-flow basins (storms). The basins must then allow the water to be drawn off in volumes spread out over several hours or days so it can be dealt with in the purification facility.
- Storage for effluents with high but variable concentrations at relatively low flow rates. Pollution is generally in dissolved form:
 - Spent caustic that is stored for a few days.
 - Process WW from a variety of sources (petrochemicals) that will be mixed in-line.
 - Sour process condensates stored sometimes from one to two days (e.g. due to upstream stripper breakdown).

The closed basins are relatively compact and do not cause any adverse solubilization or oxidation effects (aging of insoluble HC).

- Lagoons, located after preliminary oil removal and before physicochemical purification, can provide one to several days' residence time. They are common in the United States and sometimes even replace physicochemical purification. They are used for facultative aeration and for equalizing concentrations

In this instance where relatively oily water is involved (50 to 150 mg·l⁻¹ of HC), the danger of HC solubilization should be pointed out. In other words pollution is transferred in the dissolved phase, a form that could be less rapidly degradable. It also generates biological sludge which is less readily dewatered. Lysys and Russel (Water Research, Vol. 8, pp. 863-868, 1974, Pergamon Press) showed that the soluble emulsion TOC grew and could double in eight to 12 days, particularly with gasoline or fuel oil. Lagoons' unsightly appearance and foul smells are two reasons why they are being phased out as a solution (except for particular geographical constraints). Meanwhile managing physicochemical purification has become easy since the end of the 1970s thanks to the use of organic coagulants.

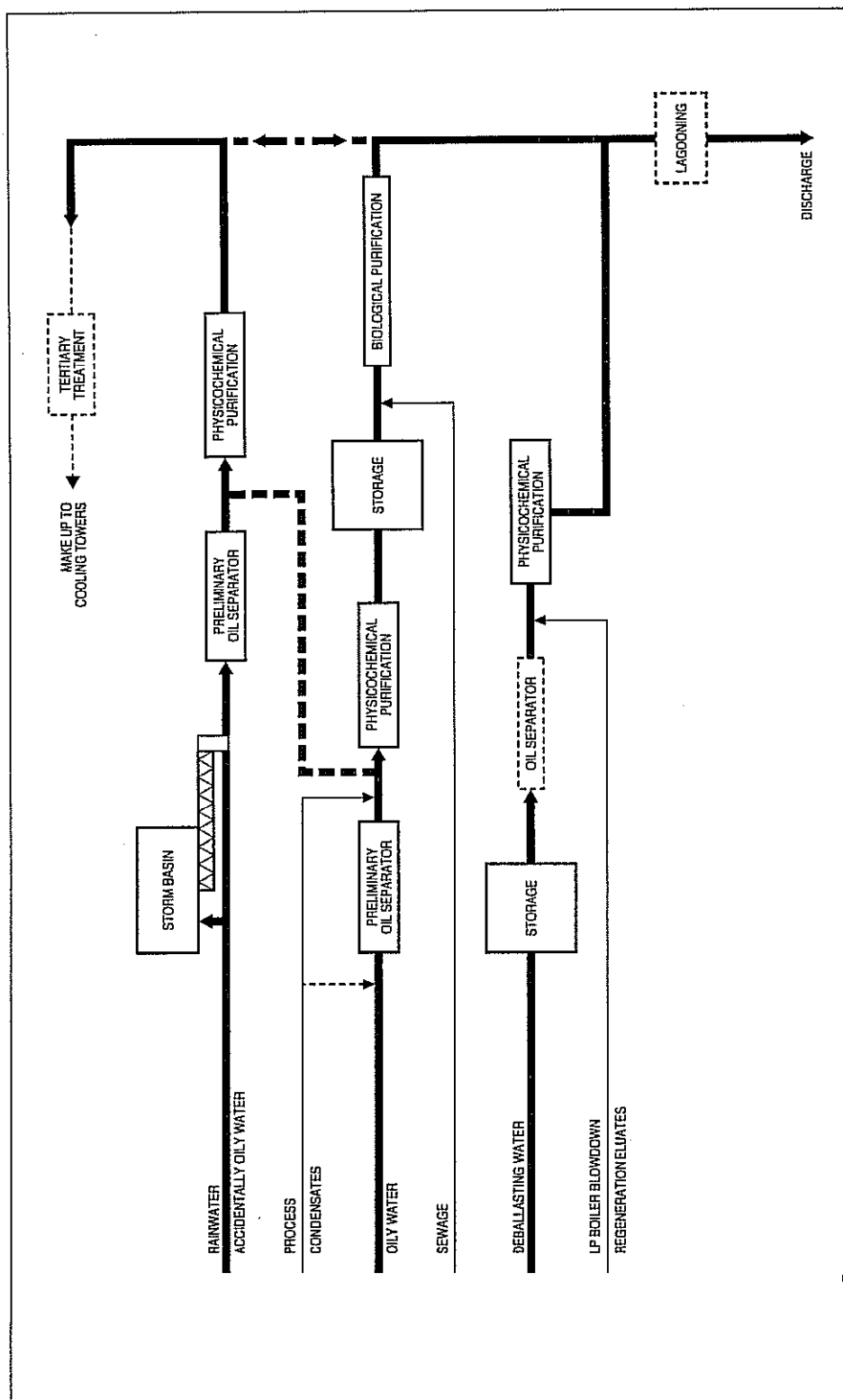


Fig. 13 Schematic diagram of refinery sewer system setup

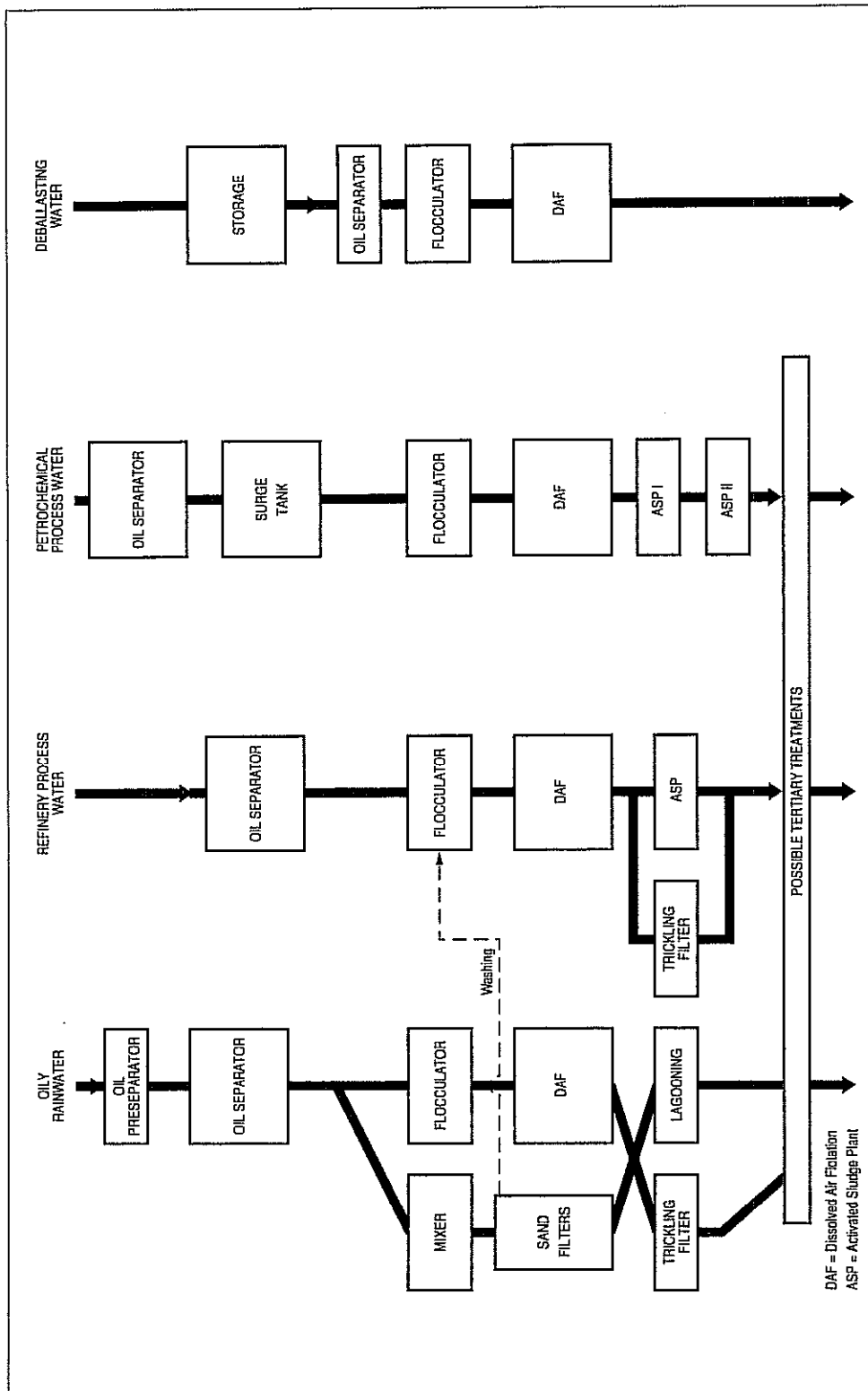


Fig. 14 Choice of treatments

2.4 Pretreatment of sour condensates

This step takes place before recycling to the desalter or before discharge into the general effluent, upstream from physicochemical purification. In the first case, it consists of a stripping operation. In the second, it may be limited solely to oxidation of the water, making sure there is no transfer of pollution to the air. Accordingly, only the effluents from the FCC and hydrocracker, if not from hydrodesulfurization, must be stripped. On the other hand, in a mixture with the other topping condensates, a drop in the S^{2-} level to below a concentration of $300 \text{ mg} \cdot \text{l}^{-1}$ means that an atmospheric oxidation treatment can be contemplated, provided precautions are taken.

2.4.1 Stripping

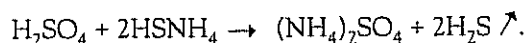
Since FCC condensates are too NH_4^- rich, they can not be directly recycled to the desalter where the NH_4 would cause the pH to rise in the water condensed in the topping overhead drum. This pH must be kept between 5.5 and 7 and recycling the S^{2-} input is also to be avoided.

As a result, there is a need for separate stripping for FCC condensates and this can be done in a closed system on the FCC with a main blowdown to the desalter (see Fig. 10b).

The stripping fluid can be steam that may or may not be associated with flue gas or fuel gas.

2.4.1.1 Preacidification

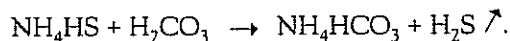
The purpose of preacidification is to dissociate volatile ammonium salts. It is carried out with a strong acid at a pH of 5.5 to 6:



Because H_2S is much more volatile than NH_3 and because its combinations with weak acids (Henry constants at 100°C respectively 150 and 15 MPa), the stripping temperature can be lowered to less than 80°C (in deacidizers), whereas rapid elimination of NH_3 itself often requires a temperature level of around 105°C .

The current need to reduce NH_4 discharge or recycling has caused acidification by strong acids to be phased out.

Flue gas can supply the CO_2 capable of displacing the H_2S from the ammonium hydrogen sulfide:



Flue gas with 12% by volume of CO_2 , on the basis of 30 volumes per volume of condensate, can displace H_2S stoichiometrically from a condensate that contains $5 \text{ g} \cdot \text{l}^{-1}$.

Practically speaking, the displacement efficiency is not as high as with a strong mineral acid. Flows of 90 volumes per volume may be required to displace 1 to $2 \text{ g} \cdot \text{l}^{-1}$ of H_2S at 85° .

The main advantage of flue gas is that it reduces steam consumption, but some of this advantage is lost because piping, valves and overpressure fan must be sized up.

Another constraint is the need for dust to be removed from the gas before it enters the stripper.

Likewise, the use of cold fuel gas requires overly high flows (>500 volumes per volume) and could be contemplated only if it is combined with preacidification of the condensate.

2.4.1.2 Steam stripping

Steam stripping is carried out either in coated columns or in black steel columns having a very high corrosion allowance. These columns are filled with plastic or stainless steel ring packing. Their height varies between six and 12 theoretical trays and they have the following operating conditions (Fig. 15):

- Make up stripping steam: 85 to 130 $\text{kg}\cdot\text{m}^{-3}$ of condensate.
- Water percolation velocity: 15 to 35 $\text{m}^3\cdot\text{h}^{-1}$ per square meter.
- Temperature at the bottom of the column: 103 to 106°C.
- Very partial dephlegmation of vapors emitted at the top of the column.
- Vapors sent off to be flared.

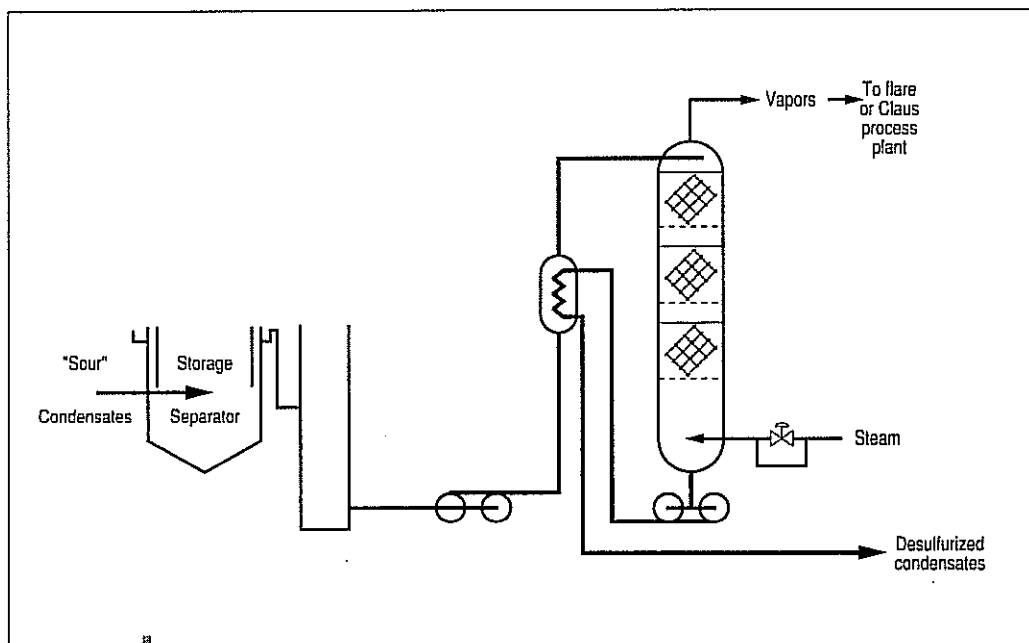


Fig. 15 Steam stripping of process condensates

It is generally not necessary to concentrate the vapors in a reflux condenser and this should be taken into account for added corrosion protection.

With refluxing, special high-cost steel is no guarantee against rapid perforation. It is preferable to utilize a thick Teflon- or furan resin-based coating, a tried and true solution.

Stripping eliminates 90 to 98% of the sulfides in a wide range of temperatures (75 to 110°) and 92 to 97% of the volatile ammonia but in a higher temperature range and with steam make up. Phenols themselves are stripped fairly little, especially if there is no reflux.

2.4.1.3 Air stripping

Air stripping consists in acidifying condensates to pH 5.5 if not 4.0 (in the presence of RSH) so as to free H_2S totally and to carry it off in an air counterflow.

The oxygen-based vapors that are produced can not be sent to the flare and must be incinerated locally.

Good preliminary oil removal from effluents is also a must so that no "pockets" of aromatic or light HC are sent to stripping, as they can be dangerous in off-gases. This is why some refineries may prohibit air stripping.

Table 19

Stripping processes for sour condensates

Process	Steam stripping	Air stripping	Flue gas
Initial S^{2-} content ($\text{g}\cdot\text{l}^{-1}$)	1-10	0.2-0.5	1-5
Temperature	80-110°C	ambient	85°C
Final S^{2-} content ($\text{mg}\cdot\text{l}^{-1}$)	20-100	5-15	
S^{2-} removal efficiency	96-99%	90-96%	90-98%
Volume per volume			
without acidification	60-200	—	—
with acidification	30-45	40-80	40-100

The advantages of the process are that it can be run cold and that at a first glance it entails the least expensive construction and operating conditions. It is designed to deal with very dilute condensates ($\text{S}^{2-} < 0.5 \text{ g}\cdot\text{l}^{-1}$) and to operate as follows:

- Packing height: 2 to 3 m.
- Percolation velocity: 30 to 40 $\text{m}^3\cdot\text{h}^{-1}$ per square meter.
- Air volume/water volume: 40 to 80.

The resulting residual S^{2-} content is about a few milligrams per liter.

Because of a number of negative points, e.g. NH_4 not eliminated, costly incineration of residual air, new standards on off-gas emissions and risks of explosion, this technique which used to be very widespread in Europe is now being phased out.

2.4.2 Air oxidation of sour condensates

This operation involves oxidation of sulfides initially present in the form of NH_4SH along with low coexisting $(\text{NH}_4)_2\text{S}$ and NH_4OH content.

Workable for S^{2-} concentrations of 30 to 300 $\text{mg}\cdot\text{l}^{-1}$ but involving instantaneous flows of about 20 to 200 $\text{m}^3\cdot\text{h}^{-1}$, air oxidation does not serve the same purposes as when spent caustic is oxidized.

It has relatively low concentrations of S^{2-} to oxidize, usually in the absence of mercaptans, and the condensates contain very few oxides and SS.

It is acceptable that a certain amount of H_2S may escape during the treatment, provided the polluted air is deodorized. Alternatively, if it does not meet standards, it must be used

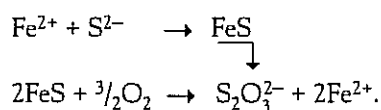
as secondary make up air in incineration, since emission volumes are currently much lower than during stripping.

Catalytic oxidation by air ensures oxidation to the thiosulfate $S_2O_3^{2-}$ stage of sulfides. Process kinetics are accelerated by adding a catalyst (divalent metal Mn^{2+} , Fe^{2+} , Co^{2+} or trivalent Fe^{3+}).

This oxidation process is carried out in a basin at **atmospheric pressure**. The basin may be open or equipped with a draw-off, with a compressed or blowered air distribution network in the bottom. When no catalyst is used, the reaction is very slow and may involve faster intermediate formation of polysulfides.

The oxidation velocity, which is at a maximum between pH 7 and 8.5, then decreases and reaches another maximum from pH 11 to 12 (exactly where spent caustic is located).

Catalysts are added in the form of ferrous or ferric iron:



Depending on pH conditions, Fe^{2+} remains precipitated in the colloidal state or partially oxidized in the form of $Fe(OH)_3$.

The amount of iron that needs to be added depends on the waste's initial concentration in miscellaneous colloidal metallic oxides. The concentration is often sufficient (many corrosion products in raw FCC condensates) and any excess dosage should be avoided.

Reactors

Because flow rates and residence time are considerable, the basins are usually open and made of concrete (Fig. 16).

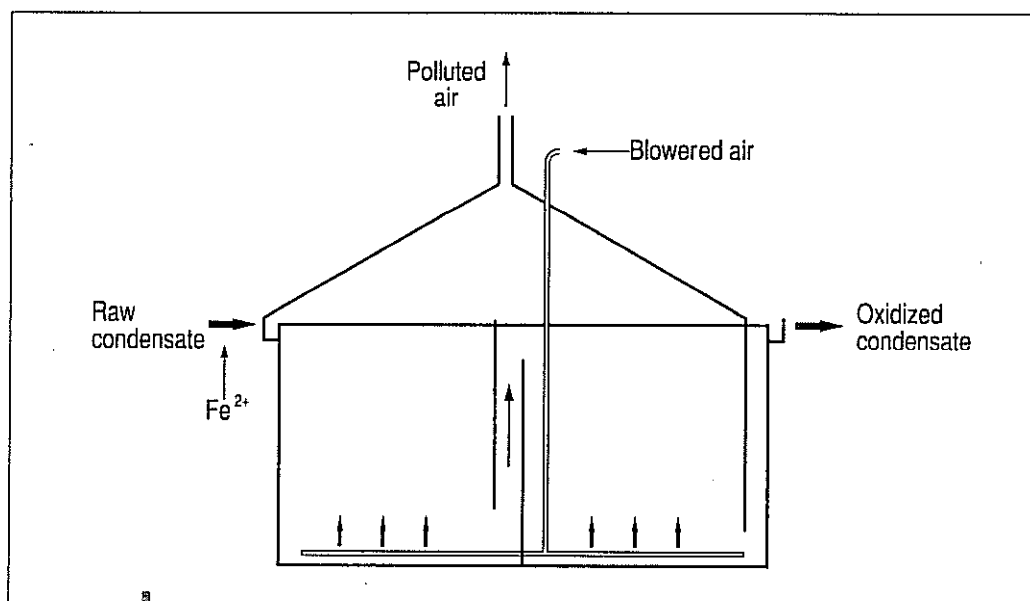


Fig. 16 Oxidation basin with two in-line reactors

For water temperatures of 20 to 35°C, the residence time T in a homogeneous reactor depends on the target oxidation efficiency and on the temperature: $KT = \frac{S_o}{S_f} - 1$.

For concentrations of $S_o < 300 \text{ mg} \cdot \text{l}^{-1}$, the oxidation velocity is said to be at a chemical rate, since it is limited by the reaction and not by the oxygen transfer.

	S_o/S_f	20°C	40°C
$\frac{S_o}{S_f}$	50%	1 hour	0.6 hour
	90%	6 hours	3.5 hours

The make up air (five to 10 volumes per volume) represents four to eight times excess O_2 . At a pH of 6.5 to 7, a parallel stripping effect prevails. At a higher pH, the fraction of free H_2S is small ($8 \text{ mg} \cdot \text{l}^{-1}$ at pH 8 and 2 at pH 9 for $S_{\text{total}} = 100 \text{ mg} \cdot \text{l}^{-1}$). Emissions into the atmosphere become negligible (calculation based on the diagram in Fig. 9a).

Whether the reactors are covered or not depends on the pH range chosen.

The choice of two in-line reactors means that the total basin capacity can be reduced by 30% and that gaseous emissions can be selectively disposed of.

2.5 Preliminary oil separation

Preliminary oil removal or natural gravity oil removal is the first step in a refinery's general treatment, which will be implemented by quite different means according to the objectives that have been set.

2.5.1 Principles of preliminary oil separation

2.5.1.1 Objectives

The first purpose is to eliminate floating HC and a fraction of the HC in mechanical emulsion. The resulting water must be sufficiently oil-free to run through downstream physicochemical purification simply and with economical amounts of reagents.

The second purpose is to eliminate sands and alluvia which are not wanted in physicochemical purification where they would hinder proper collection, concentration and final disposal of floated oily sludge.

Oil separation therefore usually works without reagents. It is designed to equalize residual HC levels at the physicochemical purification inlet by reducing peak HC arrivals, whereas before it often used to be the only purification step and had to be sized up considerably. Depending on how fine the existing emulsions are, the resulting levels of insoluble HC may in fact vary from 20 to 150-200 $\text{mg} \cdot \text{l}^{-1}$ (in petrochemical plants). In principle, they can not be anticipated or calculated. A certain approach can, however, be acquired in the case of simple effluents (deballasting, produced water).

2.5.1.2 Processes

Preliminary oil separation can be carried out by two processes:

- Natural gravity: settlers and separators that droplets of oil rise through at a given upward velocity defined by their specific gravity.
- Artificial gravity: centrifuges and cyclones that cause an increased field of gravity and can be used for produced water.

The first process, which is the only one discussed, is designed for all oily effluents while the second one is generally used for produced water (compactness and energy consumption).

Depending on the origin of the effluent and the treatment downstream, there are two possible oil separator designs:

■ Safety oil separators

They are designed for effluents which have already undergone good separation and their function is mainly to intercept surges of HC due to faulty control of the water-oil interface in facilities upstream. Examples of effluents are the following:

- Deballasting water which has stayed a few days in its tank.
- Desalting water that has stayed a few hours in the desalter.
- Previously stored process water.

These oil separators can be very compact (10 to 20 min depending on the type). Average HC content on inlet varies from 50 to 100-150 $\text{mg}\cdot\text{l}^{-1}$ and is not readily reducible below 40-50 $\text{mg}\cdot\text{l}^{-1}$.

■ Normal oil separators

They deal with effluents that arrive directly without prior storage and that are loaded with HC according to malfunctions due to manufacturing and maintenance. The effluents constantly exhibit strong, mainly mechanical emulsions and unexpected slicks of oil. The effluent categories involved here are oily water and accidentally oily water whose average daily HC concentration can vary between 0.1 and 2 $\text{g}\cdot\text{l}^{-1}$, or more.

The oil separators must be sized to allow the settling of fine droplets to develop completely. Even so, thresholds of 50 to 150 $\text{mg}\cdot\text{l}^{-1}$ of insoluble HC, depending on the origin of the water, must be reached before physicochemical purification becomes more attractive.

These functions are no longer the same as the ones that governed the choice and sizing of longitudinal separators, especially API separators (i.e. designed according to American Petroleum Institute standards) before the 1960s. There are two reasons for this:

- At the time, environmental constraints were not a crucial issue and, with the exception of the FCC stripper, the separator was the main if not the only component in refinery WW treatment. Accordingly, in the oldest European refineries, groups of big longitudinal basins can be seen. They are not covered over or scraped and provide residence times of three to eight hours. They are sometimes followed by hay filters, i.e. barred cages filled with a layer 0.5 to 1 m thick of hay that a current of water runs through. Once it was saturated, this excellent adsorbent was removed and burned.
- Since the 1970s, organic coagulants have been available on the market (see Section 2.6) and have efficiently replaced inorganic coagulants (Al^{3+} and Fe^{3+}). Organic coagulants offer a dual advantage: they can deal with emulsions that are more concentrated in HC and they produce much less sludge that is not as hydrophilic. This widened the scope of physicochemical purification (by dissolved air flotation and also by filtration) by requiring less efficiency from gravity oil separators.

2.5.1.3 Rising velocity of oil droplets

The principle of gravity separation is obviously based on the difference in density between water and insoluble oil. Under the laminar flow conditions that characterize industrial separators and correspond to Reynolds numbers of less than 800, the rising velocity v of an oil droplet can be calculated based on Stokes' law:
$$v = \frac{g}{18\eta} d^2 (\rho - \rho')$$

with:

- ρ density of water
- ρ' density of oil
- g acceleration of gravity
- η dynamic viscosity of oil (in poise, i.e. 10^{-1} Pa·s)
- d diameter of the droplet.

Therefore v is a function of:

- The square of the diameter d .
- The difference $(\rho - \rho')$.

Theoretical sizing of an oil remover therefore requires data on:

- The water temperature and dynamic viscosity (Fig. 17).
- The water (Fig. 18) and oil density.
- The size distribution of oil droplets in the water.

Any increase in water temperature that can be detected decreases the viscosity and increases the velocity (Figs. 19 and 20). A difference in density of at least 0.15 is desirable so that separators do not have to be sized too big.

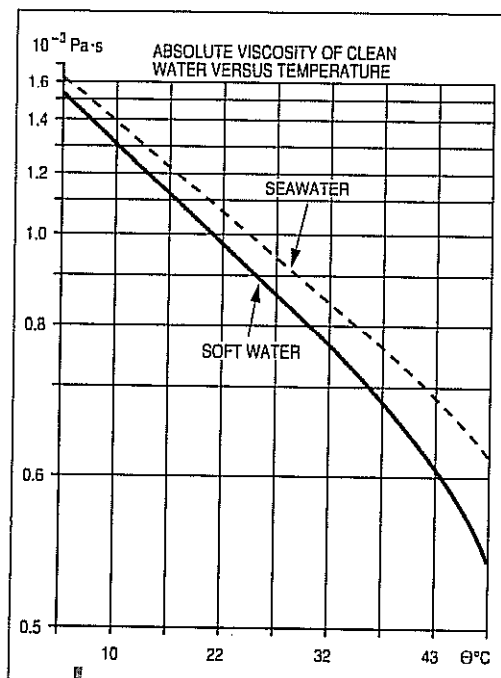


Fig. 17 Absolute viscosity of water

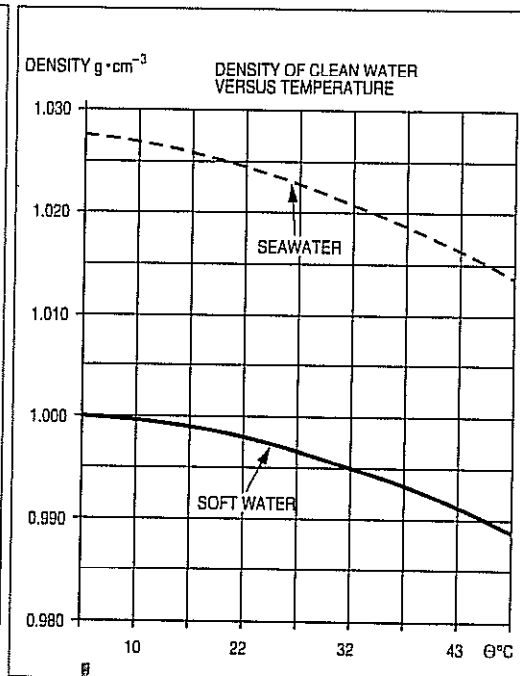


Fig. 18 Water density

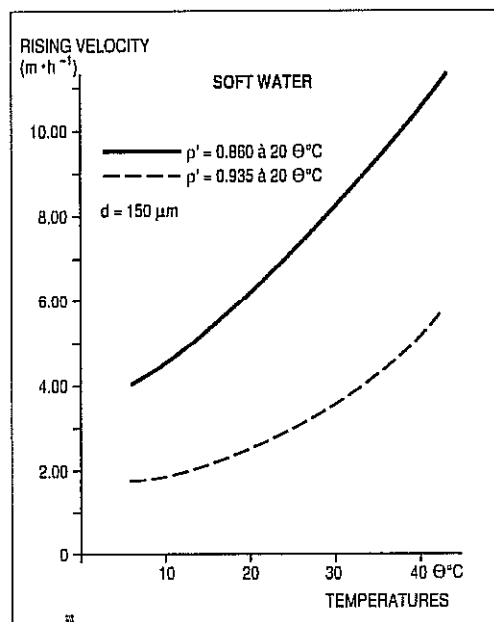


Fig. 19 Rising velocity of oil droplets in an emulsion. Diameter 150 μm . Soft water

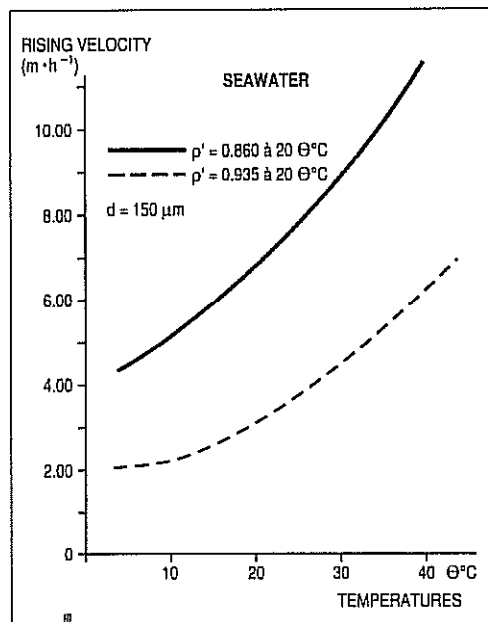


Fig. 20 Rising velocity of oil droplets in an emulsion. Diameter 150 μm . Seawater

With seawater (Fig. 20), the favorable effect of a higher density is offset by a higher viscosity than for soft water.

HC density poses a problem. It is well known during production which involves one or more well-defined crudes and is still more or less predictable during tanker transportation. However, it can no longer be assessed in oily water and accidentally oily water effluents where the nature of the HC, crude, intermediate cut or finished product varies according to malfunctions and routine operations. The choice of a maximum density for use in designing an oil separator facility would hardly be reasonable if the range of specific gravities is recalled:

Crudes:		Products:	
Hassi Messaoud.....	0.8	Motor fuels.....	0.71-0.73
Agha Jari	0.85	Petroleum spirits	0.78
Qatar.....	0.86	Kerosine	0.79
Kuwait	0.88	Diesel oil	0.81-0.89
Nigeria	0.90	Fuel oils.....	0.90-0.93
Tijuana	0.989		

For reference, slops collected and dewatered in refineries often vary in specific gravity between 0.82 and 0.85.

Tradeoffs in designing normal oil separators

The reference basis for designing oil separators is given by API standards described in the "Manual on Disposal of Refinery Wastes", Volume I of 1959, 6th edition. Sizing is based on an attempt to eliminate droplets of an oil of given specific gravity and a size greater than or equal to 150 micrometers.

HC specific gravity in a refinery has already been seen to vary from 0.8 to 1 in gradual increments and an arbitrary choice must be made that will not affect separator sizing adversely.

Monitoring the efficiency of a separator, i.e. counting the number of droplets over 150 micrometers, is based on a very complex API procedure. It resorts to three sequences (addition of a detergent solution, concentration of droplets by filtration and examination under a microscope) and probably induces a coalescence process which would throw off the measurement. Moreover, in what are termed lamella separators, the coalescence process can be developed to a greater or lesser extent and improve separation more than lamella sizing alone.

Practically speaking, except when companies impose their own ideas, separators are designed or chosen by manufacturers based on their own experience. When the separators are integrated in a complete treatment setup, they seldom have a specific operating guarantee, which would be hard to establish.

They must be expected to give good operating reliability as far as cleaning frequency, fouling risks, odor emission and water content of resulting surface slops are concerned.

2.5.2 Construction of gravity oil separators

Two types of separators are found in refineries and their efficiency can be boosted by supplementary means:

- **Settler separators** where the oil is directly collected from the surface of the water. These include longitudinal API separators and circular separators.
- **Lamella separators** or plate separators where the oil is collected directly by the lower surface of oblique plates and then brought up to the surface. The plates have a dual function. They define very short routes for the droplets and they have a coalescence effect. Both of these functions are due to the close interlamella spacing.

2.5.2.1 Longitudinal API separators

A. Design

The separators are designed to eliminate oily droplets over 150 micrometers in size. The rising velocity equation mentioned earlier becomes: $v = \frac{0.44 (\rho - \rho')}{\eta}$, expressed in $\text{m} \cdot \text{h}^{-1}$.

The API standard defines three main parameters:

1. The useful horizontal area S of the body of water, such that: $S = \frac{FQ}{v}$ with:

Q flow rate of raw water

F correction coefficient equal to $F_d \times F_t$ where F_t , the turbulence factor, is defined as a function of $\frac{V}{v}$ (V is the horizontal velocity of the water going through the settler and F_d , established distribution factor, is around 1.2. V should not exceed $54 \text{ m} \cdot \text{h}^{-1}$).

$\frac{V}{v}$	F_t	F
6	1.14	1.37
10	1.27	1.52
15	1.37	1.64
20	1.45	1.74

2. The minimum vertical cross section A , such as: $A = \frac{Q}{V}$.

V should preferably not exceed $45 \text{ m} \cdot \text{h}^{-1}$ assuming distribution is very good at the settler inlet.

3. A height to width ratio ranging between 0.3 and 0.5.

These hypotheses explain why the separators are built as several parallel shallow basins. API recommends remaining within the following limits for proportions:

- Width between 1.8 and 6 m.
- Depth between 0.65 and 2.4 m.

Since the separators were theoretically not designed with a bottom scraping system, API recommended placing a second parallel basin to be available while the first is undergoing maintenance.

Operation in this way with an increasing sludge level for several months or a year means that transit velocity is accelerated and separation efficiency is decreased at the same time, independently of unwanted floating matter which can come from anaerobic fermentation developing in the bed of sludge.

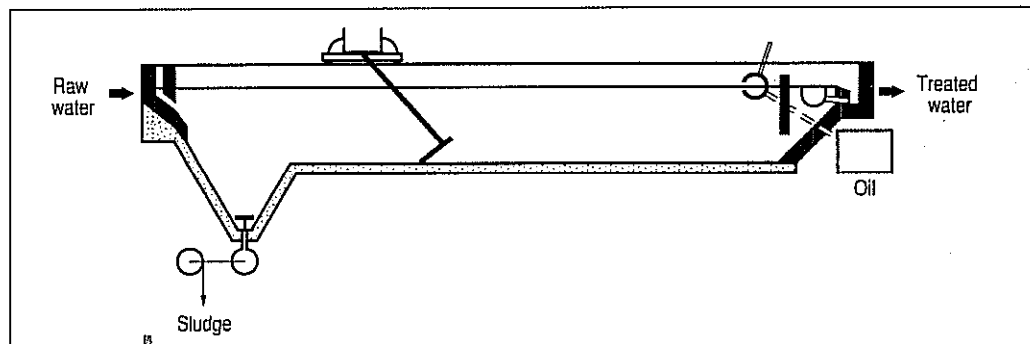


Fig. 21a API separator with a bottom scraping device

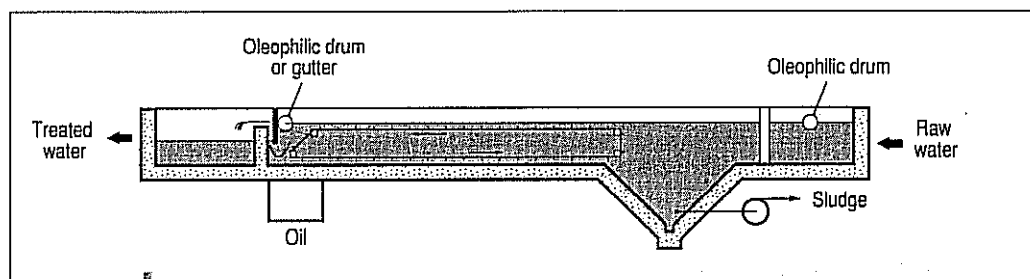


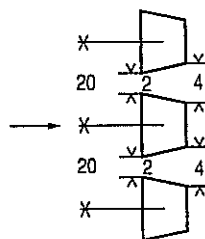
Fig. 21b API separator with a chain and a drum oil collector

In practice, new separators should always be equipped with a bottom scraper, whether bridge suspended (Fig. 21a) or chain-driven (Fig. 21b).

B. API separator feed

A vertical grid with bars spaced 4 cm apart as proposed by API should be considered for process water. In contrast, accidentally oily water can cause fouling more rapidly and requires a mechanical scraping device. In this case there can be an added preliminary grid with 10 cm spacing, followed by a automated screen with trapezoid-shaped bars more finely spaced, i.e. 2 cm, with 20 cm between axes. The advantage of this grid system is to allow a regular distribution of the raw water. With a 5% gap between the bars at the inlet and a 10% gap at the outlet, the following maximum velocities can be maintained:

- Input velocity: $0.3 \text{ m} \cdot \text{s}^{-1}$.
- Output velocity: $0.15 \text{ m} \cdot \text{s}^{-1}$.

**C. Outlet weir**

The water outlet's siphoid baffle must be submerged to a depth roughly equal to half the useful depth of the separator. This is a minimum as priority is now given to oil removal and not desanding. It can be built of asbestos board, of Epikote-coated steel or of plastic.

Hydraulic loads of 30 to $50 \text{ m}^3 \cdot \text{h}^{-1}$ per meter of outlet weir are defined for throughput velocities of 25 to $45 \text{ m} \cdot \text{h}^{-1}$. The loads are relatively large and to improve the chances of collecting the oil layer by skimmers, less variation in the height of the water head at the outlet weir is advisable. This is possible if the outlet is doubled or equipped with perpendicular notches. The Francis formula is used by API to calculate the height of the water head:

$$H = 3.2 \frac{Q^{\frac{2}{3}}}{0.3L}$$

where:

- Q throughput flow rate in cubic meters per second
- L developed length of the weir in meters
- H height of the water head in meters.

The water falling downstream from the weir has no adverse effect on the physicochemical purification operation. It may, however, cause foaming and aerosols, or even odors.

D. Disposal of bottom sludge

This is a critical point in operating the separators. If the bottom is not scraped, sludge is pumped out periodically into a low-pressure suction tank. If the bottom is scraped, the scraping system (alternating bridge or continuous chain) does not reach the concentration pit located at the head of the separator. If the bed of sludge tends to set in a viscous, fairly stable gel, suction by a pump or a piping system then creates a "chimney" of clear water and the gelled sludge surrounding it does not cave in toward the center.

The means of preventing this kind of trouble (and the less often the sludge is pumped out, the more frequent it is) is to install a scraper screw across the whole width of a single concentration pit or to have a number of square truncated pyramid-shaped concentration pits all across the width of the basin with an equal number of suction devices.

E. Disposal of oil and floating matter

Originally, API oil separators were equipped with cylindrical gutters or manually- or pneumatically-controlled troughs for periodical extraction. This caused quite a considerable amount of water to be carried off with the slops. Gutters can be built with diameters of 200 to 300 mm, or even 360 for double basins. The gutters must be adjustable in a downstream or upstream direction so as not to leave a layer of stagnant oil. Widespread use of drum oil collectors nowadays has solved these problems (Fig. 21 b).

In very windy areas, the orientation and direction of the water current in uncovered basins must be chosen carefully, but all new facilities should be covered.

When there is no cover on the basin, the layer of oil on the surface is subjected to a fair amount of entrainment depending on the water temperature and the wind speed. As a result, the air may be polluted by volatile HC, in addition to the odors produced by mercaptans. A covered forebay built in the shape of a truncated pyramid allows the lightest and most volatile HC that have collected to be extracted simply and continuously. Sludge is extracted in batch operations by an immersed pump. API gives the general layout example in its manual as it appears in Fig. 22.

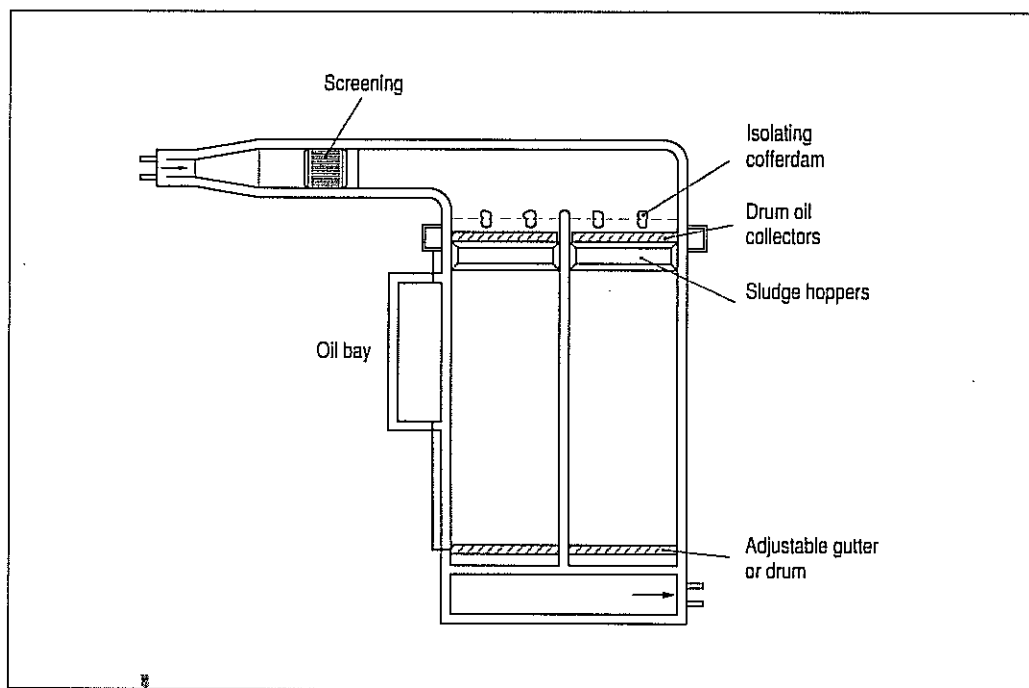


Fig. 22 General layout of API separators (After API Manual example, 1959)

Table 20
API sizing example for heavy HC

Water temperature	50°F 10°C			70°F 20°C			105°F 37°C		
Oil specific gravity	0.94	0.90	0.87	0.94	0.90	0.87	0.94	0.90	0.87
Droplet velocity 150 μm ($\text{m}\cdot\text{h}^{-1}$)	1.98	3.24	4.14	2.9	4.5	5.7	5	7.4	9
Longitudinal V of water ($\text{m}\cdot\text{h}^{-1}$)	30.6	48.6	54	43.2	54	54	54	54	54
F factor	1.64	1.64	1.59	1.64	1.56	1.50	1.52	1.44	1.38
Flow rate in $\text{m}^3\cdot\text{h}^{-1}$ per m^2 of area	1.21	1.94	2.6	1.77	2.94	3.9	3.37	5.22	9.6
Area in m^2 treating $227 \text{ m}^3\cdot\text{h}^{-1}$	184	115	86	126	76	58	67	43	34

Table 20 shows an example given by API for relatively heavy hydrocarbons. It indicates the minimum horizontal area versus the water temperature and the specific gravity of the HC under consideration (API, Vol. I, 1959).

F. Example of design

An quick sizing example can be given for a separator for a heavy crude oil:

Raw water: Flow rate = $400 \text{ m}^3\cdot\text{h}^{-1}$
 Temperature = 40°C
 Specific gravity = 0.995.

HC : API degree = 20 at 60°F
 Specific gravity = 0.925.

- Rising velocity v of the $150 \mu\text{m}$ droplet = $5 \text{ m}\cdot\text{h}^{-1}$
- Maximum acceptable velocity $V = 45 \text{ m}\cdot\text{h}^{-1}$
- Correction coefficient F for $\frac{V}{v} = 9$: $1.2 \times 1.27 = 1.54$.

Separator dimensions:

$$\text{Useful area: } \frac{400 \times 1.54}{5} = 123 \text{ m}^2$$

$$\text{Vertical cross section: } \frac{400}{45} = 8.9 \text{ m}^2.$$

Width = 4.5 m

Depth = 2 m

Length = 27 m.

Considering the space necessary upstream for distribution and downstream for the water to spill out and the oil to be collected, the separator has a total length of around 30 m and a useful volume of somewhere near 280 m^3 . It defines a theoretical residence time of 40 min.

2.5.2.2 Circular oil separators

A. Principle

API also points out that it is possible to build circular oil separators whose profile fits the profile of make up water clarifiers. However this does require the addition of a very deep, siphoid peripheral wall.

Although this technique requires more costly civil engineering work, it is now making a comeback as it can solve a number of the problems posed by longitudinal separators:

- The separator bottom is completely scraped and the central sludge concentrator is partially scraped by a scraper bridge with central or peripheral drive. This means that it covers the whole area, even the inaccessible parts and leaves no blind zones.
- The peripheral weir has a development of $3.14 D$ which defines variations in water head height of a few centimeters for considerable variations in the throughput flow rate. Hydraulic loads of 3 to $15 \text{ m}^3 \cdot \text{h}^{-1}$ per meter of weir are in fact maintained depending on the increase in oil separator diameter D .
- The central baffle where raw water is introduced may be covered and equipped with a continuous oil draw-off. In a residence time of two to five minutes, the oil layers and the larger droplets of the lighter oil can be gathered together. The oil is protected from the wind during extraction and accordingly odors are considerably curtailed.
- The peripheral zone is therefore used to settle the sludge and float the heavier oil and the oil-coated SS.

The volume defined for this secondary separation, between the siphoid wall and the central baffle can represent an average residence time of 30 to 40 min and corresponds to a surface load of 3 to $6 \text{ m}^3 \cdot \text{h}^{-1}$ per square meter.

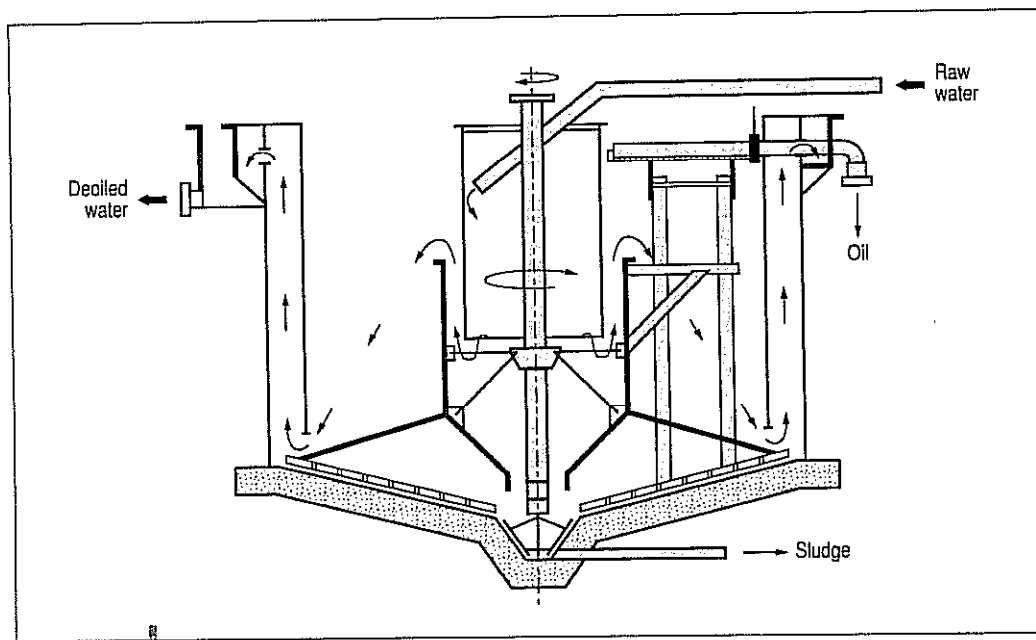


Fig. 23 Degremont circular oil separator

However, the raw water inlet causes problems. If piping runs overhead, the water must not fall which would generate emulsions.

If piping runs underground, the inlet profile must be designed so as to minimize clogging risks or to allow maintenance without building costly underground access tunnels.

B. Implementation

Buried structures

The circular separator with scraping at two separation steps can be considered for diameters greater than 6 m and therefore flow rates of at least 75 to $100 \text{ m}^3 \cdot \text{h}^{-1}$. Building a "preliminary oil removal well" outside simplifies construction for oil separator diameters of 4 to 6 m but requires a sunk pump to extract the sludge from the well.

Elevated structures

Since they are fed under pressure, unscrapped, cylindroconic tanks can be considered provided that the water is warm or that the HC have a low pour point. They can be built up to a diameter of 5 to 6 m and can deal with warm process water without needing a preliminary oil removal well.

2.5.2.3 Lamella oil separators

The principle of separating oils by means of plates has been applied for some time and PPI oil separators (Parallel Plate Interceptors) were developed as far back as the 1950s by the Shell Group.

The technique then developed greatly for use in clarification of turbid or waste water thanks to the manufacture of one-piece plastic plate packages. Interest in applying lamellar separation to oily water was immediately revived.

A. Principle

Since the theory of these separators is discussed in specialized treatment literature, we will confine ourselves to a reminder of some of their characteristics.

A group of parallel plates, usually slanted at a 45° or a 60° angle in an oil-removing separator provides a three-pronged improvement in operation:

- By lowering the Reynolds number of the water flow and causing more even distribution. Numbers from 400 to 1600 are encountered depending on the temperature and the capacities used. Meanwhile, these values rise above 5000 in longitudinal separators at maximum allowable velocities.
- By dividing up the average rising vertical route for oil droplets in as many portions as there are intervals of plates located in the useful height of the settler. The plate intervals are 10 cm in PPI, two or four centimeters in CPI (Corrugated Plate Interceptors) and in TPS (Tilted Plate Separators). As a result, there is a considerable decrease in the route covered by a droplet before it is picked up. Additionally, the structures are compact, at least as regards the land area they require, i.e. three to four times less than that of normal separators. An API with an average water depth of 1.6 m can be compared to a PPI or to a CPI which can respectively provide eight separation stages or nearly forty for the same useful height.
- By promoting a coalescence process, i.e. enlargement of oil droplets by contact between the water and an oily film developed over a considerable area. This is an asset that longitudinal or circular separators can not provide.

On the contrary, close plate density with cold dirty water, especially if it is loaded with paraffins, promotes development of considerable deposits or "fattens up" the plates. This leads to a reduction in the free cross section and can double the flow velocity in separators with 2 cm intervals. As a result, separator efficiency is impaired.

With accidentally oily water that is relatively colder and dirtier, it is necessary to clean the plate packages every three to four months. This requires them to be taken apart outside the separator. With hot process water (condensates, etc.) the congealing problem is nonexistent and deposit growth warrants preventive maintenance only once a year. Two-centimeter intervals therefore become possible, but are still borderline.

A second limit on their use comes from their modular construction. With four-centimeter spacing and a nominal capacity of $30 \text{ m}^3 \cdot \text{h}^{-1}$ per assembly, around ten prefabricated packages are used to treat a maximum flow rate of $300 \text{ m}^3 \cdot \text{h}^{-1}$ of accidentally oily water. When so many modules are lined up parallel fashion, there are problems:

- Of equal distribution on inlet, i.e. of modules that it is advisable but difficult to cover;
- Of scraping the relatively deep bottoms;
- Of operating costs due to periodical cleaning;
- Of covering.

B. Implementation

Among the numerous available lamella separators, the following can be mentioned according to the direction of oil and water circulation:

Counterflow separators (Fig. 24)

The CPI with modules measuring $1 \times 1 \times 1.75 \text{ m}$ and plates spaced 2 or 4 cm apart (space occupied $2.2 \times 4.95 \text{ m}$, depth 3.85 m) and the TPS.

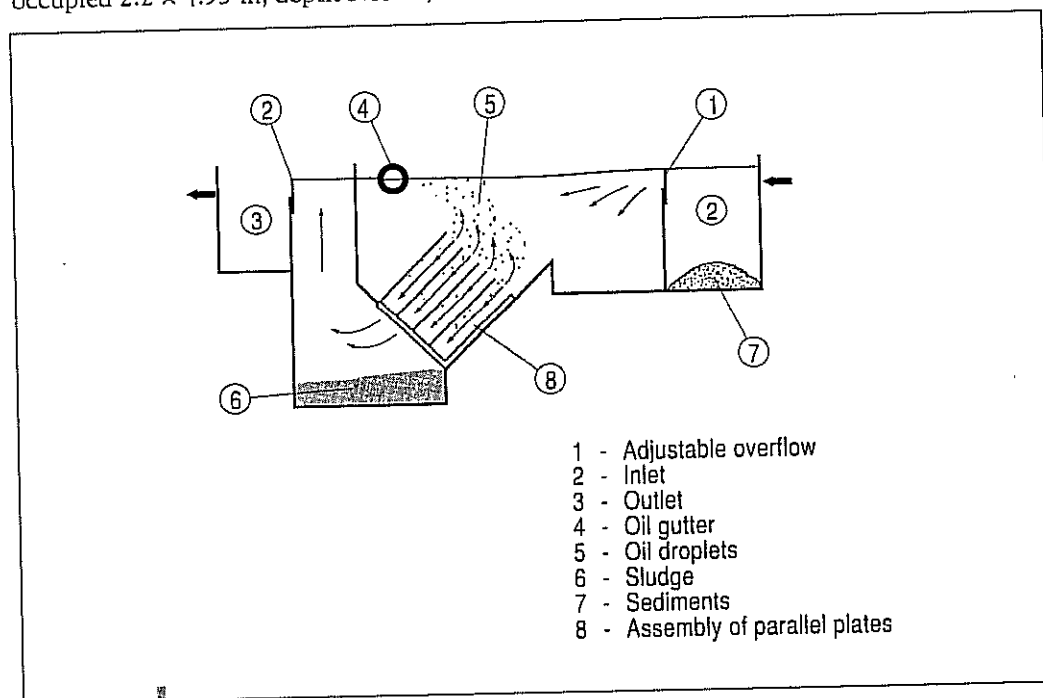


Fig. 24 CPI separator

Water and oil cocurrent flow separators

Skimovex separators, for example, with special "fingers" to collect the oil (Fig. 25).

Plate equipment is made of fiberglass-reinforced polyester resin or some other noncorrodable material.

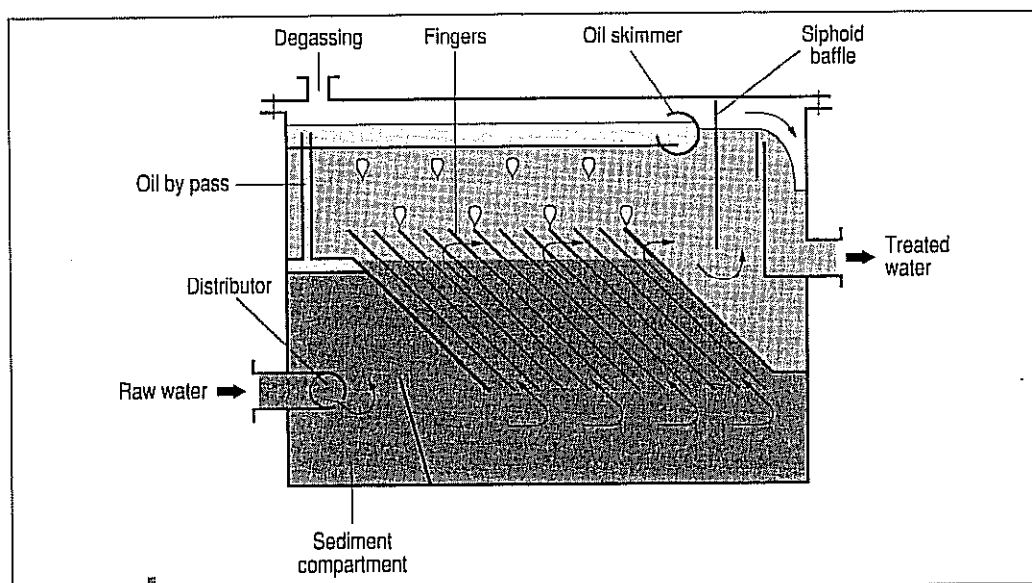


Fig. 25 Skimovex separator

Crossflow separators

PPIs with 10 cm spacing (Fig. 26) and a removable heavy metal plate assembly.

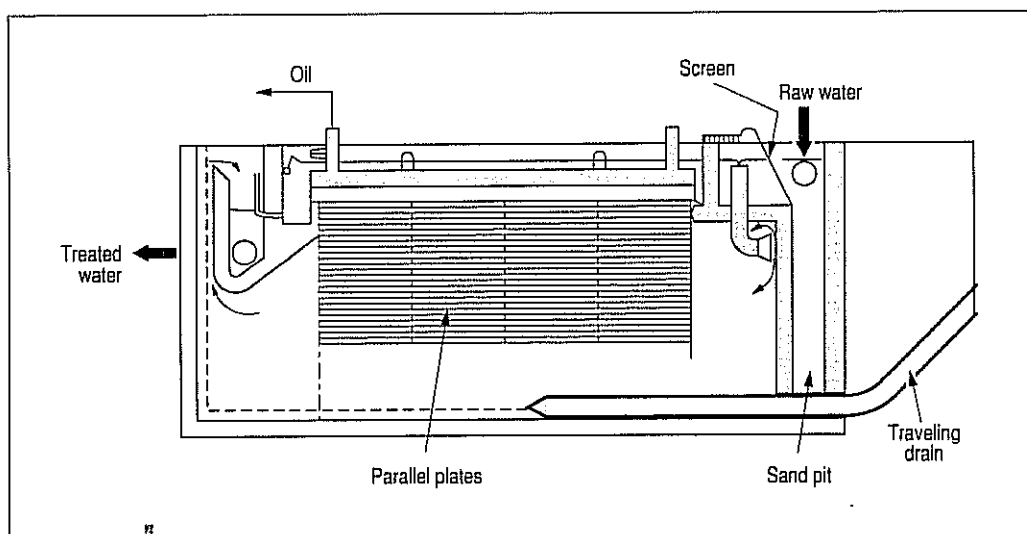


Fig. 26 PPI separator

C. Efficiency

As for all separators, lamella separator efficiency is hard to forecast since effluents can vary widely and mainly because of the measurement of emulsion grain-size dispersion.

Residual concentrations of 20 to 50 $\text{mg}\cdot\text{l}^{-1}$ are put forward when the separators treat so-called "easy" effluents such as deballasting or produced water. It generally constitutes unstable mechanical emulsions that are more readily treatable than some refinery WW, or petrochemical WW in particular. It should also be pointed out that the potential efficiency is seldom given in correlation with the HC measurement method (see page 80).

The main point to remember is how well these separators work on a lot of hot process water and produced water and that they are suitable for low flow rates.

2.5.3 Choosing oil gravity separators

Assessing a separator and its sizing depends on the type of effluents experienced. General guidelines alone can be given:

- Lamella systems serve to ensure safety on hot, relatively oily, low-SS process condensates.
- Scraped systems are suitable for accidentally oily water that is irregular, cold and loaded with SS.
- The safety role prevails with relatively nonoily but cold deballasting water. To cope with the odd, unexpected slug of oil, simple oil-removing wells offering a residence time of 12 to 20 min at a limited horizontal flow rate of $200 \text{ m}\cdot\text{h}^{-1}$ can be built (what is termed the API Special-purpose Separator).

Generally speaking, controlling physicochemical purification processes, especially by dissolved air flotation, prioritizes the separator's safety function at the expense of the polishing function, which in any case has often become redundant.

2.5.4 Oil collectors and skimmers

There are a large number of devices designed to collect or "sponge up" oil layers. The scope of use ranges from equipment in API separators to applications in ports or for oil spills.

They are in no way used to purify water in depth and do not modify an emulsion. They are placed at the surface of a body of water that is assumed to be as calm and constant as possible and can only "recover" a preexisting, fairly thick slick of oil.

According to the area involved (API, lagoon, port) and the water agitation (waves, wind), the device is chosen based on the manufacturer's actual experience. Among the models used in the refining and iron and steel industries, i.e. on a stable body of water, the following can be mentioned:

2.5.4.1 Static collectors

- Adjustable gutters (reminder).
- Upright Serep skimmer for fairly constant levels (small basins).
- Circular Serep skimmer for large, variable-level tanks.

2.5.4.2 Oil collectors

- With discs or drums (for constant levels, API, etc.).
For example: SAPEC Oil Drum Skimmer, VIKOMA KEBAB Skimmer, etc.
- With metal belts (for small level differences).
For example: SANDVIK, REXbelt.
- With "sponge"-type rope (for variable levels).
For example : OIL MOP, BRILL Skimmer M610.

2.5.4.3 Dynamic stationary separators

- Vortex Elf Bertin, where the sheet of oil accumulates in a vortex induced by a submerged turbine.
- Megator, Rheinwerft, where the sheet of oil is carried away by forced water circulation.
- Autostable SEREP MOBY DUCK Skimmer.

2.5.4.4 Dewatering surface slops

The water content in surface slops is lowest with oil drums and highest with pump-induced water circulation systems. Nevertheless, some dynamic skimmers such as the autostables can draw off a thin enough water layer to be fairly rich in oil.

Surface slops must have a low water content in order to be sent to the refinery's slop tanks. If there are no oil drum or disc collectors (often a heavy investment), the oil compartment attached to the separators and usually fed by gravity from the collectors must be set up and operated rationally.

The means to this end may be:

- Water-oil interface sensors.
- Flow controller and/or gravity controller on the transfer pump discharge.
- Moderate heating of the oil layer in the compartment, provided there is a steel lining and, more important, as long as the refinery's safety regulations are complied with.

2.6 Physicochemical purification of effluents from preliminary oil separators

This purification process is the intermediate phase between preliminary oil removal (API or lamella separators) and biological purification.

It has to treat effluents which still contain:

- From 30 to 100-150 $\text{mg}\cdot\text{l}^{-1}$ of hydrocarbons in a fine emulsion.
- Colloidal or suspended matter.
- Dissolved or suspended metals.
- Possibly sulfides.

It involves flocculation of these effluents by chemicals and solid-liquid physical separation of the sludge produced by flocculation.

2.6.1 Aims of physicochemical purification

- First to eliminate insoluble hydrocarbons to possible residual concentrations of 2 to 20 $\text{mg}\cdot\text{l}^{-1}$ depending on regulations and methods.
- Then to perform several important joint operations required either for direct discharge or to supply the biological purification process:
 - Neutralize the pH.
 - Precipitate toxic heavy metals.
 - Oxidize or precipitate excess sulfides by an iron salt.
 - Clarify the water.

For many years, this purification process was carried out in three stages, by analogy with river water clarification:

- Coagulation based on aluminum or iron salts, with possible lime make up (coprecipitant) so as to densify the floc, and an anionic polyelectrolyte make up (flocculating agent).
- Separation of the oily metallic hydroxide floc by slow settling initially, then exclusively by dissolved air flotation.
- Thickening, dehydration and incineration of bulky hydrophilic sludge.

As far back as the 1970s, dissolved air flotation (DAF) was mastered and organic coagulants became available on the market. This modified and simplified flotation conditions:

- By precluding the need for lime, a reagent that is difficult to handle.
- Then by replacing the inorganic coagulant by an organic coagulant that produces less, and less hydrophilic, sludge. As a result, DAF facilities became simpler and less expensive to run.

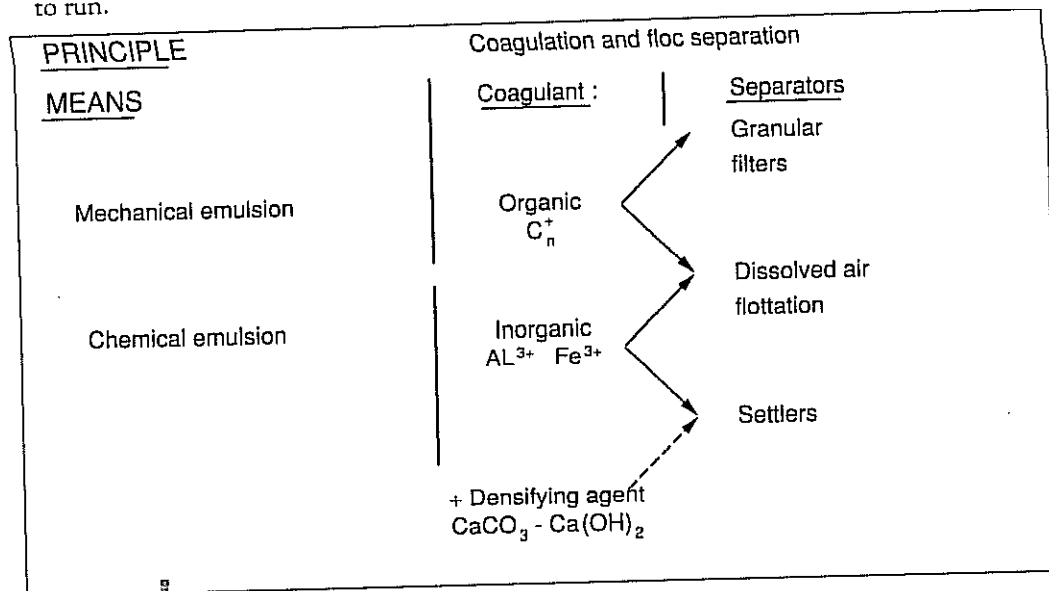


Fig. 27 Physicochemical purification processes

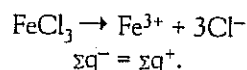
Physicochemical purification can therefore be defined as the combination of flocculation using two possible processes and separation of the resulting (or potential) floc by two physical mechanisms: flotation or filtration (see Fig. 27).

2.6.2 Notes on coagulation and flocculation

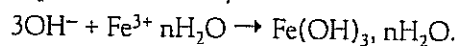
2.6.2.1 Conventional flocculation

This process is used to clarify a lot of river water and includes:

- Dissolution and ionization of the inorganic coagulant whose electropositive charges neutralize the electronegative charges of the emulsion or the colloids which are accordingly destabilized:



- Precipitation of the hydrophilic metallic hydroxide:



- Flocculation by enlargement of the hydroxide floc on which the destabilized colloids or micelles are adsorbed. An anionic flocculant is often added.

Amounts: 50 to 100 $\text{mg}\cdot\text{l}^{-1}$ of 50% FeCl_3 which precipitates 17 to 35 $\text{mg}\cdot\text{l}^{-1}$ of $\text{Fe}(\text{OH})_3$.

This hydroxide increases the sludge weight by 20 to 40% and mainly decreases its concentratability by two or three times, since it is very hydrophilic.

2.6.2.2 Flocculation by organic cationic coagulant

- Dispersion of the type 2 liquid cationic polyelectrolyte which only partially neutralizes the electronegative charges in the emulsion.

Amounts of coagulant (active matter): 0.2 to 3 $\text{mg}\cdot\text{l}^{-1}$ of water.

- Agglomeration of the micelles that have been destabilized by coalescence.
- Flocculation of oily agglomerates together by addition of a cationic flocculant or by contact on a granular mass.

Amounts: 0.5 to 1.5 $\text{mg}\cdot\text{l}^{-1}$ of flocculant (type 1 polymer) generally in powder or sometimes anionic polymer.

These polymer doses do not significantly increase the mass of the sludge and, more important, do not impair its good initial concentratability.

In order to choose these polyelectrolytes, it is useful to know the characteristics of the four different types given in Table 21.

Table 21

Main types of polyelectrolytes

Type	Structure	Molecular weight	Commercial form
Anionic	Acrylamide and acrylic acid copolymers	10^6 to 10^7	Flocculants Powders or emulsions
Nonionic	Polyacrylamides		
Type 1 Cationic	Copolymers of acrylamides and a cationic monomer		
Type 2 Cationic = coagulant	Melamine, formaldehyde EPI, DMA, poly DAD MAC	10^4 to 10^5	Coagulant 10% aqueous solution or emulsion

The first three polymers, the flocculants, are generally chosen on the basis of their "antagonism" with the flocs that are being formed:

- Anionic for flocs of electropositive-tendency metallic hydroxides.
- Cationic for electronegative colloid-based flocs (OM, activated sludge).
- Nonionic in intermediate situations (sometimes CaCO_3).

These products must be distributed in-line at concentrations of 0.05 to 0.1 $\text{g}\cdot\text{l}^{-1}$.

2.6.2.3 Specific features of organic coagulants

The organic coagulant (type 2 cationic polymer) with a strong cationic nature provides a coagulation mechanism fairly close to the metallic coagulants' mechanism but does not include the subsequent flocculation stage.

It achieves only very partial neutralization of the electronegative charges of the oil micelles at the homeopathic doses in which it can be used. However, this allows initiation of the process that coalesces the micelles together by modifying interfacial tension forces.

Flocculation as such can be achieved only through contact with a granular mass (infinite number of velocity accelerations and decelerations) or through the reticulating effect of a separately added flocculating agent. The flocculant is:

- Usually a type 1 cationic polymer which acts by electric complementarity. This is the case for emulsions.
- Sometimes an anionic polymer which acts by antagonism. This can be true of suspensions where there is a prevailing metallic hydroxide floc and not oils.

As a matter of fact, this arbitrary explanation summarizes complex phenomena which are still not very well understood. They can be mastered only by experience or, even better, by experimenting and testing (jar tests).

In industry, this form of flocculation coagulation where coalescence prevails can be performed:

- Fully in coalescing filters.
- Along with flocculation upstream from dissolved air flotation or through downflow filters.

There are several important rules on the use of cationic coagulants:

- Considerable dilution of the commercial liquid is required in-line (1 $\text{g}\cdot\text{l}^{-1}$ of active matter) with water whose salinity is compatible with the coagulant (or vice versa). It is preferable to use soft water.
- High mixing energy is needed with the water to be treated (velocity gradients of 500 to 1000 s^{-1} for a few seconds). Mixing can be achieved through the water transfer centrifugal pump or through an in-line mixer.
- Flocculation time depends on the nature of the emulsion and especially on the temperature which is often an asset in refinery WW. Above 20°C, the time is often from two to four minutes. It can go up to about 15 min at around +12°C.
- The velocity gradient in the flocculating facility must not be excessive, i.e. it is around 50 to 150 s^{-1} .

Some organic coagulants can be listed: Kemazur 4516 and 4521, Cyanamid 507, Nalco 3364, Alchem 7607, Tetrolite J 121 and WC 14.

Direct demulsifiers

Their purpose is to destabilize water-in-oil emulsions found in production. However, they may be of interest in refining upstream from filters or coalescer filters, where processes different from simple coagulation are likely to develop. Organic coagulants are also called "inverse demulsifiers" in production.

2.6.2.4 Limits of organic coagulants

The coalescence process, i.e. the collision-encounter-agglomeration of oily droplets can develop:

- Either on a continuous oily film, if it is established in contact with a granular medium (sand, anthracite) and this is the case for granular coalescers or even filters.
- Or between more or less fine droplets maintained in suspension in a flocculator by steady stirring. To promote minimum agglomeration, traces of flocculant must be added after the coagulant is added.

There is therefore no more HC adsorption on an Al metallic hydroxide and no more Fe hydroxide which is known to be hydrophilic, and hard to thicken and to dehydrate.

There is no more mineralization by Cl^- or SO_4^{2-} anions provided by the inorganic coagulant.

However, in the absence of this highly adsorbent hydroxide gel, fine colloids (with FeS among them) do not flocculate as well and water clarified by an organic coagulant alone does not exhibit the limpidity and shininess given by metallic salts. Turbidity may be from 2 to 3 NTU, often 0.5 to 1 in the second instance.

If rare but nevertheless possible chemical emulsions occur in the second case, due to asphaltenic or even naphthenic compounds, the organic coagulant may not be effective enough. It will need to be replaced or supplemented by strong doses of inorganic coagulant or by dramatic lowering of the pH. This involves heavy chemical consumption.

2.6.2.5 Desulfurization by precipitation of FeS

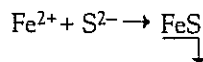
Earlier (in Section 2.4), desulfurization was seen to be performed by oxidation or by stripping. Carrying out oxidation is seldom necessary for general effluents, it would more likely be used for process water mainly comprising sour condensates (0 to 300 $\text{mg}\cdot\text{l}^{-1}$ of S^{2-}).

Chemical precipitation at the head of a flocculation-separation facility in fact involves water whose S content ranges between 10 and 50 $\text{mg}\cdot\text{l}^{-1}$. The aim here is to achieve water containing less than 1 or 0.5 $\text{mg}\cdot\text{l}^{-1}$ of S^{2-} after this separation operation.

Depending on whether dissolved oxygen is present or not, the products of precipitation by an iron salt are different. But in both cases, coprecipitation of iron hydroxide is required so that flocculation of FeS or S_0 (both of which are highly colloidal) can be controlled.

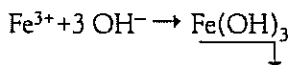
1. Without dissolved oxygen

- Precipitation of FeS:



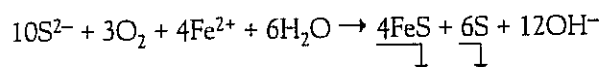
For 1 mg of S^{2-} :

- Consumption of $\text{FeSO}_4, 7\text{H}_2\text{O}$: 8.7 mg.
- Precipitation of 2.75 mg of FeS.
- Coprecipitation of FeS by the required iron hydroxide, i.e. 1 mg per milligram of FeS:



which requires 8.5 mg of $\text{FeSO}_4, 7\text{H}_2\text{O}$ or 8.1 mg of 50% FeCl_3 .

2. In the presence of dissolved oxygen (disproportionation)



For 1 mg of S^{2-} :

- Consumption of $FeSO_4, 7H_2O = 3.5$ mg.
- Consumption of 50% $FeCl_3 = 1.2$ mg.
- Precipitation of 1.7 mg ($FeS + S$).
- Required coprecipitation of 1.5 to 3 mg of $Fe(OH)_3$ or $Fe(OH)_2$ which needs 4.6 to 9.2 mg $FeSO_4, 7H_2O$ or 2.2 to 4.5 mg of 50% $FeCl_3$.

Three chemical conditioning setups are therefore possible (Fig. 28):

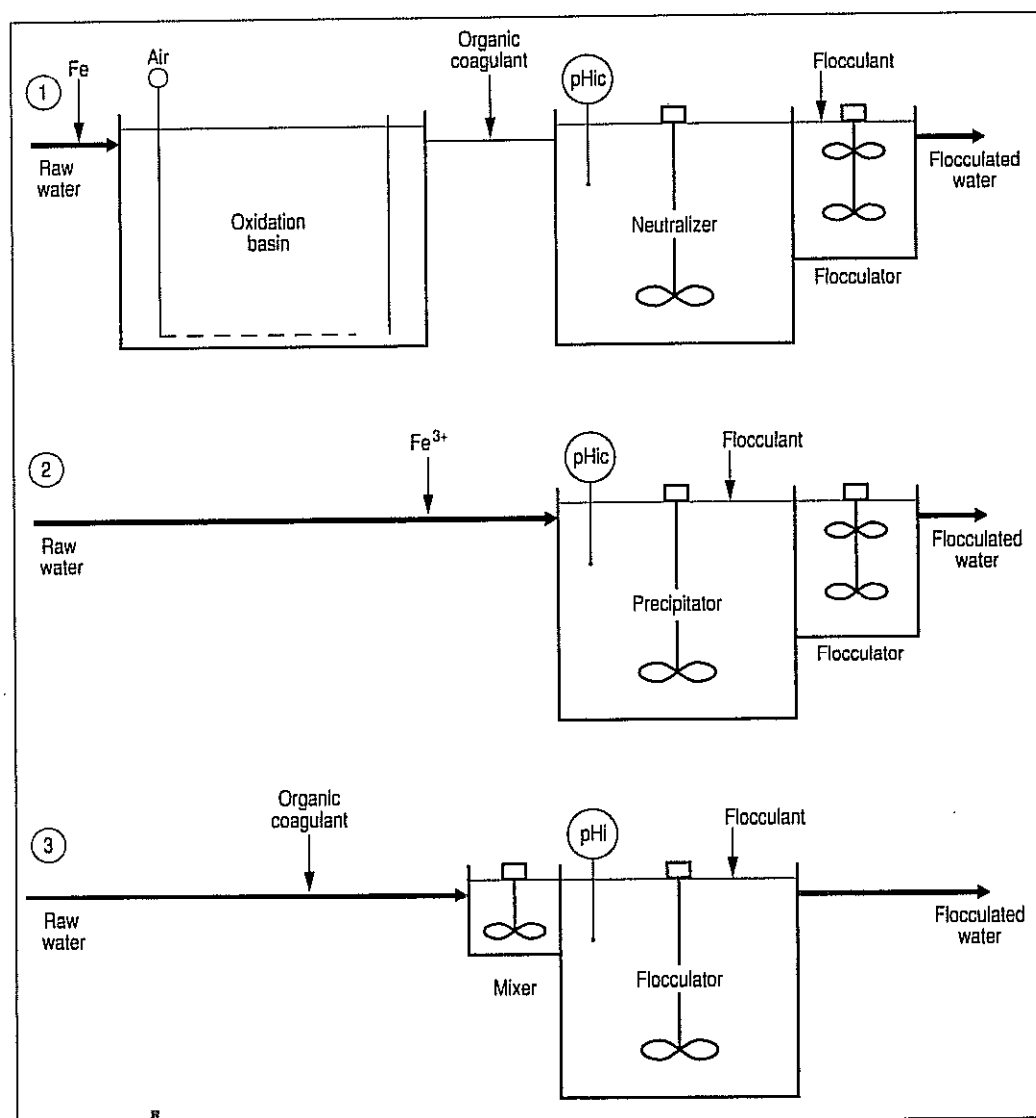


Fig. 28 Diagrams showing chemical conditioning before DAF

The first diagram is the least common and involves oxidation of sulfides in water where process condensates prevail. The water is often slightly alkaline. The pH may have to be corrected in the neutralizer which also performs coagulation and must allow a sufficient residence time (10 to 15 min). Residence time itself in the oxidation basin (see Chapter 2, Section 2.4) lasts some 30 to 90 min.

The second diagram corresponds to precipitation of FeS as previously defined. This usually entails the use of an inorganic coagulant. The precipitator, which can include another neutralization operation, also provides ten to 15 min' residence time.

The third diagram shows the general effluent treatment setup. It includes a quick mixer (one to two minutes) followed by a flocculator. This device, depending on the temperature, provides a residence time of 6 to 12 min and is equipped with a pH indicator since the neutralization function is often unnecessary.

These treatments produce sludge and must be carried out in relatively large reactors. They are always located upstream from a DAF station and not at the head of a filtration process that could not accommodate the amount of sludge produced with an inorganic coagulant.

2.6.3 Floc separation by settling-sedimentation

This process is hardly ever used any more but should still be cited. Because floc densification is necessary, lime or CaCO_3 (50 to 100 $\text{mg}\cdot\text{l}^{-1}$) were used and scraped settlers were designed with low surface loads of around 0.4 to 1 $\text{m}^3\cdot\text{h}^{-1}$ per square meter of settling. The coagulant is always inorganic.

Internal or external recycling of sludge to enhance flocculation is not necessary as long as the floc produced has at least 150 to 200 $\text{mg}\cdot\text{l}^{-1}$ of SS. The flocculator can be incorporated in the center of the settler. The sludge produced is rich in CaCO_3 with 40 to 60 $\text{g}\cdot\text{l}^{-1}$ DS and this may correspond to 0.25 to 0.45% of the volume of treated water.

2.6.4 Separation by dissolved air flotation (DAF)

In refineries this is the most common process used. Furthermore, as far as sludge production and handling is concerned, it is often the most advantageous. The DAF process consists in sticking very fine air bubbles onto the floc (50 to 100 μm) and creating very light aggregates that exhibit considerable rising velocities in water, e.g. 7 to 15 $\text{m}\cdot\text{h}^{-1}$ at 20°C.

These fines air bubbles are produced by recycling a fraction of the water clarified by flotation (20 to 50%) at a pressure of 4 to 6 bar. Compressed air is dissolved in the water to saturation (in what is called a pressurizing drum), then the water is expanded in contact with the flocculated raw water and at flotation cell backpressure (0.2 to 0.4 bar). Expansion and mixing with flocculated water should be performed with care. The delicate floc must in no case be sheared. This is why the design of potable water flotation cells (where the use of organic flocculants is sometimes prohibited, whereas the floc is labile), is very different from the design of WW flotation cells.

The flotation cell is cylindrical or rectangular. It is equipped with a device to scrape off surface scum, or more commonly to scrape bottom sludge (Fig. 29).

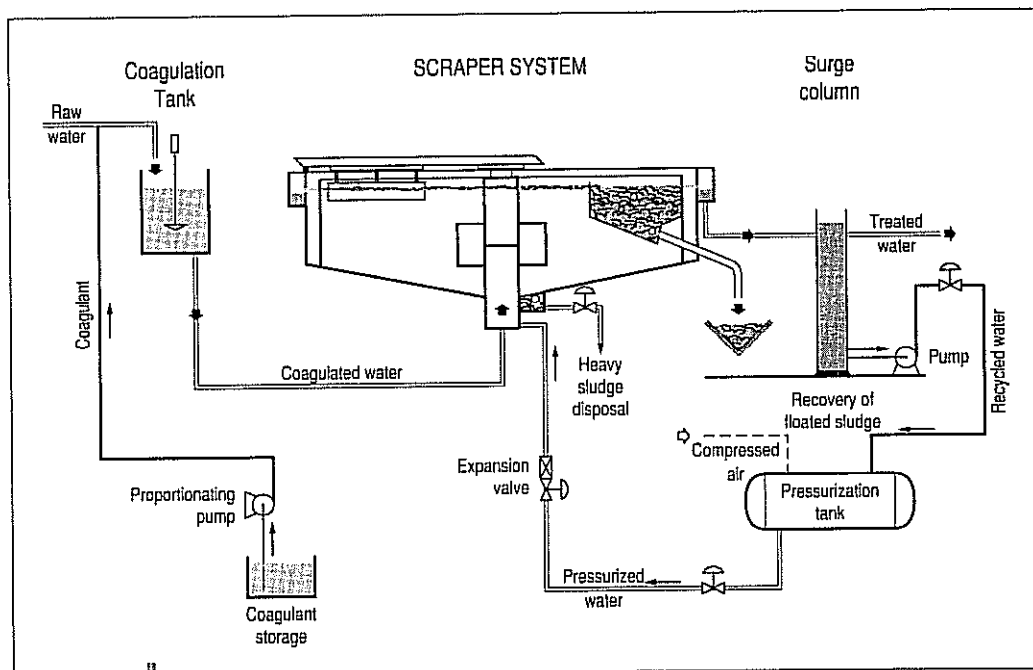


Fig. 29 Flotazur flotation unit for industrial waste water

The flocculated water goes in the lower central part and comes out under a peripheral siphoid wall. A fraction (20 to 50%) of the floated water is sent back to a pressurizing system that includes:

- One or two pumps that discharge the appropriate fraction of floated water to the saturator at 4 to 6 bar.
- The saturator which is a contact drum where a dynamic air-water level is maintained with energetic mixing of the inlet water and air.
- A controlled air flow make up device.
- An outlet and expansion valve for the pressurized water supersaturated with air.

Proper control of the expansion valve allows air bubbles of 50 to 80 micrometers to be formed. This size distribution is particularly suited to trapping the floc. At the same time it ensures air dissolution efficiency of over 70% in the drum.

The expansion energy is dissipated in a conical chamber whose profile is designed in order to offer the best probability for the floc and air bubbles coming in contact.

The floated sludge has concentrations of 50 to 100 g·l⁻¹. It represents 0.15 to 0.30% of the volume of treated water for an inorganic coagulant. With an organic coagulant, concentrations of 80 to 200 g·l⁻¹ can be achieved.

For a flow of 500 m³·h⁻¹ of an average type of water, the typical installation and operation characteristics for each of the two separation processes can be summarized as shown in Table 22. The differences due to the use of an organic coagulant rather than FeCl₃ can be seen.

Table 22

Comparison of the two settling techniques for oily flocs. Flow rate $500 \text{ m}^3 \cdot \text{h}^{-1}$

Separation process		Sedimentation	DAF	
			with FeCl_3	with organic coagulant
Separator area (m^2)		660	150	100
Consumption in $\text{kg} \cdot \text{h}^{-1}$	Lime	20-50	—	—
	50% FeCl_3	20-60	10-50	—
	Organic coagulant	—	—	0.5-1
	AM (active matter)	—	—	0.1-0.5
Power (kW)		5-8	25-30	20-30
Sludge volume (m^3/day)		36-48	24-36	5-10

When refinery WW is treated, DAF operating conditions may be as follows:

- Useful surface load = 4 to $6 \text{ m}^3 \cdot \text{h}^{-1}$ per square meter (clarification).
- Pressurized water recycling:
 - Clarification recycling = 15 to 30% of the useful load.
 - Thickening recycling = 30 to 60% of the useful load.
- Compressed air consumption in clarification = 250 to 50 $\text{Std.l} \cdot \text{m}^{-3}$ of water.
- Compressed air consumption in thickening = 0.01 to $0.02 \text{ kg} \cdot \text{kg}^{-1}$ of DS (HC + activated sludge).

DAF flotation cells are advantageous in that they can perform a remarkable thickening function that is used for oily sludge. However, it can also be used on activated sludge in addition to biological purification if the two types of sludge are slated to serve the same final purpose.

The sizing of the flotation cell is therefore imposed by the mass load in kilograms of DS allowable per square meter of area and hour. Maximum activated sludge mass flow rates of 50 kg of DS per square meter per day should be envisaged if the quality of the flotation product, the prime objective, is to be maintained.

The flocculator-flotation cell can be used together in both organic and inorganic coagulation as long as the energy gradients and appropriate residence time are complied with in flocculation.

DAF is a versatile tool in refineries. It can cope with the treatment of mechanical emulsions by organic coagulant or rare chemical emulsions by inorganic coagulant.

This is why many instances of implementation feature flotation cells equipped for the eventualities described above with both types of coagulants stored. Final sludge incineration has either become unnecessary (recycling is possible for organic coagulation sludge), or been reduced to a small scale or done elsewhere.

Table 23 gives the results for a large petrochemical complex that refines around 8 Mt/year. It includes a large number of units (steam cracking, sulfonic acids, propylene polymerization, bitumen unit) and has an effective throughput of around $800 \text{ m}^3 \cdot \text{h}^{-1}$.

Prior operation with aluminum sulfate produced 18 to 30 m^3 of sludge per day which was directly incinerated. Use of organic coagulants alone reduced this volume to 3 to 5 m^3 per day of reusable matter, i.e. 0.17% of the volume of treated water.

Table 23

DAF efficiency in a petrochemical complex

Flotation	Flotation cell inlet		Flotation cell outlet		Sludge concentration
	Hydrocarbons ($\text{mg} \cdot \text{l}^{-1}$)	SS ($\text{mg} \cdot \text{l}^{-1}$)	Hydrocarbons ($\text{mg} \cdot \text{l}^{-1}$)	SS ($\text{mg} \cdot \text{l}^{-1}$)	
With $10 \text{ mg} \cdot \text{l}^{-1}$ of aluminum sulfate... + $1 \text{ mg} \cdot \text{l}^{-1}$ of anionic polyelectrolyte	150	70	21	24	$70\text{-}80 \text{ g} \cdot \text{l}^{-1}$ DS
	120	59	18	20	$70\text{-}80 \text{ g} \cdot \text{l}^{-1}$ DS
	130	63	16	28	$70\text{-}80 \text{ g} \cdot \text{l}^{-1}$ DS
With $0.7 \text{ mg} \cdot \text{l}^{-1}$ AM of organic coagulant	160	173	13	17	$120\text{-}180 \text{ g} \cdot \text{l}^{-1}$ DS
	112	70	18	17	$120\text{-}180 \text{ g} \cdot \text{l}^{-1}$ DS

2.6.5 Separation by filtration (downflow on granular material)

Filters operate under pressure, or occasionally they are open and gravity fed. They are similar in principle to the filters used in clarification of industrial make up water even though they do have some particular features specific to WW treatment.

The filtering material is made up of a homogeneous layer of sand (single medium) or a layer of anthracite on top of a layer of finer sand (dual media).

Filtration occurs in depth and the retained particles are deposited in the inter-grain voids which represent around 55% of the bulk volume of the filtering mass. Practically 100 to 110 liters per cubic meter is available for storing retained matter (SS and oils). This useful volume therefore defines the maximum storage capacity. It should never be reached in downflow filtration because the pressure drop would be too great or more importantly, because the quality of the filtrate would decline dramatically. When this capacity is saturated, the filtering mass must be washed in runs by clean water return and blown with blowered air.

The duration of the cycles depends on the nature of the SS retained and their concentratability which is fairly variable (ultimately, a filter can be considered to be made up of an infinite number of "microsettlers").

Orders of magnitude for concentratability of a number of types of sludge:

Fe or Al hydroxides	10 to $15 \text{ g} \cdot \text{l}^{-1}$
Iron oxides depending on fineness	25 to $200 \text{ g} \cdot \text{l}^{-1}$
Oils and hydrocarbons	100 to $300 \text{ g} \cdot \text{l}^{-1}$

Oil concentration is in fact limited by the presence of a water-in-oil emulsion.

A void of 80 liters available in one cubic meter of sand can store:

- 0.8 to 1 kg of hydroxides.
- 2 to 16 kg of oxides.
- 8 to 24 l of oil.

Experience has in fact shown that for filtration of refinery or production oily water, one-layer or two-layer filters can store the following in beds 1.5 to 2 m deep:

- 15 to 25 l of oil and HC per cubic meter of bed.
- 2 to 3 kg of SS.

However, a comment must be made as to these values. The stored SS are fairly stable and quickly generate high pressure drops whereas oil is mobile and unstable in storage. Depending on its viscosity and coalescence capability, the oil mass can migrate and "run off" with the filtered water at the smallest surge in pressure, or if there is a substantial sudden variation in the filtration velocity.

The use of an organic coagulant or reticulating flocculants can still ensure good cohesion of the retained SS/oil "cake" if the ratio between the two components remains fairly high (0.5 to 1, at least).

However, in **upflow filtration** on a noncompact granular medium, the aim is to associate the cyclic filtration of SS retained at the bottom of the filter bed with the limited and deliberate migration of oil. This corresponds in fact to the enlargement and breakaway of the thick oil film which has fed on the coalescence of HC droplets on the sand walls.

Additionally, in this filtration process no flocculating polymers at all are needed to the exclusive benefit of the organic coagulant. Velocities are from 10 to 18 $\text{m}\cdot\text{h}^{-1}$.

In **downflow filtration**, the aim is to fix maximum amounts of SS and HC while keeping a trade-off between the possible velocities and the increased pressure drops due to the use of a coagulant and/or flocculant.

A pressurized filter is not limited in pressure drop and as a result is an ideal filtration implement (Fig. 30).

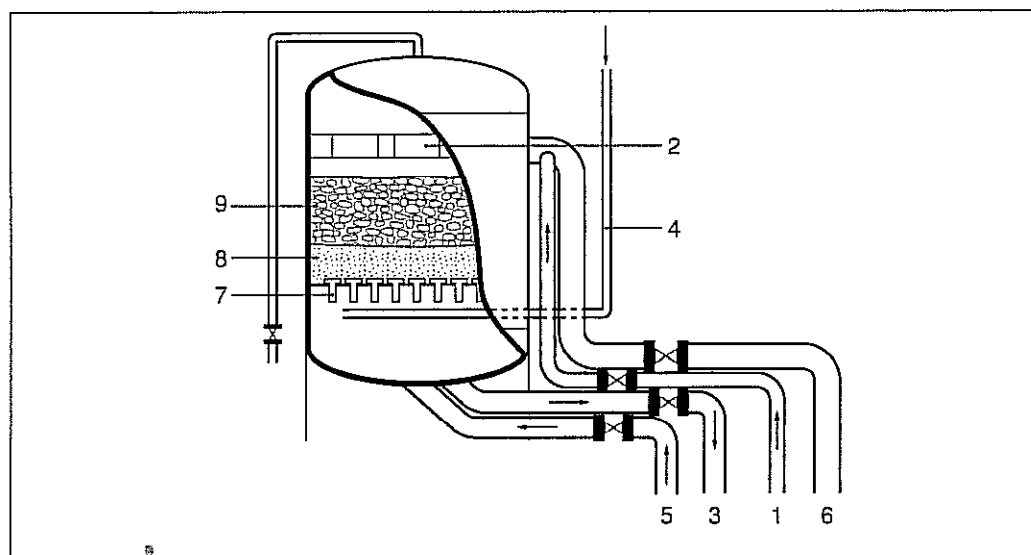


Fig. 30 UHR-type two-layer filter

These filters are either vertical cylindrical metallic vessels with diameters of up to 5 or 6 meters, or horizontal vessels with diameters of 2.5 to 3.4 m. They include:

- A metal support floor (7) equipped with plastic nozzles. Design allows the distribution of washing air and water.
- A one-layer filtering bed of sand or a two-layer bed of sand and anthracite, from 1.5 to 2 m deep (8) and (9).
- A raw water inlet collector (1).
- A raw water supply and sludge collecting basin (2).
- A filtered water outlet collector (3).
- A blowered air inlet (4).
- A washing water inlet (5).
- A washing water outlet collector (6).

The one-layer bed is made up of sand grains with an effective size of 1.35 to 1.8 mm depending on the use.

The two-layer bed is made up of sand grains with an effective size of 0.85 to 1.35 mm and, in an opposite size ratio, of anthracite of 1.6-2.6 mm or 2.5-4 mm.

The maximum pressure drops considered range from 0.6 bar sometimes up to 1.5 bar, with a filtration velocity of 15 to 20, or even $25 \text{ m} \cdot \text{h}^{-1}$.

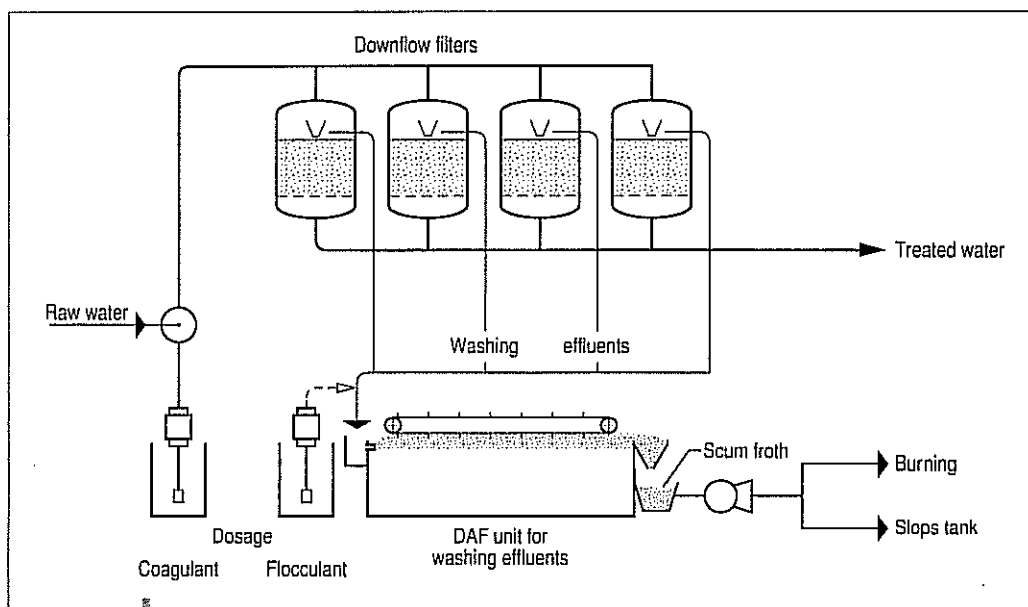


Fig. 31 Filtration of oily water

The treatment sequence by conditioned filtration includes (see Fig. 31):

- Introduction of reagents to destabilize the emulsion and coagulate the colloid.
- A contact chamber or an in-line mixer.
- Downflow filtration (a battery of pressurized filters).
- A hydropneumatic washing device in counterflow to the filters.
- Washing water conditioning upstream and/or downstream from the washed filter.
- Thickening of washing effluents usually by flotation, or by sedimentation if the oil/SS ratio in the raw water is too low.

Table 24 gives the results obtained in a hydroskimming refinery.

Table 24
Filtration efficiency in a
hydroskimming refinery

	Hydrocarbons ($\text{mg} \cdot \text{l}^{-1}$)		
	Before filter	After filter	Efficiency (%)
Without coagulation	270	43	84
	110	14	87
	150	17	89
	90	17	81
	110	14	87
	180	23	87
	100	10	90
	130	13	90
	115	10	91
Average	139	17,8	87

Although efficiency is high without conditioning, it remains nevertheless at about 84 to 91%.

With the use of an organic coagulant, efficiency rises to above 90% but at the expense of a faster increase in pressure drop.

Filter washing water is generally in the form of a fairly stable emulsion that must be flocculated. Layouts combining the repeated use of the initial coagulating agents allow the sludge to be separated

by high velocity flotation. Then filter washing effluents can be reduced. They usually account for 3 to 6% of the volume of the raw water and can be reduced to the flotation scum alone, which itself represents less than 1% of the volume of the raw water.

The number of units comprising a filter battery is defined so as to prevent overly-high velocities that would be unacceptable for the filters when one of them is being washed. This is why the batteries have at least three filters with a maximum of eight filters per battery. Regulating valves equipping each filter can also limit the percolation velocities which would otherwise exceed the limit of 20 to $30 \text{ m} \cdot \text{h}^{-1}$ on a filter that has been washed and put back on stream. Above the 20 to $30 \text{ m} \cdot \text{h}^{-1}$ limit, there would be entrainment and leaks of HC depending on the effluent. This process is basically designed to separate oil + SS aggregates and not fouling hydroxide flocs.

2.6.6 Separation by coalescence

Filtration with coalescence by upflow filters can be contemplated when there is no interference by an overly-high SS concentration and when the HC present do not have too high a viscosity (hot water) or too high a pour point (paraffin risk). The required conditions are fulfilled by many types of produced water and all heating condensates, but less often by oily or accidentally oily refinery water.

The coalescer (Fig. 32) has a lower percolation zone with sand that has been made oleophilic, and an upper zone for oil droplet separation by differential settling.

In the lower zone, the aim is to promote coalescence of pre-coagulated and destabilized oils on an oil film coating the grains and becoming gradually thicker toward the top of the medium. At the top of the medium, the joint forces of gravity and entrainment cause shear and discontinuous breakaway of the film which frees large droplets (0.5 to 5 mm).

The droplets move at a rising velocity of 50 to $100 \text{ m} \cdot \text{h}^{-1}$ and can be readily separated from the treated fluid which circulates concurrently at a velocity of 20 to $25 \text{ m} \cdot \text{h}^{-1}$. In this way separation is complete in the upper zone.

This process is mainly designed to separate oil and not SS or flocs.

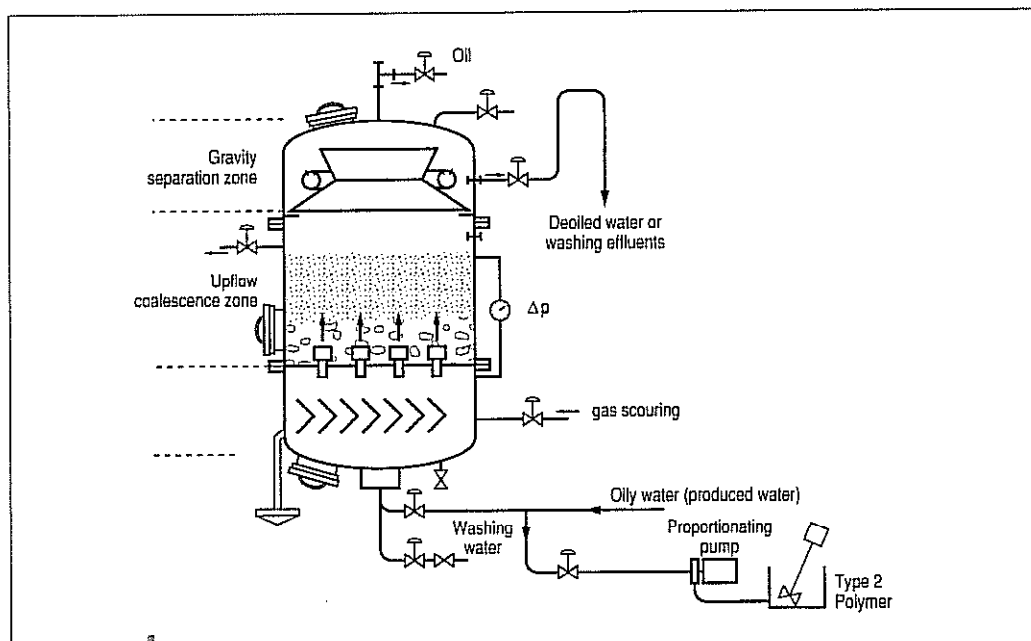


Fig. 32 "Collexer" coalescer filter

2.6.7 Choosing separation processes

Relevant areas of application are defined in Table 25 for common orders of magnitude of pollution in refineries and petrochemical plants.

Table 25

Choosing a physicochemical purification process for oily WW

Type of emulsion	Insoluble HC (mg·l ⁻¹)	SS (mg·l ⁻¹)	S ²⁻ (mg·l ⁻¹)	Separation
Cold mechanical emulsion	20-100	20-50	< 10	Organic coagulant + filtration or flotation
Hot mechanical emulsion (40-90°C)	50-500	< 20	—	Organic coagulant + coalescence or flotation < 50°C
Chemical emulsion	50-200	50-100	20-300 Oxidation	Al-Fe coagulants + flotation
			10-50 Precipitation	Fe coagulant + flotation

2.6.8 Induced air flotation (IAF) or mechanical flotation

This technique is used to treat a lot of formation water but very little refining and deballasting water, at least in Europe. It should be mentioned to avoid any confusion with FAD. It is derived from ore beneficiation techniques used in hydrometallurgy. An impurity is eliminated by frothing through a large number of in-line reactors, after a number of chemical agents (collectors, depressors) have been introduced. In each reactor, very high agitation energy is developed by a stator-reactor which mechanically induces formation of very large air bubbles (0.5 to 2 mm) (Fig. 33).

Fig. 33
"Hydroclean"
dispersed air flotation cell

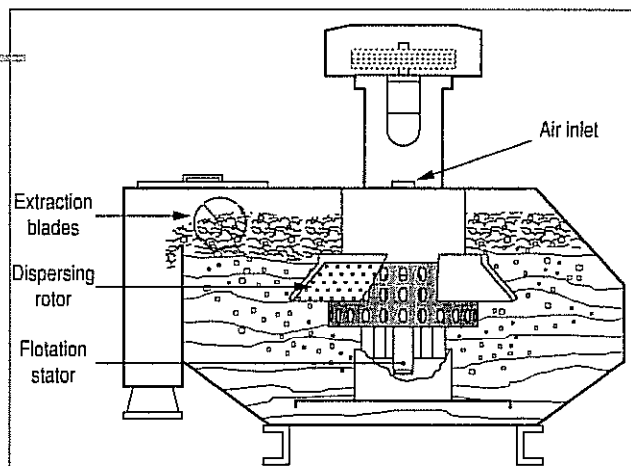


Table 26
Comparison of DAF and IAF in treating oily IWW

	Dissolved air flotation (DAF)	Induced air flotation (IAF)
Size of air bubbles	50-100 μm	0.5-2 mm
Equipment	Flocculator + flotation + pressurizing	4 in-line mechanical flotation cells
Hydraulic retention (min) including flocculation	30-60 min	4-16 min
Power required ($\text{Wh} \cdot \text{m}^{-3}$ treated water)	50-60	100-150
Circulating air flow rate ($\text{Std m}^3 \cdot \text{m}^{-3}$ of water)	0.02-0.06	1
Chemical conditioning	Organic coagulant $\pm$ flocculant	Collecting agent or demulsifier or organic coagulant
Clarification	Yes	No
Residual insoluble HC ($\text{mg} \cdot \text{l}^{-1}$)	3-20	15-40
Sludge production (% of treated water)	0.3-0.4 (inorg. coag.) 0.1 (org. coag.)	3-5

Aerobic biological purification and tertiary treatments for refinery and petrochemical plant effluents

Chapter

3

Biological purification is the second main purification stage for refinery and petrochemical plant WW. It is designed initially to eliminate the soluble BOD_5 that subsists after physicochemical purification and particularly the phenols.

However, with the incentive of new regulations it is engineered from the beginning or equipped after construction so that it can eliminate NH_4 (Europe) or toxic compounds (U.S.) to a certain extent. The attempt to achieve lower COD (or TOC) levels can also lead to an improvement in efficiency.

By way of an example, French requirements according to refinery complexity are recalled below:

Mean BOD_5	30 to 40 $mg \cdot l^{-1}$
Entrainable phenols	0.5 to 1 $mg \cdot l^{-1}$
COD	120 to 150 $mg \cdot l^{-1}$

Biological purification process design in refineries, in contrast to MWW design, must take three original factors into account:

- All the BOD_5 is in dissolved form.
- The $\frac{COD}{BOD_5}$ ratio varies widely, with an extra fraction of the COD becoming biodegradable with increasing sludge age.
- Dissolved BOD_5 values are often low in refineries (60 to 90 $mg \cdot l^{-1}$), but not in petrochemical plants. In both cases, there are considerable irregular variations over a one month period. Purification processes must accordingly be highly specific to each particular situation.

3.1 Aerobic biological purification systems

Three main types of process are used in the petroleum industry:

- Suspended growth in activated sludge, with medium load, low load or extended aeration.
- Attached growth on trickling filters (random or ordered fill materials).
- Attached growth on granular biological filters.

The principle of each process is summarized below along with the conditions governing application to refinery and petrochemical plant WW. Specialized literature (see References) should be consulted for a more thorough understanding of biological purification processes.

3.1.1 Activated sludge (Fig. 34 a)

This system is the most well known since it is the most commonly used for MWW. It is often used in petrochemical plants, but more seldom however in refineries where BOD_5 levels are lower.

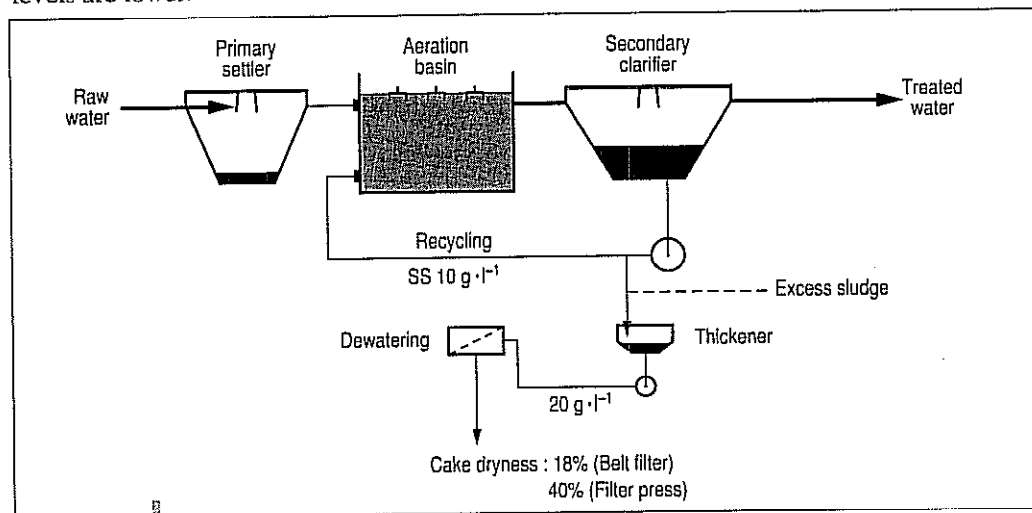


Fig. 34a Biological purification by activated sludge

It uses suspended growth in an aeration tank in the presence of air or oxygen, followed by a secondary settler or clarifier. The clarifier fulfills the dual function of clarifying the water that is being treated and of concentrating the activated sludge so that it can be continuously recycled upstream from the aeration tank. Recycling is necessary in order to rescue the water and guarantee a high activated sludge concentration compatible with the planned load for the purification facility. Recycling also ensures sufficiently advanced activated sludge age, which is particularly required for maximum elimination of the COD and aromatic HC.

The air make up in the aeration tank is designed to meet the need for dissolved oxygen (around $2 \text{ mg} \cdot \text{l}^{-1}$) to satisfy the BOD_5 and so that the bacterial mass can breathe. It is also designed to contribute to stirring and keeping the activated sludge in suspension.

The concentration in dry solids (DS) in the aeration tank can range between 2 and $12 \text{ g} \cdot \text{l}^{-1}$ depending on the situation. The activated sludge recirculation flow rate is of the same order of magnitude as the average water circulation flow rate. The dry solids are basically living matter that can be measured only in the form of volatile solids (VS).

Aeration can be carried out in tanks 4 to 5 m deep by:

- Surface aerators (turbines, rotating discs).
- Blown air nozzles for big air bubbles.
- Porous distributors of fine-size bubbles.

There are drawbacks however. In the first system in particular there is a considerable aerosol production and some stripping of aromatic HC. In the second and third systems, basins 8 to 10 m deep can be designed which will still involve the use of air injectors, however (Dipair, Kenics). In addition to the fact that the facilities are compact, there are two further advantages:

- Greatly increased air dissolution efficiency.
- Greatly reduced stripping effect.

The use of oxygen in aeration depends on whether a supply by oxygen pipeline is conveniently available. To date this has been possible solely in petrochemical plants. The oxygenation tanks are closed, the oxygen is recycled and no stripping occurs during purification.

3.1.1.1 Removing carbonaceous pollution

The growth of a bacterial mass, M , develops according to the availability of a nutrient substrate, L , in several characteristic periods:

- Initial period for seeding and acclimatizing the microorganisms.
- Period of what is termed exponential growth where the increase in mass is proportional

to its concentration:
$$\frac{dM}{dt} = KM.$$

- Period of declining growth where the decrease in nutrient concentration L may be a major constraint:
$$\frac{dM}{dt} = K'LM.$$

- Endogenous period or negative growth where the microorganisms age, are self-oxidized and self-digested:
$$\frac{dM}{dt} = -bM.$$

In aerobic purification as currently under discussion, the changes in bacterial mass versus the initial supply of nutrient L (here represented by the BOD in the medium) can be illustrated as shown in Fig. 34b. Since bacterial activity varies with the age of the bacteria, the three loads often considered in sizing activated sludge can be approximately located on the diagram. These three loads are the high and medium loads and extended aeration (see 3.2.1) where very advanced age makes the sludge mineralize and reduces its production.

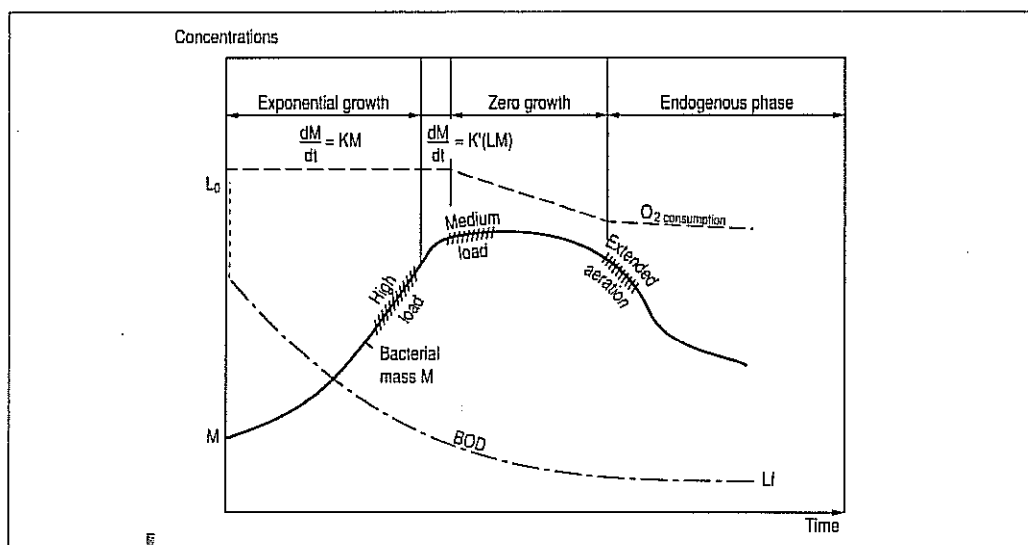


Fig. 34b Growth of an aerobic bacterial mass

3.1.1.2 Removing nitrogen biologically

WW from refineries, and generally from petrochemical plants as well, has a N content lower than $100 \text{ mg} \cdot \text{l}^{-1}$ and so does not warrant stripping. Instead, a biological purification process that is frequently used for MWW can lower (N.NH_4) nitrogen levels to 10 or $5 \text{ mg} \cdot \text{l}^{-1}$ depending on regulations in different countries.

This purification process is completely carried out in two main stages: nitrification and denitrification.

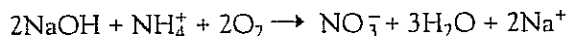
1. Nitrification

Ammonification of organic N into ammonia N must be performed before nitrification of NH_4 , which in turn occurs in two stages:

- Oxidation of NH_4 into NO_2 (Nitrosomonas bacteria).
- Oxidation of NO_2 into NO_3 (Nitrobacter bacteria).

These bacteria are autotrophic, i.e. they grow by oxidation of inorganic compounds. Nitrosomonas bacteria reproduce much more slowly than Nitrobacter, so the first reaction is determining.

The overall reaction is acidifying and therefore consumes the alkalinity of the water which must be offset:

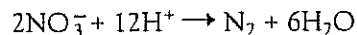


The theoretical O_2 demand is $4.2 \text{ mg} \cdot \text{mg}^{-1}$ of nitrogen. The equivalent acidity produced is around $0.11 \text{ meq} \cdot \text{l}^{-1}$ per mg of nitrified N.NH_4 . Advanced sludge age is necessary and the volume of the activated sludge aeration tank should define a low load or an extended aeration, with plug flow feed. This type of feed entails simultaneous inlet of raw water and recycled sludge at the basin inlet. The N loading that can be considered ranges from 50 to $240 \text{ g} \cdot \text{day}^{-1}$ per kg of volatile solids, since relatively tight pH and temperature conditions must be maintained within a relatively long acclimatization time.

2. Denitrification

Denitrification occurs due to the action of facultative anaerobic heterotrophic microorganisms that get their nourishment from an organic substrate and use the oxygen from nitrates.

The presence of dissolved oxygen inhibits their growth. The reaction that accordingly develops in anoxia in a tank or a filter is:



In MWW, denitrification consumes from 4 to 6 mg of BOD_5 per mg of N.NO_3 removed. In refinery WW, the naturally existing BOD_5 may not be sufficient and so the organic substrate must be supplemented by an outside source (ethanol, methanol, molasses, etc.). Phenol input is not advisable since at certain concentrations phenols have an inhibiting effect on the nitrifying bacteria themselves.

An activated sludge nitrification-denitrification sequence includes an anoxia tank, possibly with an added organic substrate input and an extended aeration tank with an added neutralizing agent. On start-up, acclimatization may require many weeks depending on the quality of secondary settling, which accordingly requires particular care.

3.1.2 Trickling filters

3.1.2.1 Principle

The operating principle consists in allowing water to trickle continuously through masses of materials contained in towers where an air countercurrent circulates by natural draft. The material requires a large specific area and high crushing strength. It supports a thick film of microorganisms that are much more varied than in activated sludge. Along with the main mass of one-cell heterotrophic bacteria in common with activated sludge, there are coexisting anaerobic or facultative aerobic microorganisms, more elaborate organisms such as green algae, fungi and predatory fauna such as protozoans, nematodes and arachnids. Added to the aerobic purification mechanism there is therefore an anaerobic mechanism deep down in the film, which breaks down the cells formed by the aerobic process, as well as consumption of excess sludge by predators. This explains why very little sludge is produced by these trickling filters, they release small amounts of sludge sporadically.

The beds were formerly made of heavy natural materials (pozzolana, coke) with a small specific area which limited the height of the bed and the percolation velocity to low values. They are now made of plastic fill whose light weight and large specific area allow increased heights (4 to 10 m) and percolation velocities. Two categories of materials that can provide void ratios of over 90% are used:

- Random fill materials, made up of rings or discs several inches in size:
 - Glitsch's cascade miniring and Pall-ETA.
 - Norton's Actifil 90.
- Ordered fill materials in tubes or frames:
 - 80 or 100 mm tubes (Cloisonyle), with $225 \text{ m}^2 \cdot \text{m}^{-3}$ of specific area.
 - Square $600 \times 600 \text{ mm}$ cross section modules (Flocor), with $85 \text{ m}^2 \cdot \text{m}^{-3}$ of specific area.
 - Criss-cross herringbone (Plasdek) with $100 \text{ m}^2 \cdot \text{m}^{-3}$ of specific area.

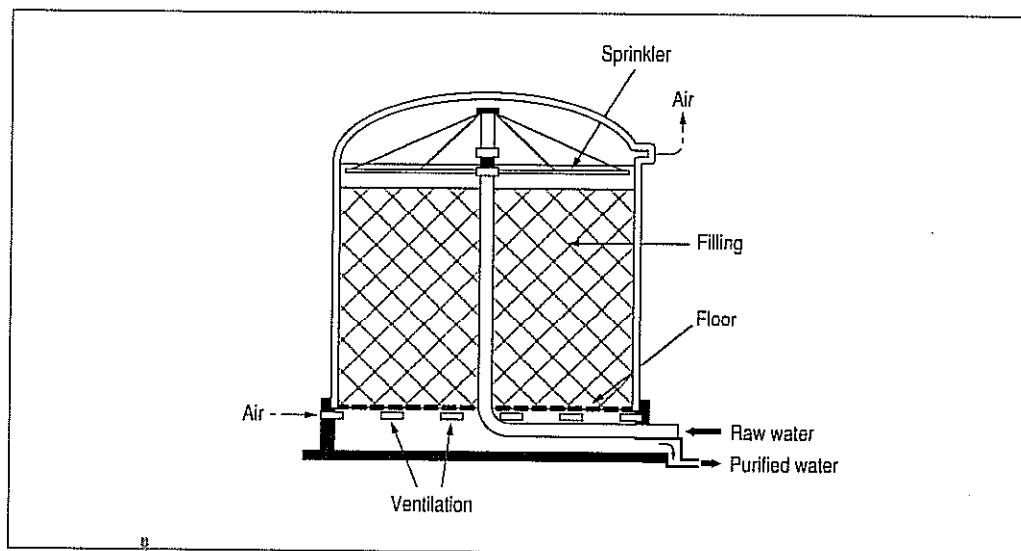


Fig. 35 Circular trickling filter with random fill material

The water is dispersed on the surface of the bed by a rotating jet device, the sprinkler, and collects on the bottom of the structure (Fig. 35).

A secondary settler is optional downstream from the trickling filter. The water directly downstream from the filter is often recycled upstream from it to keep hydraulic flushing at a minimum.

Trickling filters can run under the following operating conditions in refinery WW treatment:

- Hydraulic load: 1 to 4 $\text{m} \cdot \text{h}^{-1}$ (i.e. 0.2 to 0.8 space velocity for a height of 5 m).
- Volume load: 1 to 3 kg BOD₅ per cubic meter of fill per day.
- Efficiency is closely related to the composition of the water and ranges from 50 to 75% of the BOD₅ or phenols, depending on feed and recycling.

The low efficiency, though often high enough to remove the required BOD₅, could sometimes justify two trickling filters set up in line for phenols to be removed to required levels.

3.1.2.2 Operating the trickling filter with refinery WW

After colonizing the support medium, a thick biofilm develops. It looks particularly gelatinous if there is a supply of insoluble HC. When the water percolates, the dissolved oxygen is diffused to a shallow depth in the film and does not reach its core. So there are two coexisting zones: an outer one in aerobiosis and an inner one in anaerobiosis. The biological sludge produced aerobically can therefore be broken down anaerobically. Anaerobic action, which enables the sludge to be mineralized, is carried out in beds with a low percolation load and the growth of the film is limited by the predators mentioned above.

In beds with a high hydraulic load maintained by recirculation there is a self-scouring phenomenon that keeps a thick film from forming and the bacterial flora that develops is more homogeneous. Sludge digestion is slight and a secondary settler will become necessary depending on downstream treatment.

These facilities are economically attractive despite the costly plastics because they are simple, there is often no secondary settler and, theoretically, no frequent measurement. In practice however, difficulties in operating some of them have caused the bed mass to become clogged in the space of a few months. As a result, the bed material has had to be cleaned either in situ or after removal from the unit.

Clogging may be due to several reasons in a refinery:

- An overly large amount of hydrocarbons coming from physicochemical purification, which is particularly likely when the purification step consists of filtration without coagulation.
- An inadequate anaerobic process to break down the sludge produced in the bed, a process which is necessary in a trickling filter.

As a matter of fact, the still too common presence of insoluble HC coming from physicochemical purification obviously enriches the film in HC which in turn are not prone to anaerobic degradation. They are capable of making a barrier to the migration of microorganisms or even enzymes. As a result, there may be an exaggerated densification of the film which becomes a sludge bed and increases the water flow pressure drop by increasing the mass of the trickling filter. Hence purification efficiency can gradually decline and a poorly designed support floor can collapse.

These malfunctions occurred mainly with random fill materials that tend to compact dramatically (10 to 20%) in a well-nigh irreversible process after a few months' operating time.

In the agrifood industries, similar difficulties occurred due to attendant causes: precipitation of CaSO_4 , massive development of fungus mycelia, etc.

The use of the random fill material technique in refineries must therefore be contemplated only with a number of modifications:

- Bed height must be limited and packing material must be chosen accordingly.
- The support floor and the ventilation device must be improved.
- A perforated cylindrical basket in a fixed perforated cylinder must be installed. This allows periodical "coring" to take a vertical sample of the material.
- Pressure drops must be monitored throughout the bed.
- Periodic hydraulic cleaning sequences must be scheduled with appropriate equipment along with exceptional chemical cleaning (chlorine bleach, NaOH).

Ordered fill materials are a less sensitive but more expensive alternative.

3.1.3 Attached growth on granular beds-biofilters

Here the contact mass is made up of grains several millimeters in size: sand, anthracite, slags or lighter materials.

The mass is placed in fairly small diameter tanks on support floors that may be equipped with a water and air countercurrent washing system. It can be methodically washed depending on bed head losses. This allows the excess sludge to be disposed of, thereby avoiding the causes of clogging.

The development of these filters originated from the fact that tertiary filtration existed for purified effluents and was considered advantageous. Tertiary filtration includes sand and/or anthracite filters whose job is to remove residual suspended solids and the insoluble BOD_5 related to them. Implementation of these filtration processes made it possible to observe the filter medium's behavior and to develop an intermediate range of biofilters. The new filters are required to remove a fraction of the soluble BOD_5 as well. Certain specific pollutants present in low concentrations may also be eliminated by using added outside air.

There are two kinds of biofilters designed for treatment of water that is fairly poor in SS:

- Pressurized oxygen saturation filters.
- Upflow filters with cocurrent blowered air flow.

3.1.3.1 Pressurized oxygen saturation filters

The added oxygen required for aerobic purification to develop is provided by saturating the raw water in air at the inlet to the filter battery along with:

- Operating pressure raised to 5-6 bar in order to dissolve up to $40 \text{ mg} \cdot \text{l}^{-1}$ of O_2 .
- Filtered water recycled upstream from the battery if the resulting effective hydraulic load of the filters allows. Recycling is generally 50 to 100% of the useful flow rate and this can double the O_2 input at a given pressure.

Given the impact of recycling, BOD_5 of 40 to $50 \text{ mg} \cdot \text{l}^{-1}$ can be satisfied by the O_2 input. The BOD_5 fraction removed with the SS is low, inasmuch as these colloidal, almost unfilterable SS can escape filtration. As a result, the filtered water can still contain 15 to $30 \text{ mg} \cdot \text{l}^{-1}$ SS.

The cost of treatment is governed by the power used for pumping: around 8 kWh per kilogram of oxygen transferred.

Metallic filters have diameters ranging up to 5 or 6 m and are used in batteries of several parallel units with the following operating conditions:

Pressure	2 to 6 bar
Real percolation velocity	5 to 15 m·h ⁻¹
Allowable increment in pressure drop	0.5 to 1 bar
Filter bed depth	1.5 to 2.5 m

In addition to the filters themselves, the facility includes (Fig. 36):

- An aeration chamber.
- Feed and recirculation pumping.
- A nutrient (PO_4^{3-}) metering station.

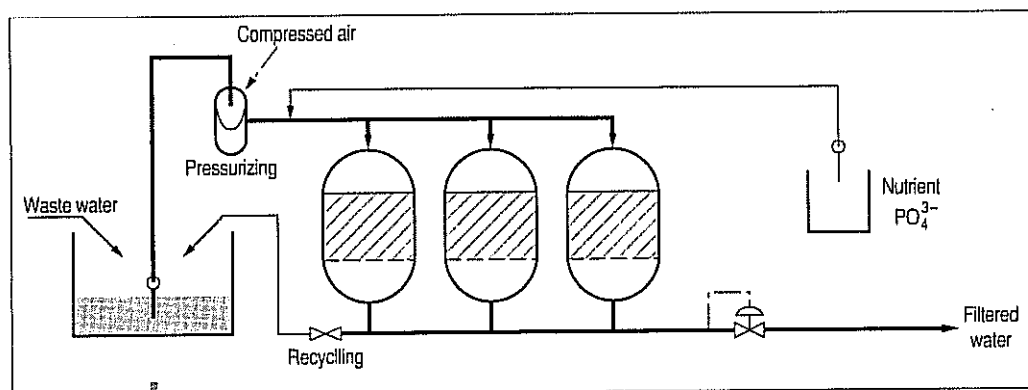


Fig. 36 Battery of oxygen saturation biofilters

3.1.3.2 Water and air upflow biofilters (Biofor, for example)

The added oxygen required for aerobic development is provided by maintaining an air cocurrent jointly with the rising water current through the filter. The filter is generally open and can be built of concrete on a larger scale than pressurized filters. The facilities must nevertheless be made up of several units because excess velocities when a unit is being washed are even less acceptable than in pressurized facilities.

The filter (Fig. 37) includes:

- A support floor made of prefabricated slabs or steel.
- A mass of filtering material with an effective size of between 1.5 and 2.5 mm, a bulk specific gravity of 1.4 to 1.8 in a layer 2 to 3 m thick.
- A process air distribution collector located on the floor.
- A scouring air supply collector located under the floor.
- Weirs to recover the treated water and the washing water.

This technique can be used in refineries:

- To remove the soluble BOD_5 :
 - Volume loads from 2 to 5 kg/m³·day.
 - Filtration velocities from 1 to 5 m·h⁻¹.
 - Efficiency from 70 to 85%.
- To oxidize ammonium into nitrate (layer 3 m thick):
 - N.NH_4^+ volume loads around 1 to 1.5 kg/m³·day for temperatures from 20 to 30°C.
 - Filtration velocities from 1 to 3 m·h⁻¹ for NH_4 concentrations of 60 to 150 mg·l⁻¹.

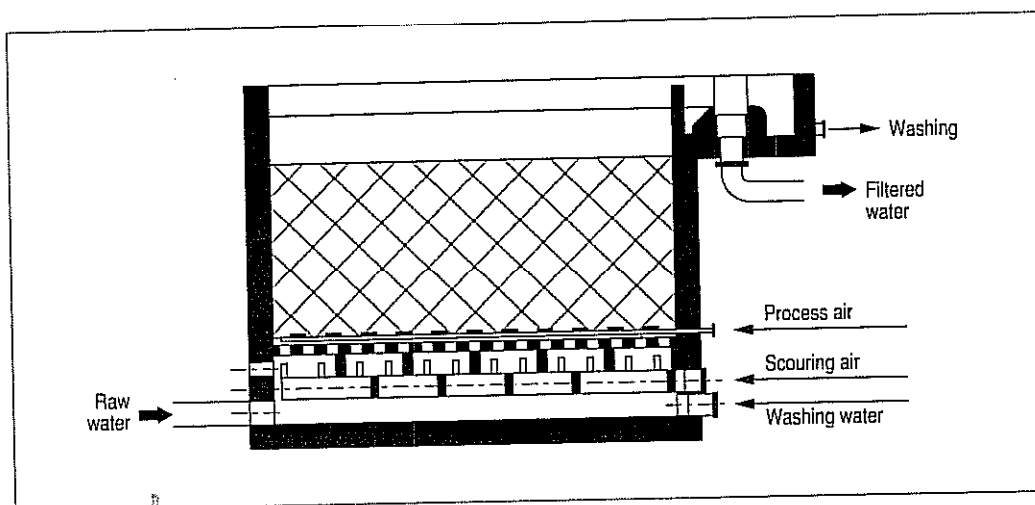


Fig. 37 Biofor filter

Forced process air flow amounts to 4 to 15 $\text{Stdm}^3/\text{m}^2 \cdot \text{h}$ with an air dissolution efficiency of about 20%. This defines an oxygenation capacity of 0.25 to 0.9 kg of oxygen per square meter per hour.

The duration of cycles between washing operations corresponds to a SS storage capacity (initial + activated sludge) of 1 to 2 kg per cubic meter of material.

3.2 Implementation of biological purification by activated sludge (ASP)

3.2.1 Sizing activated sludge aerobic biological purification facilities

Aerobic biological purification is the only type of purification used in refineries, but petrochemical plants could, albeit rarely, use anaerobic purification by methanization. The general mechanisms, which are the same as for MWW, will not be discussed here but the sizing parameters should be understood. They are calculated based on the following data, as for ASP:

- L_o raw water BOD_5
- L_f purified water BOD_5
- S_v Mass of living matter in the reactor
- a_m Mass of cells produced by the removed BOD_5 , $L_o - L_f$
- a Fraction of the BOD_5 used to oxidize all the living matter
- a' Fraction of the BOD_5 used for bacterial synthesis
- b Fraction of the bacterial mass broken down by endogenous respiration (death rate)
- b' Amount of oxygen required to degrade fraction b with $a + a' \leq 1.46$
($b' = 1.42$ considering the living matter in the $\text{C}_5\text{H}_7\text{NO}_2$ form).

- **Production of excess biological sludge.** This is the difference between:

$$\begin{array}{ccc} \text{Production of biomass} & & \text{Destruction of biomass} \\ \text{by synthesis} & - & \text{by endogenous respiration} \end{array}$$

$$\text{or: } a_m(L_o - L_f) - b \cdot S_v$$

- **Oxygen demand.** This is the sum of:

$$\begin{array}{ccc} \text{Demand} & + & \text{Demand} \\ \text{for bacterial synthesis} & & \text{for endogenous respiration} \end{array}$$

$$\text{or: } a' \cdot (L_o - L_f) + b' S_v$$

It varies with the mass load applied to the reactor.

- **Hydraulic residence time (in hours):**

$$\frac{\text{Volume of reactor (m}^3\text{)}}{\text{Flow rate of effluent (m}^3\text{·h}^{-1}\text{)}}$$

- **Sludge age (in days):**

$$\frac{\text{Masse } S_v \text{ of living matter in the reactor}}{\text{Production of excess biomass per day}}$$

- **Mass load (C_m) of a reactor (in kg of BOD₅/kg of SS.day):**

$$\text{Ratio } \frac{\text{Mass of BOD}_5 \text{ entering per day}}{\text{Mass of activated sludge in the reactor}}$$

- **Volume load (C_v) of a reactor (in kg of kBOD₅/m³ of reactor per day):**

$$\text{Ratio } \frac{\text{Mass of BOD}_5 \text{ input per day}}{\text{Volume of reactor}}$$

Table 27 shows the correspondence between the loads that can be maintained.

Table 27

Activated sludge processes used in refineries

	C_m Mass load	C_v volume load	Sludge age (days)
Extended aeration	0.07	0.40	20-35
Low load	<0.2	<0.5	10-20
Medium load	$0.2 < C_m < 0.4$	$0.5 < C_v < 1.5$	4-10

Table 28 shows the comparative impact of operating with high or low loads in MWW treatment (activated sludge plants).

Table 28

Characteristics of municipal waste after ASP with high or low loads ($\text{mg}\cdot\text{l}^{-1}$)

	Raw water	Purified water	
		High load	Low load
BOD ₅	150-400	20-30	10-20
COD	300-750	60-200	30-100
SS	200-500	30-40	10-15
N-NTK	25-50	20-30	5-8
N-NH ₄	20-40	15-18	0.2-2
N-NO ₃	0	0	20-35
Total P	10-20	3.5-10	3.5-10
Anionic detergents	20-15	10	5 mg·l

The following values can often be considered for energy demand and sludge production coefficients for refinery IWW:

- Coefficient a_m varies from 0.45 to 0.70 depending on the substrate and on the temperature.
- Coefficient b is a relatively linear function of the temperature and from 15 to 35°C it varies from 0.03 to 0.07-0.1 $\text{kg}\cdot\text{day}^{-1}$ per kg of volatile solids in the aeration tank for a given substrate.
- In petrochemical plants some effluents can generate more sludge, with coefficients close to those for MWW ($a_m = 0.6$, $a' = 0.5$).

With IWW coming from physicochemical purification and BOD₅ of over 100 $\text{mg}\cdot\text{l}^{-1}$ justifying activated sludge purification, the mass S_v of volatile solids can be replaced by the mass S_T of total SS. This is because the inorganic or inactive SS input is then considered as being of second order ($S_T = \text{aeration volume} \times \text{total SS}$).

3.2.2 Means of aerating activated sludge tanks

Aeration fulfills the dual function of providing added oxygen to the bacteria and of stirring the activated sludge. There are two types of system:

3.2.2.1 Surface aerators

Vertical axis, low speed (40 to 100 rpm) aerators driven by a reducer motor are mainly used in Europe. Meanwhile, in the U.S. aerators (lagoons) are often directly driven, i.e. at high speed (750 to 1500 rpm) and located inside a tank. Manufacturers are careful to minimize noise and reduce aerosol entrainment by the use of a deflecting skirt. The systems are mounted in stationary positions or on floats.

Calculating oxygenation capacities requires data on the temperature of the water, its salinity, and the altitude (physicochemical conditions and T factor) and shape (hydraulic conditions and F factor) of the tank. First the specific input is defined in standard conditions in terms of kilograms of dissolved oxygen per gross (at the motor) or net (at the transmission shaft) kWh consumed. Power consumption data are provided by the

manufacturer. The net nominal inputs can range from 1.6 to 2.4 kg of O_2 per kWh, depending on the model. Effective O_2 demand is deduced from the theoretical demand by applying the T and F factors (possible increment of 10 to 50%).

The stirring power developed in the tanks is around $40 \text{ W} \cdot \text{m}^{-3}$ of tank for MWW, but can often reach or exceed 60 W for IWW (high sludge concentrations).

3.2.2.2 Blowered air

Air is supplied by a pressurizing device or compressors and injected into the bottom of the aeration tanks where it is distributed by diffusers that are classified into three groups according to the average size of the air bubbles they produce (Table 29).

Table 29

Aeration by forced air

	Gross specific input in kg of O_2 per kWh	Dissolution efficiency (%)
4 m immersion		
Big bubbles (>6 mm) (collectors, tubes)	0.75-0.85	5-6
Medium-size bubbles (4 to 6 mm) (valves, Vibrairs)	1.1-1.2	6-12
Small bubbles (<3 mm) (porous devices)	2.5	15-25
8 to 10 m immersion		
Ejectors-diffusers (Dipair, Kenics)	2.4	22-28

The noise made by blowers means that they must be placed in a well sound-proofed place. Constraints of size, drift and noise have led to covered and increasingly deeper design for aeration tanks.

3.2.2.3 Example of medium load activated sludge sizing

- IWW flow rate = $4\,800 \text{ m}^3 \cdot \text{day}^{-1}$, BOD_5 $430 \text{ mg} \cdot \text{l}^{-1}$ to be cut to 30.
- Daily BOD_5 load: $L_o - L_f = 1920 \text{ kg} \cdot \text{day}^{-1}$.
- Volatile solids concentration in the aeration tank = $3 \text{ g} \cdot \text{l}^{-1}$.
- Mass load chosen: $C_m = 0.3$.
- Aeration tank volume required: $V = 1920 / 3 \times 0.3 = 2133 \text{ m}^3$.
- Residence time = 10.66 hours.
- Known experimental coefficients: a_m , a' and b' respectively 0.5, 0.6 and 0.1.
- Theoretical amount of O_2 to be supplied:

$$a'(L_o - L_f) + b'S_v = 0.6 \times 1920 + 0.1 \times 6400 = 1792 \text{ kg} \cdot \text{day}^{-1} \text{ of } O_2.$$

- Production of excess activated sludge:

$$a_m(L_o - L_f) - bS_v = 0.5 \times 1920 - 0.07 \times 6400 = 512 \text{ kg} \cdot \text{day}^{-1}, \text{ (i.e. 0.266 kg of volatile solids per kg of BOD}_5\text{)}.$$

- Living matter entrained in suspension by settled water: $40 \text{ mg} \cdot \text{l}^{-1}$, i.e. $192 \text{ kg} \cdot \text{day}^{-1}$.

- Excess sludge to be drained off: $320 \text{ kg} \cdot \text{day}^{-1}$.

- The actual amount of O_2 to be supplied is calculated after two series of corrections:

- a. Correction factor T related to effective physicochemical conditions of air dissolution: T_p (nature of the water and of the aeration system) $\times T_t$ (O_2 transfer versus temperature) $\times T_d$ (Oxygen deficit). This last coefficient $\frac{C_s - C_x}{11.25}$ often brings about the most substantial correction.

C_s = saturation in O_2 under effective salinity, temperature and pressure conditions.

C_x = oxygen content in the purification water, often chosen between 1 and $2 \text{ mg} \cdot \text{l}^{-1}$.
 $11.25 \text{ mg} \cdot \text{l}^{-1}$ = saturation in O_2 of pure water at 10°C .

With $C_s = 10$ and $C_x = 1.5$, $T_d = 0.76$ at 15 to 20°C . Disregarding the two other parameters, the corrected amount of oxygen becomes $2\,358 \text{ kg} \cdot \text{day}^{-1}$.

- b. Correction factor F related to the shape of the aeration tank and to hydraulic conditions.

Depending on the type of surface aerator and the shape of the tank, the second F factor $12 = F_1$ can be calculated (shape of the tank) $\times F_2$ (ratio between width and depth) $\times F_3$ (specific stirring power) that can be 0.9 for example. A nominal net specific aerator input measured at the shaft of $2 \text{ kg} \cdot \text{kWh}^{-1}$ of O_2 becomes a real input of 1.8. Four aerators, with 20 kW of absorbed power, therefore supply $4 \times 20 \times 1.8 = 144 \text{ kg}$ of O_2 per hour for a total of 74 that are required on the average. They can be run intermittently and still ensure a maximum stirring power of $37 \text{ W} \cdot \text{m}^{-3}$ of tank.

3.2.3 Biological treatability of refining and steam cracking effluents

3.2.3.1 Composition of effluents and importance of BOD_5

After proper physicochemical treatment, the effluents are free of sulfides and HC. Their pollution is almost exclusively dissolved and is defined by the four usual parameters:

COD	Phenols
BOD_5	NH_4

as well as the TOC which it would be advisable to add to the list (monitoring).

Earlier the COD was seen to be divided up into four fractions corresponding to:

- Intermediate S^{2-} oxidation products which are still capable of further oxidation: sulfites, thiosulfates and polysulfides in varying concentrations. In fact they constitute an inorganic O_2 demand and satisfaction of this demand is however made easier by enzymatic processes.
- A "biological" origin COD corresponding to the following different compounds:
 - Aldehydes, acetic and formic acids, coming more particularly from steam cracking or even FCC condensates.

- Miscellaneous phenol compounds coming mainly from FCC and often from leaks of spent caustic.
- Highly soluble and fairly biodegradable furfural and MEK sometimes coming massively from lube oil plants.
- Sulfonates in variable added amounts that may come from spent acids and acid tars, which are relatively hard to biodegrade and produce foam.
- Low CN^- concentrations which are often 50 to 80% broken down.
- Aromatic HC which are especially present in petrochemical plant and natural gas treatment effluents.
- Nonbiodegradable compounds that are hard to oxidize cold. Among them, the following should be mentioned:
 - Chlorinated and phosphorated organic compounds.
 - Chlorinated solvents.

The BOD_5 values (Table 30) seen in refineries in the 1970s were widely variable depending on the networks and dilutions. However since then, the limits set on make up water consumption have nevertheless tended to cause a substantial increase as discussed in Chapter 6.

Table 30

Dissolved pollution in refinery effluents

Type of refinery	Simple, 4 Mt. $\cdot\text{y}^{-1}$ + cooling water	Simple 3 Mt. $\cdot\text{y}^{-1}$	FCC 2 000 t. $\cdot\text{day}^{-1}$	Simple 3 Mt. $\cdot\text{y}^{-1}$ + lube oil plant	Complex, 8 Mt. $\cdot\text{y}^{-1}$ without FCC condensates
Effluent flow rate	400 $\text{m}^3\cdot\text{h}^{-1}$	40 $\text{m}^3\cdot\text{h}^{-1}$	40 $\text{m}^3\cdot\text{h}^{-1}$	450 $\text{m}^3\cdot\text{h}^{-1}$	850 $\text{m}^3\cdot\text{h}^{-1}$
BOD_5 ($\text{mg}\cdot\text{l}^{-1}$)	45-70	35-50	350-580	80-180	75-200
COD ($\text{mg}\cdot\text{l}^{-1}$)	200-350	120-150	800-1 650	160-400	200-350
Hydrocarbons ($\text{mg}\cdot\text{l}^{-1}$)	5-10	5-10	8-15	5-10	18-30
Phenols ($\text{mg}\cdot\text{l}^{-1}$)	<1-3	<2	150-500	<1-3	<1-3

NB: All examples without discharges of untreated spent caustic.

The table shows that average BOD_5 levels are relatively low, but that there are strong peaks that have to be dealt with.

Need for nutrients

The two elements N and P required for bacterial development exist naturally in MWW. In refinery WW, N is also already present in sufficient concentrations in the form of NH_4^+ . Added amounts of P must therefore be provided, often in the form of H_3PO_4 at a rate of 0.5 parts of P per 100 parts of BOD_5 .

3.2.3.2 Removing aromatic hydrocarbons

In the effluents of simple refineries or even petrochemical complexes, concentrations in benzene or ethylbenzene do not exceed 30 to 50 $\text{mg}\cdot\text{l}^{-1}$. The hotter and more agitated the water is, the more readily these HC can be volatilized.

Laboratory tests reproducing the maximum stirring energy sustained in the facilities show a decrease in concentration of C_6H_6 from $50 \text{ mg} \cdot \text{l}^{-1}$ to 20 after about ten minutes and to 5-10 after twenty minutes. Of course this is stripping that can be produced in open tanks with surface aerators or large bubbles generated by blowered air. Eckenfelder also mentions research on the relative importance of stripping and biodegradation of BTX (see References). This effect can also develop with free NH_4^+ in cooling towers, when they are fed by IWW make up.

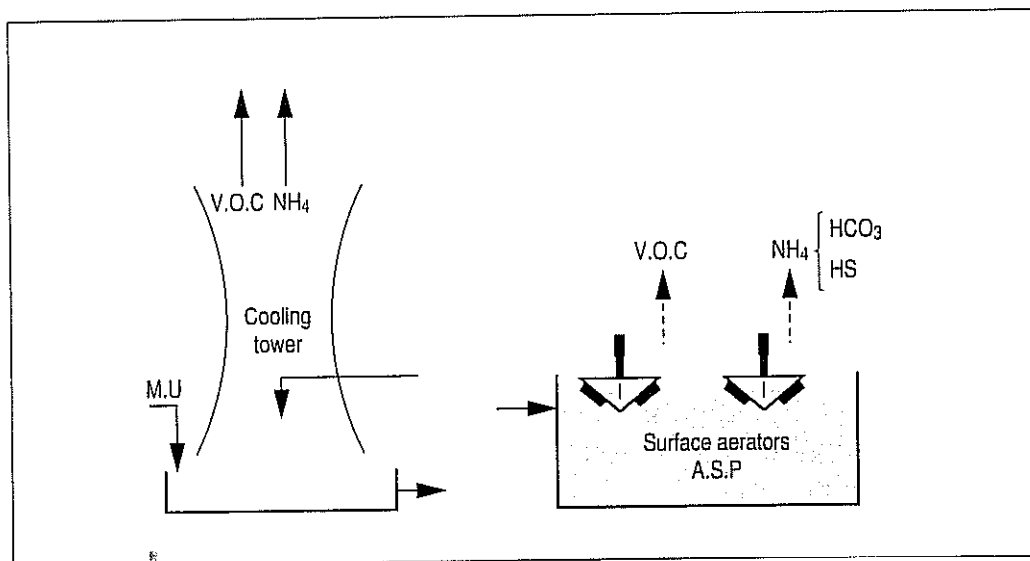


Fig. 38 Two possible sources of pollution transfer by air stripping

This adverse effect occurs much less in tanks 8 m deep where air percolation flow is four or five times less powerful.

It does not occur at all in the rare purification processes with pure oxygen, but these facilities must keep the activated sludge at a very advanced age. In this way, bacteria families capable of digesting these hydrocarbons can be selected. Any hazardous BTX concentration must also be discarded.

Prior steam stripping of condensates rich in BTX is therefore the most effective means of preventing any transfer of pollution to the atmosphere.

3.2.3.3 Causes of upsets in biological purification

First of all the insoluble HC must have been properly removed by physicochemical purification. Otherwise they could throw off the settling of activated sludge or plug up a trickling filter. A concentration of over 10% of HC in activated sludge is unacceptable whatever system of purification is used.

Toxic metals (Cu, Zn, Pb) can also have been removed by the same physicochemical purification.

Four remaining causes of trouble in biological purification should be avoided: temperature, pH, shock effects and sludge "leaching".

Temperature

Aerobic purification by mesophile bacteria can be carried out in a wide range of temperatures from 10 to 35°C, but load and efficiency conditions are optimum between 18 and 32°C. Also to be avoided are dramatic variations in temperature in a time frame of a few hours.

pH

The pH should usually be kept at 6.8 to 7.8, and acidification to below 6.5 should be avoided as it may cause the activated sludge to deflocculate and make it hard to settle out. A supply of strongly bicarbonate make up water will be advantageous in this connection. If there is none, pH may have to be regulated at the biological purification inlet. The possibility of acidifying fermentation (nitrification or oxidation of thiosulfates) must be prevented.

Shock effect

This effect can be due to sudden variations in salinity (modification in the osmotic pressure on cell membranes), in relatively inhibiting compounds or even in readily biodegradable compounds. Phenols are routinely degraded in coking plants from concentrations of $2.5 \text{ g} \cdot \text{l}^{-1}$, which are high but kept constant. Meanwhile in refineries, purification must deal with concentrations of some 20 to 100 $\text{mg} \cdot \text{l}^{-1}$ and could in no way cope with a sudden discharge of phenol-bearing spent caustic for a couple of hours. The same holds true for S^{2-} above 20 to 30 $\text{mg} \cdot \text{l}^{-1}$.

Leaching

Leaching or considerable periodical dilution of process water by rainwater or even cooling water occurs frequently in countries with heavy or intermittent rains when there is a single sewer network. It washes away a large proportion of the sludge mass in the aeration tank and the mass can not be built back up as long as the BOD_5 level at the tank inlet remains low.

3.2.3.4 Operating difficulties

The precautions mentioned above may not prevent a number of operating difficulties that will therefore have to be overcome.

A. Poor settleability of activated sludge

The problem makes itself felt by a high SS rate in decanted water. This high rate occurs frequently with petrochemical plant effluents and may have two major causes:

■ Sludge bulking

Bulking is due to predominant development of filamentous bacteria (*Sphaerotilus*) which is a form of adaptation that affords maximum surface area. The configuration is conducive to the best oxygen transfer during massive input of a highly biodegradable source of carbon. The Mohlman index, normally lower than 100, can rise to 300. There is a variety of measures that can be used to kill the filamentous bacteria or to select the bacterial medium differently:

- Addition of an oxidizing agent in the recycled sludge to especially target filamentous bacteria. In Europe Cl_2 may be used (but be careful chlorophenols do not form!) or H_2O_2 in the U.S.

- Development of anaerobiosis in the clarifier.
- Reactivation tank for sludge before purification (a few minutes aerated residence time).

■ Colloidal SS structure

Whereas interstitial water is limpid during bulking, it can in contrast be in a very colloidal dispersion if:

- The salinity is high (petrochemical plant).
- The temperature is too low (this is seldom true).
- The stirring energy is continuous and too vigorous (above 50 watts per cubic meter of tank).
- There is a considerable amount of thiosulfates or surfactants present.

B. Foaming

Besides the trouble caused in operations, foaming also reduces the oxygen transfer coefficient and causes a fine-textured floc to form that is nonsettleable by activated sludge. A positive effect could sometimes be the removal of fine particles by foaming that would then have to be controlled. It is a much more common drawback in petrochemical plants and in gasification facilities than in refineries. There are a number of origins:

- Presence of cationic or anionic surfactants, such as sulfonates in fairly low concentrations.
- Excessive use of demulsifying reagents or certain organic flocculants during a prior step in the treatment sequence.
- Development of filamentous bacteria, as mentioned earlier, associated with sludge bulking.
- Excessive concentrations of intermediate products from carbohydrate compound metabolism.

Corrective action can be to:

- Increase the stirring energy and added oxygen input.
- Resort to careful addition of antifoaming agents and water sprinkling.
- Modify the tank feed changing from plug flow to completely mixed if need be.
- Resort to preventive use of aluminum sulfate in physicochemical purification to precipitate up to 3 to 5 mg·l⁻¹ of anionic detergents.

3.2.3.5 Monitoring biological purification

It is possible to use reliable sensors and necessary to curb laboratory measurements. As a result there is a minimum amount of equipment for the monitoring and recording of:

■ Activated sludge purification

In the aeration tank:

- pH, temperature and concentration of the sludge.
- Possibly, conductivity and redox potential.

In the clarifier:

- Sludge bed level (ultrasonic probe).
- Possibly, turbidity of decanted water (UV turbidimeter).

■ Trickling filter purification

- pH and temperature at the inlet, possibly resistivity and turbidity at the outlet.
- Monitor pressure drop or sludge mass.

■ Laboratory monitoring

Daily monitoring of an average sample (inlet and outlet) is advisable for TOC (or COD) and phenols. Slightly less frequent monitoring of BOD₅ then becomes possible, except if regulations dictate otherwise. The same holds true for the Mohlman index.

The Mohlman index or sludge volume index (SVI) expresses the volume of 1 g of activated sludge settled for 30 min and is calculated by the ratio:

$$\frac{\text{Volume of settled sludge in ml}}{\text{Mass of the sludge in g}}$$

The index is easy to assess and can vary from 50 to 100 (good settleability) to 200 to 250 in petrochemical plants (poor settleability warranting preflocculation in a tertiary clarification treatment).

3.2.4 Areas where aerobic purification is used in refineries and petrochemical plants

3.2.4.1 Purification by activated sludge

Purification by activated sludge with residence time of ten to 24 hours and a sludge mass of advanced age has a buffer effect which allows:

- The breakdown of 90 to 97% of the BOD₅.
- The catalysis of complete oxidation of sulfides and thiosulfates.
- A better elimination of phenols, cyanides and sulfocyanides than with other processes.
- The reduction of the COD beyond the simple equivalence with the eliminated BOD₅ (but often with two purification stages).

It generally involves water which, after physicochemical treatment, still exhibits a BOD₅ of at least 100 mg·l⁻¹, i.e. that may be equivalent to production of at least 40 to 50 mg·l⁻¹ of activated sludge.

In contrast, the disadvantages of activated sludge are:

- The unsettability of hydrocarbon-loaded sludge.
- The large surface area occupied by the aeration tank and the settler.
- The need to monitor purification and excess sludge by a number of measurements (Mohlman index, dissolved oxygen, volatile solids mass).
- The risk of atmospheric pollution by aerosols.
- The sensitivity to the shock effect.

Progress in engineering and implementation technology for this process in the past ten years has found answers to most of these objections:

- First of all, good reliability of preliminary flotation purification thereby preventing any unplanned occurrence of hydrocarbons.
- Possibility of using deep tanks (6 to 10 m) thanks to air injectors.
- Installation of deflecting skirts to curb spattering of water droplets by surface aerators.
- Increased surface loads for secondary settlers by making them deeper, building a degassing prechamber or using an organic flocculant.

- Construction of buffer tanks for irregular concentrated effluents.
- Better maintenance of automatic devices to measure pH and dissolved oxygen.

Nevertheless, operating simplicity along with limited performance requirements suggest using attached growth systems in simple refineries. Especially effective are trickling filters that need only very little monitoring and can be followed either by a second in-series trickling filter stage or by biofilters that improve a number of water characteristics such as SS or even NH_4^+ .

Table 31

Efficiency of activated sludge purification versus the refinery effluent load (examples)

Type of activated sludge	BOD ₅	C _m	Excess sludge (kg of BOD ₅)	Sludge age (days)	BOD ₅ efficiency (%)
Low load	380	0.40	0.25	11	88
Medium load	325	0.65	0.32	5.5	90

3.2.4.2 Trickling filters

These filters have become a common means of biological purification in Western Europe in existing refineries that have been equipped since the 1970s. Meanwhile, refineries under construction still resorted to activated sludge. This is because of the frequent overestimation of forecast soluble BOD₅ levels in the effluents. As a result, in these refineries in contrast to petrochemical plants, activated sludge stations are often undernourished as regards flow rate and BOD₅ concentration and it is hard to maintain sufficient activated sludge concentration in the aeration tank. With potential production of 0.4 kg of activated sludge per kilogram of BOD₅ eliminated, it is easy to understand that 40 mg·l⁻¹ of SS in clarified water makes it difficult to maintain a sludge blanket when raw water exhibits a BOD₅ of 100 mg·l⁻¹.

Trickling filters are not subject to this type of constraint and their efficiency therefore becomes acceptable to meet usual discharge standards.

In the refining context, their phenol efficiency needs to be known. Phenols are usually present only in small initial concentrations of less than 20 mg·l⁻¹, especially if the FCC condensates are treated separately.

Phenol removal efficiency of 99.2 to 99.5% is achieved in coking plants with effluents having strong and constant phenol levels (1000 to 2000 mg·l⁻¹), but can not currently be matched in refinery effluents. This is true especially if the associated BOD₅ does not contain any phenols.

In a single trickling filter stage, efficiency of 80 to 90% can be contemplated for initial concentrations of 10 to 40 mg·l⁻¹ that can thus be reduced to 3 to 8 mg·l⁻¹. A second trickling filter bed allows a 60 to 80% reduction on the preceding concentrations.

Table 32
Purification efficiency with
trickling filters
Refinery effluent examples

	Inlet ($\text{mg}\cdot\text{l}^{-1}$)	Outlet ($\text{mg}\cdot\text{l}^{-1}$)	Efficiency (%)
COD	160-200	80-110	45-50
BOD ₅	80-100	30-40	55-65
Phenols	10-15	1.5-2	80-90

The efficiencies mentioned above can be achieved with a hydraulic load of 2 to $2.5 \text{ m}\cdot\text{h}^{-1}$ and a BOD₅ volume load of 0.6 to 0.9 kg of BOD₅ eliminated per cubic meter of packing fill per day (Table 32).

3.2.4.3 Biofilters

Pressurized or Biofor-type biofilters can be used in line behind a trickling filter or directly on the effluents at the physicochemical purification outlet to solve the following problems:

- Tertiary filtration to lower the BOD₅ level from 30 to 15 or $10 \text{ mg}\cdot\text{l}^{-1}$ or to lower the SS level from 40 to 25.
- Secondary biological purification of rainwater that is not heavily loaded to bring it from 40 to $60 \text{ mg}\cdot\text{l}^{-1}$ down to under $30 \text{ mg}\cdot\text{l}^{-1}$ of BOD₅.
- Phenol removal from water that is not heavily loaded. This type of water is common and its phenol content must be reduced from $2\text{-}3 \text{ mg}\cdot\text{l}^{-1}$ to under 1 or $0.5 \text{ mg}\cdot\text{l}^{-1}$.

3.2.4.4 Recent changes

Three tendencies have been seen in refinery operations in the past few years. They can have direct consequences on the quality of effluents undergoing treatment, given the fact that new legislation will probably be tougher.

- An increase in conversion operations (fluid catalytic cracking and visbreaking) which means more phenol and sulfide discharges. This is compounded by the fact that recycling spent caustic downstream from the desalter may be excluded by visbreaker feed Na requirements. This is why all prior stripping operations and flow segregations on the condensates from these units must be well planned and enhanced.
- A decrease in chemical treatments, e.g. polishing, alkaline and sulfuric washing, which cuts down on discharges of spent acids and caustic, and sulfonates.
- Separation of cooling water (since cooling is increasingly performed in open recirculating systems in atmospheric cooling towers) as prompted by legislation in a number of countries. This means less effluent volume to be treated, but at the same time generally higher pollutant concentrations.

These smaller, more saline and more concentrated flows will require more thorough purification operations that will however be easier to "feed" from buffer tanks.

Lastly, the possibility of recycling treated effluents as make up to cooling towers will allow cost-effective tertiary purification. Discharge of salts remains the last obstacle that needs to be overcome to guarantee optimum environmental protection.

3.3 Tertiary treatments

What are termed tertiary treatments in MWW are located immediately downstream from (secondary) biological purification and mainly aim to reduce phosphates or SS or to

disinfect. For IWW, especially for petrochemical plant and refinery WW, the aims are instead to reduce SS and COD and sometimes to remove traces of phenols or, in the U.S., to eliminate TOC.

In principle, there are a large number of processes to achieve these goals (Fig. 39). Some examples are: chlorination, adsorption on activated carbon, physicochemical purification with inorganic rather than organic coagulants preferred, and a variety of oxidizing agents (H_2O_2 , O_3 , etc.).

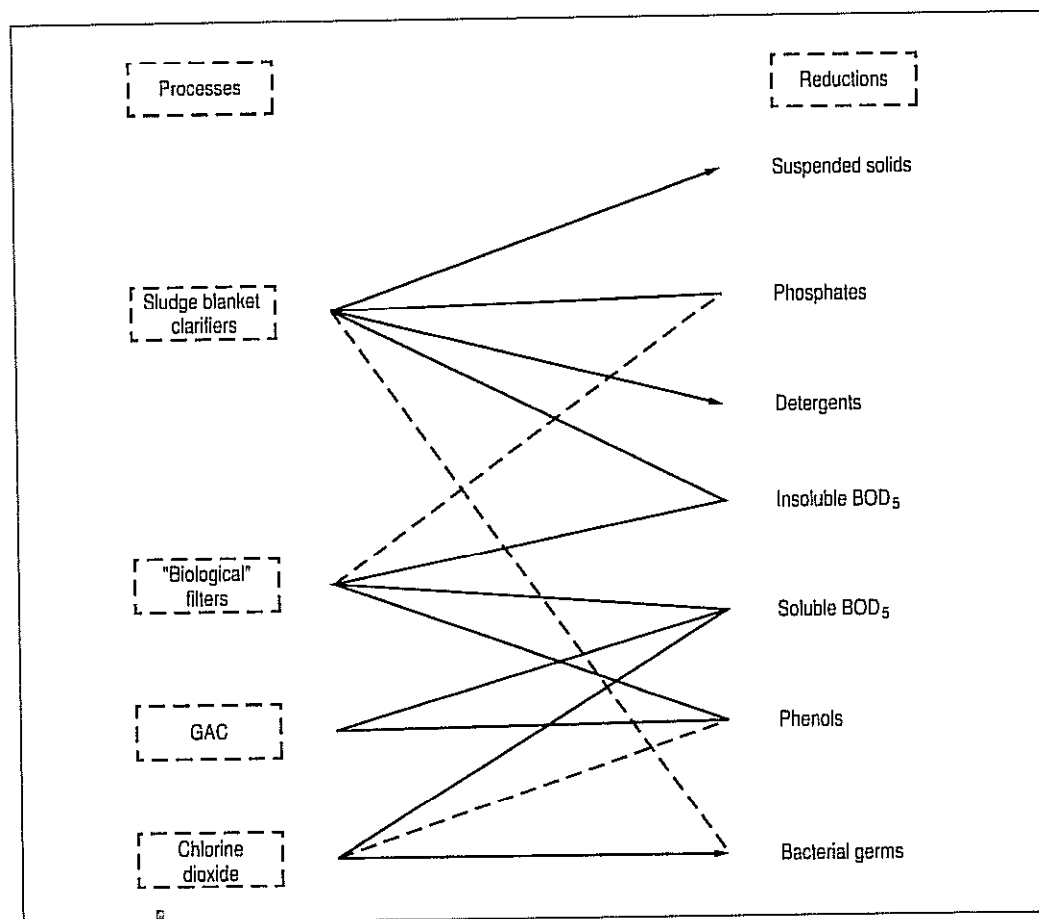


Fig. 39 Action of tertiary treatments

In an industrial context, the ends and the corresponding means applied to IWW must be separated.

3.3.1 Eliminating SS

This is a priority problem in petrochemical plants where settled water can still contain 80 to 150 $mg \cdot l^{-1}$ of SS or more after biological treatment, often in conjunction with high salinity.

The most cost-effective process from the standpoint of investments consists in distributing a nonionic or cationic organic flocculant at the inlet of the existing secondary settler.

The doses of powdered product are 2 to 4 $\text{mg}\cdot\text{l}^{-1}$.

As a result, the floc thickens and this brings about a clear-cut improvement in its settleability. Some 30 to 40% of the SS which previously escaped secondary clarification can be retained. Accordingly, a SS content in settled water of 80 to 90 $\text{mg}\cdot\text{l}^{-1}$ is cut down to 35 to 50 $\text{mg}\cdot\text{l}^{-1}$ in gasification or petrochemical facilities. Only joint use of an inorganic coagulant, Al or Fe, would make it possible to reach the threshold of 30, but the doses are high and it is not always advisable to enrich sludge in hydroxides when it is recycled to aeration.

Recycling a cationic flocculant or its monomer is also sometimes a subject of misgivings because the O_2 transfer might deteriorate. This does not seem likely with the doses used and when considerable excess sludge is produced. Industrial testing over a time frame corresponding to the age of biological sludge is in any case easy to implement.

A second process is direct filtration of water after the secondary settler with some possible help provided by an organic coagulant (1 to 2.5 $\text{mg}\cdot\text{l}^{-1}$ of active matter). When water containing 60 to 70 $\text{mg}\cdot\text{l}^{-1}$ of SS is to be treated, a filtrate with 30 $\text{mg}\cdot\text{l}^{-1}$ of SS (efficiency 50%) can be anticipated without coagulant or 20 with a coagulant. If water contains more than 80 to 100 ppm SS, a complete tertiary clarification with a DAF unit is advisable.

3.3.2 Eliminating the COD or TOC

In petrochemical plant effluents, a fairly substantial fraction of the residual COD is in colloidal form or in the form of organic macromolecules which are hard to biodegrade. In the first instance, it is necessary to resort to large doses of inorganic coagulant to destabilize the dispersion (50 to 300 $\text{mg}\cdot\text{l}^{-1}$ of 50% FeCl_3). The sludge generated must be separated in a settler or in a DAF unit. The DAF gives better thickening of the extracted sludge and is therefore preferred.

In the second instance, according to some practice in the U.S. petrochemical industry, powdered activated carbon (PAC) is added directly into the aeration tank in amounts that may vary from 10 to 50 $\text{mg}\cdot\text{l}^{-1}$. At the same time, however, advanced activated sludge age (40 to 45 days) is maintained and considerable reductions (from 10 to 20%) in TOC have been achieved.

Filtration on granular activated carbon (GAC) is also practiced in North America, but development comes up against the cost of regenerating the activated carbon. The GAC may fix only 90 to 250 kg of COD per cubic meter and so its turnover time is short. When no (thermal) regeneration is done, the filters ensure only physical purification of the SS or even a biological purification of the soluble BOD.

3.4 Recycling

A chronic shortage of available fresh water has prompted studies on reusing treated MWW or refinery WW, especially in the U.S. The situation has recently worsened with the drought and so reuse now needs to be reconsidered more in-depth.

In fact, reuse requires a certain escalation in equipment of increasingly complex design and operation, which can be chosen since needs are more sophisticated (boilers, for example). In contrast, when seawater is conveniently available it can be used to cool heat exchangers if they have been specially designed.

There are several possibilities for reusing water:

- Reusing purified MWW in cooling.
- Recycling process water itself in cooling.
- Recycling WW to LP boilers.
- Recycling heating condensates to LP and MP boilers.

3.4.1 High concentration ratios in atmospheric cooling

In the 1970s, this process was the subject of much speculation in the professional literature. First a very high "number of cycles" was mentioned, 50 for instance or even more, in order to achieve "zero blowdown discharge".

Although only power station condensers were involved, and despite the fact that they were simple, easily monitored systems, industrial applications are now confined to achieving more moderate concentration ratios of 10 to 12. The limit is due as much to the trouble caused by saline mist falling down on nearby transformer insulators as to the fact that it is technically difficult to prevent unwanted leakage throughout the system. The leakage itself of atmospheric cooling towers by drift is about 0.1 to 0.02% of the circulating water flow.

In refinery or petrochemical plant processes, there is diversity in exchanger shapes and models and the conditions they are used under, plus the geographical dispersion on the site. This explains why expectations for concentration values do not usually exceed the still ambitious figure of eight to ten times.

Nevertheless, some power plants in the U.S. state they achieve concentration ratios in excess of 20 times in systems equipped with side-stream treatments in combination with reverse osmosis or an evaporator treating the blowdown.

Even at these levels, the system must be run so as to prevent precipitation of silica (maximum solubility of around 140 to $160 \text{ mg}\cdot\text{l}^{-1}$). Additionally, conventional chemical purification of the make up water alone must be replaced by side-stream treatment of the main system water itself (Fig. 40), theoretically advantageous as to size and cost. This treatment provides for chemical precipitation of the calcic bicarbonate alkalinity and silica.

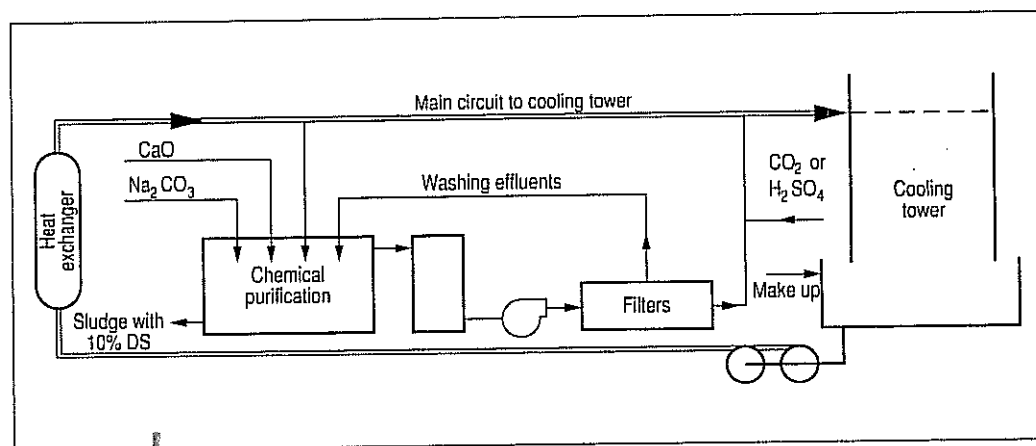


Fig. 40 Side-stream chemical treatment (SST)

3.4.2 Recycling MWW in cooling

Industry has resorted to using biologically purified MWW for part, if not all the make up water in once-through or open recirculating cooling systems. There have been several examples in Europe and more in countries that are harder hit by water shortages.

Regardless of whether nitrification was performed during the municipal biological purification operation, a tertiary treatment is necessary. It usually includes:

- Chlorination to disinfect.
- Coagulation flocculation followed by settling or DAF.
- Filtration.

Coagulation by a metallic salt is also advantageous in that it precipitates the residual phosphorus that could otherwise promote bacterial development.

The presence of ammonium can raise the potential problem of biological nitrification in the cooling tower depending on the NH_4 concentration in the water, its alkalinity and above all the conditioning of the system.

Usual concentrations of NH_4^+ after biological purification at high load are about 15 to 20 $\text{mg}\cdot\text{l}^{-1}$ of $\text{N}\cdot\text{NH}_4$. This may involve production of 68 to 98 $\text{mg}\cdot\text{l}^{-1}$ of HNO_3 (5.3 to 7.1°F) in cooling towers.

Though nitrification does not occur with "chromate-zinc" conditioning, it may become a problem with "phosphate-zinc" conditioning at pH values of 6.6 to 6.8. It will certainly be a problem with conditioning carried out at what is termed an "uncontrolled pH". Two things can then be done:

- Make sure the alkalinity input by the water itself or by addition of NaOH in the system offsets the potential nitric acidification.
- Adapt the capacity of side-stream filtration to the low extra input of SS produced by nitrification and modify periodical biocide treatments.

This is how power stations have been able to suspend softening treatments on their river water (40 $\text{mg}\cdot\text{l}^{-1}$ $\text{N}\cdot\text{NH}_4$), leaving it up to nitrifying bacterial, momentarily, to vaccinate the water in the system (Table 33).

Table 33

Changing concentrations in a nitrification system before and after stopping softening treatment of make up water

Concentrations	Make up water		System water	
	Before	After	Before	After
pH	9.6-9.0	8.9-8.2	6.6-4.8	7.8-7.1
M alk.	10°-15°	30°-15°	1°-0°	6°-2.5°
$\text{N}\cdot\text{NH}_4^+$ ($\text{mg}\cdot\text{l}^{-1}$)	40-16	40-16	1.5-0.2	1.8-0.6

3.4.3 Recycling process water in cooling

In the 1970s, direct input of phenol-bearing process water to cooling towers was tested. The towers were turned into immense "trickling filters", with biological purification accepted in the towers provided there was considerable maintenance. For example, 400 to

500 $\text{m}^3 \cdot \text{h}^{-1}$ of rainwater and phenol-bearing but desulfurized and deoiled condensates were sent into a system characterized by a concentration ratio of 1.1. The concentration in SS in the system was held at around $90 \text{ mg} \cdot \text{l}^{-1}$. The make up water contained from 10 to $30 \text{ mg} \cdot \text{l}^{-1}$ of phenols and the blowdown 0.1 to $0.5 \text{ mg} \cdot \text{l}^{-1}$, i.e. destruction of 90%. For a circulating flow of $11\,000 \text{ m}^3 \cdot \text{h}^{-1}$, a $400 \text{ m}^3 \cdot \text{h}^{-1}$ side-stream filtration ensured SS deconcentration. Countercurrent cleaning of exchangers was performed daily, sometimes with air injection.

The cost of maintenance and the reliability of biological purification now prompt operators to carry out biological purification on process water first, following up with a tertiary treatment.

The choice of purification techniques depends on local conditions, often there is much to be gained by using existing equipment.

Two French refineries have successfully applied two quite different schemes. In both cases, deballasting and desalting water was excluded (see Chapter 6).

The Shell refinery in Pauillac formerly used to need $90 \text{ m}^3 \cdot \text{h}^{-1}$ of water from the Gironde river to provide make up for the open recirculating cooling system. Recycling process WW enabled them to reduce the final discharge of effluents from $200 \text{ m}^3 \cdot \text{h}^{-1}$ to $50 \text{ m}^3 \cdot \text{h}^{-1}$, with some of the water going to other nonpolluting uses. The characteristics of the final discharge were improved as shown below:

	Before recycling	After recycling
HC	$10 \text{ mg} \cdot \text{l}^{-1}$	$1 \text{ mg} \cdot \text{l}^{-1}$
Phenols	$2 \text{ mg} \cdot \text{l}^{-1}$	unmeasurable
BOD ₅	$67 \text{ mg} \cdot \text{l}^{-1}$	$30 \text{ mg} \cdot \text{l}^{-1}$
Toxicity index	2.5	0
Cubic meter WW/ton of crude	0.4	0.1

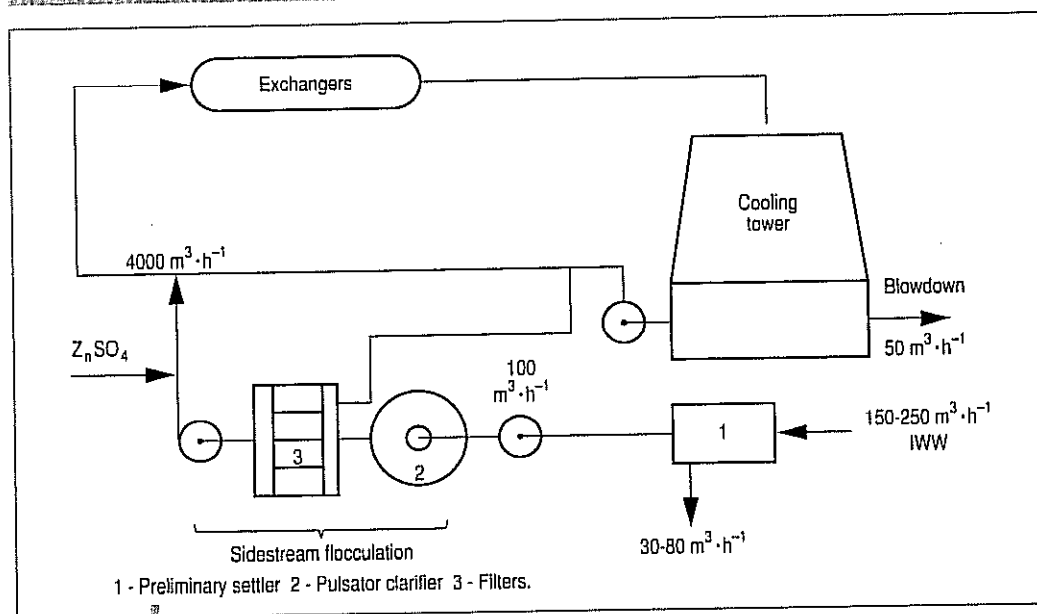


Fig. 41 Side-stream purification with process WW make up

WW treatment after low-load biological purification would include (Fig. 41):

- Flocculation with FeCl_3 .
- Clarification in a sludge blanket clarifier.
- Filtration on open filters.

MWW or process WW that has undergone extensive biological purification can be recycled more profitably than in atmospheric cooling, e.g. to supply LP boilers. This could be contemplated after a complete tertiary treatment and softening on frequently cleaned resins. But because of the often high and variable salinity of the water, simple softening is not always enough and desalting is necessary. Desalting is based on the use of reverse osmosis membranes and entails a much more severe tertiary treatment under accurate operation.

3.4.4 Reusing WW with reverse osmosis (RO) desalting

Water supply to MP or HP boilers could therefore be designed to have high requirements ($\text{SiO}_2 < 20 \mu\text{g}\cdot\text{l}^{-1}$, resistivity over 5 megohm-cm) and better justifies the heavy investment needed. Tertiary treatment must allow supply to a RO unit, then to a cation-anion polishing sequence. It can include a two-stage flocculation:

- Chlorination;
- Flocculation-clarification or lime softening;
- Filtration;
- Flocculation in line at a lower pH (6 to 6.5) and secondary filtration;
- Dechlorination.

The first stage performs some bacteriological disinfection, eliminates the phosphates, the carbonate hardness and most colloids. The second stage removes a fraction of the soluble organic matter and yields water of constant physical quality and a fouling index of less than 3. The recycled water should nevertheless exhibit low salinity and regular characteristics for reliable treatment before RO, and this is not often achieved.

3.4.5 Heating condensates

Heating steam may accidentally come into contact with light or aromatic products that it carries off into its condensates.

Refineries separate condensate streams if there is potential pollution and schedule treatment so the condensates can be recycled to LP or MP boilers.

The condensates are hot (40 to 60°C) and may contain:

- 5 to 15 $\text{mg}\cdot\text{l}^{-1}$ of SS (oxides, corrosion products).
- 10 to 20 $\text{mg}\cdot\text{l}^{-1}$ of insoluble HC on the average, but with peaks of 30 to 60.
- From 5 to 30 $\text{mg}\cdot\text{l}^{-1}$ of aromatic HC if the condensates are cold.

The pH varies from 6 to 8 but much lower values have been recorded.

Treatment is carried out according to the following two or three stages:

3.4.5.1 Oil separation by coalescence

After coagulation with an organic coagulant, this oil separation process shaves off the HC peaks and yields a filtrate containing less than 3 to 4 $\text{mg}\cdot\text{l}^{-1}$ of insoluble HC on the average. Upflow percolation velocities of 20 to 25 $\text{m}\cdot\text{h}^{-1}$ can be contemplated. Intermediate storage in a hydraulic buffer tank (one to two hours).

3.4.5.2 Polishing oil separation

a. On cartridge filters with a diatom precoat; optimum temperature from 60 to 70°C; percolation velocity from 3 to 8 m·h⁻¹ on the surface of the candles.

Since the HC pour point can be reached, the size of the mesh opening in the support material must be large enough.

Insoluble HC content after this filtration process is around 1 to 2 mg·l⁻¹ depending on the precoat and the velocity.

Silica redissolution must be limited because of the contact with the sand in the coalescer or with the diatoms. This is why the pH values must be lower than 8. Under these conditions, possible silica enrichment varies from 0.05 to 0.25 mg·l⁻¹ depending on the growing pH and temperature.

b. On granular activated carbon filters (GAC). They have a dual function:

- Adsorption of aromatic HC at limited percolation velocities.
- Polishing filtration to eliminate the residual HC subsisting after coalescence.

Possible loads go from 3 to 10 volumes per volume per hour with bed heights of 1.5 to 2 m. Sometimes two beds are in line and they are switched around after each washing.

Optimum temperature is from 30 to 40°C to keep the aromatic HC adsorbed. This often requires that the condensates are cooled beforehand.

A problem involved in using GAC is the slow redissolution of silica (from 1 to 0.1 mg·l⁻¹) and of calcium (from 1 to 0.2°F). This corresponds to carbon rinsing which may require the flow of from 1000 to 1500 volumes of condensate per volume of GAC and then enrichment in silica maintained along the lines of 0.1 to 0.2 mg·l⁻¹. Percolation of water cooled to 25-35°C and at a pH<7 slows down the SiO₂ solubilization velocity, however.

In this range of temperature, removal of total HC, both soluble and insoluble, to less than 0.5 mg·l⁻¹ can be considered with capacities of 150 to 300 g of soluble HC per kilogram of carbon. Above this figure, the GAC must be regenerated by steam or, less frequently but more expensively, by thermal means.

3.4.5.3 Thermal degassing

The condensates being treated are usually mixed with make up water and thermally degassed. Here the prior GAC stage is not necessary since the low concentrations of aromatic HC are sufficiently eliminated by the degasser.

3.4.5.4 Total demineralization

Removing traces of Ca and SiO₂ brought in by recycling seldom entails mixing the condensates with the make up water at the inlet of a series of ion exchangers. In fact the SiO₂ input by the treatment is very diluted by massive return of unpolluted untreated condensates and by make up water. To check this out, a SiO₂ balance must be set up.

Treatment of spent caustic

Chapter

4

Spent caustic is a highly specific effluent. The small volumes (0.1 to $8 \text{ m}^3 \cdot \text{h}^{-1}$) discharged vary according to a refinery's size and layout and to the sulfur content of the crude being processed. However, the harmful effects are considerable due to the concentration in S^{2-} and in phenols.

In the CONCAWE report of 5 May, 1989, production of spent caustic by 45 European refineries represents about $138,000 \text{ t} \cdot \text{y}^{-1}$ compared to an overall 252 Mt of crude refined. This should give 550 t of spent caustic for every 1 Mt of crude.

Depending on a refinery's degree of complexity, average hourly spent caustic discharge can be extremely different:

Simple $6 \text{ Mt} \cdot \text{y}^{-1}$ refinery	$0.1 \text{ t} \cdot \text{y}^{-1}$
$6 \text{ Mt} \cdot \text{y}^{-1}$ refinery with FCC, thermal or hydrocracking	$0.165 \text{ t} \cdot \text{y}^{-1}$
$10 \text{ Mt} \cdot \text{y}^{-1}$ refinery with the above plus SC or lube oil plant	$1.25 \text{ t} \cdot \text{y}^{-1}$
Complex $10 \text{ Mt} \cdot \text{y}^{-1}$ refinery	$5 \text{ t} \cdot \text{y}^{-1}$

Outside of the treatments discussed in this chapter, the ways of breaking down or disposing of spent caustic are very different. It can be sold to an outside buyer, though this is done less and less. It can be recycled downstream from the desalter, diluted with different types of water or neutralized with acid effluents.

Many of these solutions have drawbacks involving the process itself or the treatment of effluents. The negative points may not be immediately obvious and can be easily underestimated.

Recycling spent caustic downstream from the desalter can be only a limited solution. This is because of the detrimental alkalization of the crude (creation of emulsions), or if vacuum distillation residues are to serve as feed for visbreaking (standard 3 ppm of Na^+ in the feed or 8 in the crude). It can be contemplated only in simple refineries, but not in the complex ones that produce considerable amounts of spent caustic.

Spent caustic has often been discharged after dilution directly into the general effluent or into cooling water in an open system. However, this has led to more difficult and more costly water treatment (softening process initiated with dispersed precipitation of CaCO_3).

As a result, separate preliminary treatments, desulfurization or even phenol removal, are necessary.

After oxidation of sulfides into thiosulfates, a fraction of the spent caustic could, however, be recycled for alkaline scrubbing of certain cuts.

4.1 Origin and composition of spent caustic

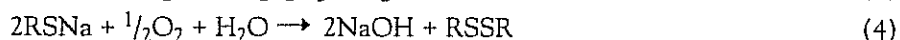
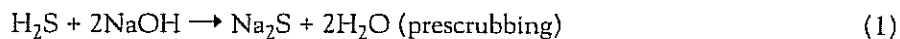
4.1.1 Nonregenerative desulfurization processes

Processes that are termed **regenerative** use amine solutions (MEA or DEA) and involve gas scrubbing alone (MEA for natural gases and DEA for sulfur-bearing refinery or steam cracking gases).

Nonregenerative processes use caustic soda scrubbing sometimes in combination with air oxidation. They generate three types of spent caustic:

- Scrubbing or preliminary scrubbing by caustic alone.
- **Catalytic sweetening** (Merox sweetening) which is a direct oxidation of mercaptans RSH into disulfides RSSR.
- **Catalytic extraction** (Merox extractive) which extracts disulfides from the gasolines being treated.

In the Merox process, cold mild oxidation of RSH by air in an alkaline environment is catalyzed by a chelating agent, cobalt phthalocyanine. Four main reactions are involved; the first two are avoided or curtailed as the reagents are expensive:



The major aim of oxidation processes is therefore to remove mercaptans. These are present in high concentrations in light gasolines and in low concentrations in gas oils where sulfides prevail.

Mercaptans can represent 1% of the total S in sour crudes, but up to 30% in sweet crudes. Possible concentrations may go up to 90 ppm (light gasolines) or 300 ppm (heavy gasolines), or even 1000 ppm in CC heavy gasolines.

The disulfides produced by mild oxidation of mercaptans are insoluble in dilute caustic or in water but dissolved in petroleum products.

Their boiling point is high but their specific gravity is low:

		Specific gravity at 15°C	Boiling point at 1 bar
$\text{CH}_3 \text{ SS } \text{CH}_3$	Dimethyldisulfide	1.057	114°C
$\text{C}_2\text{H}_5 \text{ SS } \text{C}_2\text{H}_5$	Diethyldisulfide	0.992	152°C
$\text{C}_3\text{H}_7 \text{ SS } \text{C}_2\text{H}_5$	Dipropyldisulfide	0.964	142°C

They can be separated from the spent caustic, with difficulty by natural flotation and practically by coalescence, provided there are minimum amounts of added light gasolines to disperse them.

In practice, oxidation is carried out by means of the two systems summarized in Table 34.

Table 34

The two Merox processes

Principle	Sweetening	Extractive
	Oxidation of RSH in presence of gasolines	Extraction of RSH then regeneration of caustic by air
Procedure	• Caustic, then air introduced • Caustic settled and recycled • Gasoline scrubbed or filtered	• Extraction by caustic alone • Caustic regenerated by air • Disulfides and caustic separated
Caustic solution	5-10%	12-18%
Disulfides	Remain in gasoline	Are extracted from caustic by coalescence

The flow schemes are shown in Figs. 42 (sweetening) and 43 (extraction).

Areas where nonregenerative processes are used (i.e. sources of spent caustic) are summarized in Table 35.

Table 35

Main areas involving nonregenerative treatments

Treatment	Areas
Alkaline scrubbing alone	To remove H_2S and CH_3SH from LPG To remove H_2S , CO_2 and HCN from SC gas
Preliminary caustic scrubbing before Kerox	To reduce the acidity index in kerosine (mainly due to naphthenic acids) and reduce surfactants that are harmful for Merox
Merox sweetening	For heavy gasoline, naphthas
Merox extractive	For C_4 , C_5 gases and LPG
Merox extractive + Merox sweetening	For light straight-run gasoline
Min-Alk (minimum alkalinity)	For cracked gasoline

} Low caustic consumption

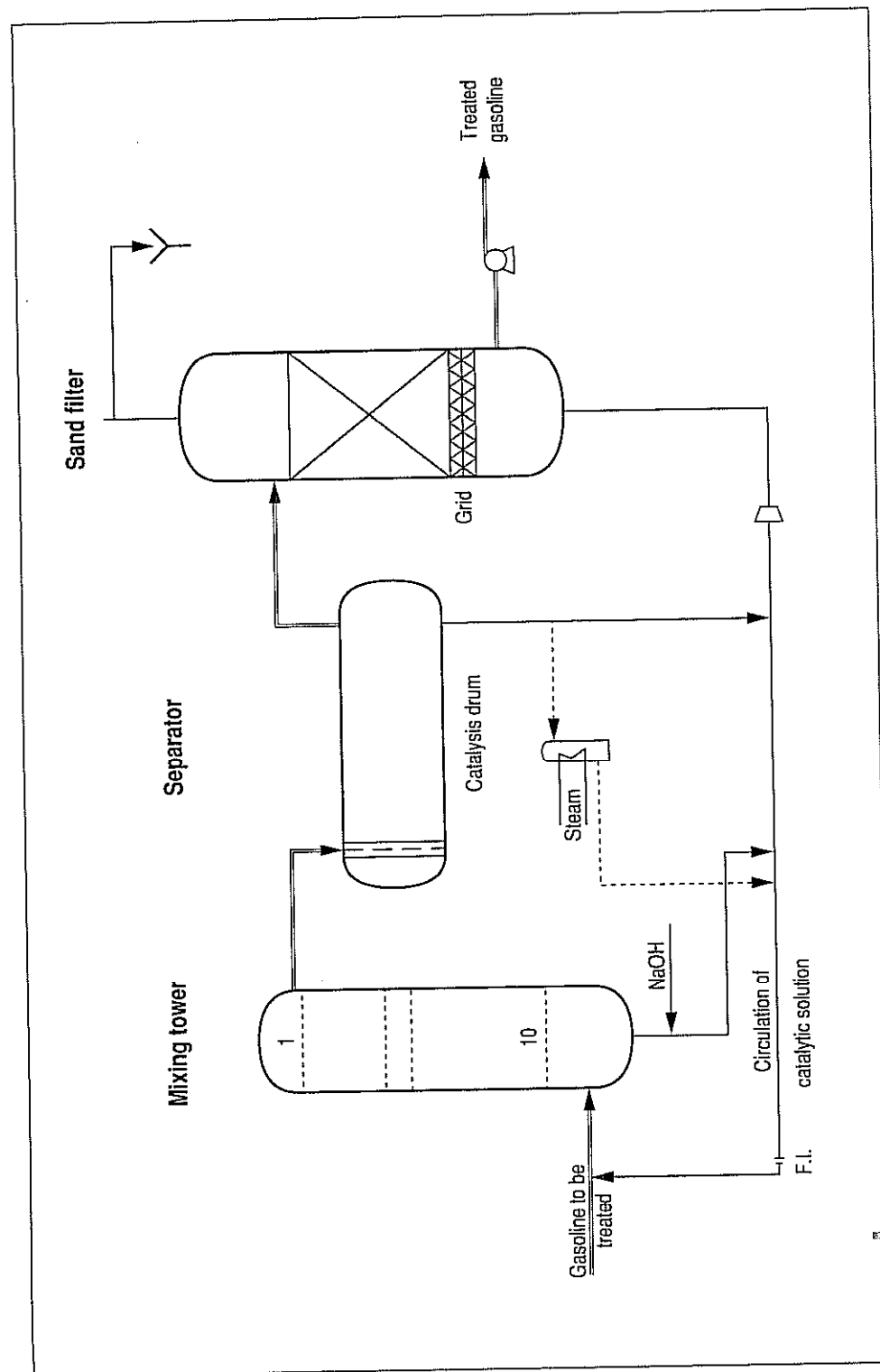


Fig. 42 Mercox-type sweetening process (From: Report 38 302, "Raffinage chimique par adoucissement", by C. Marty, Center for Refining, Petrochemicals, Gas course material, ENSPM).

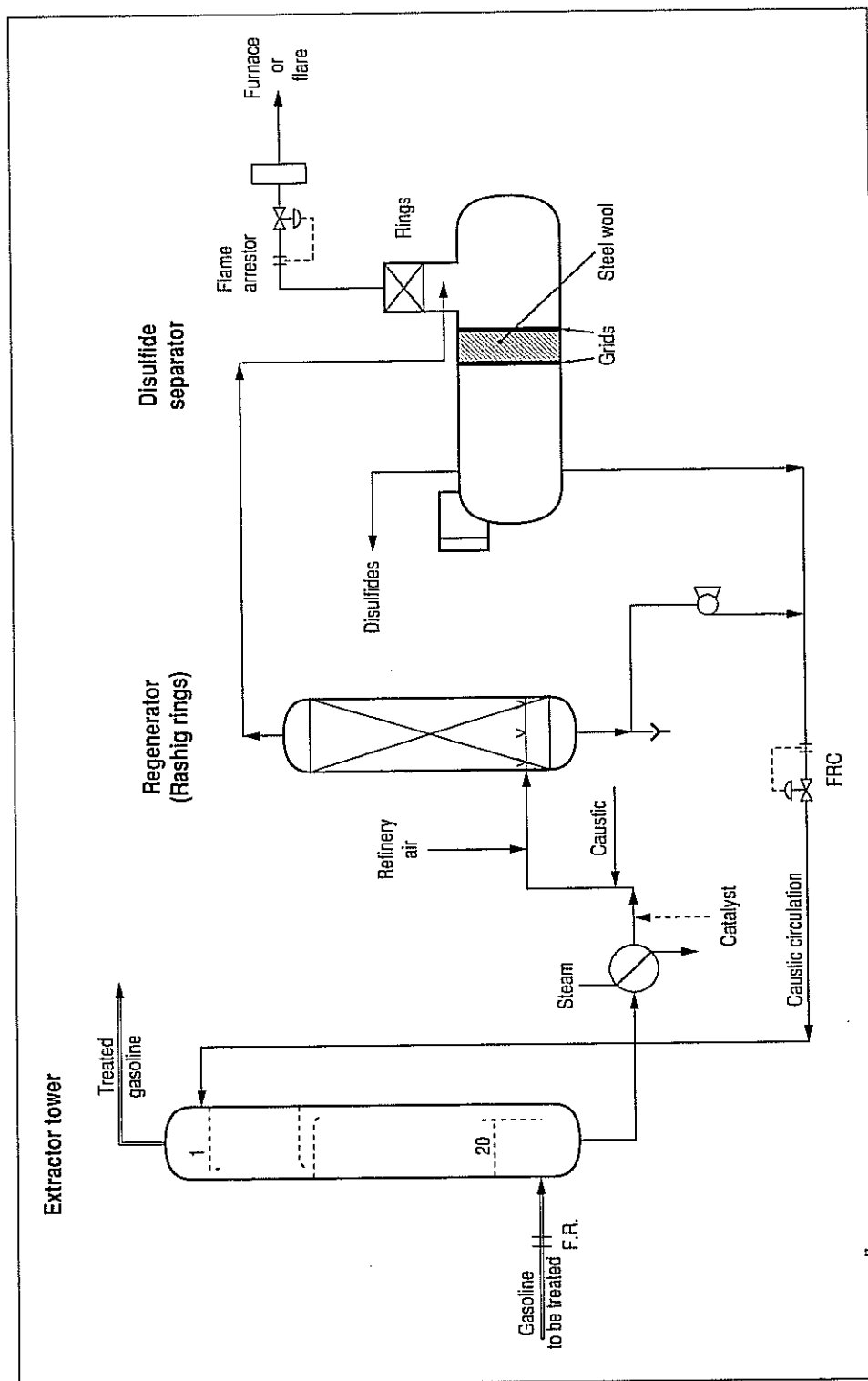


Fig. 43 Extractive sweetening process (From: Report 38 302, "Raffinage chimique par adoucissement", by C. Marty, Center for Refining, Petrochemicals, Gas course material).

4.1.2 Composition of spent caustic

Free caustic content must be kept above thresholds that are defined according to the cut and the nature of the treatment. It can vary from 5% (Merox sweetening) to 20% (scrubbing). Another aim is to keep less than 20 ppm of disulfides in regenerated solutions. The two prime causes of spent caustic deterioration are the growing Na_2S and mercaptan content and "sprung acid" concentration where phenolic compounds are the main components. Allowable concentrations increase with caustic concentrations.

Spent caustic also ages by:

- Becoming richer in emulsion-producing naphthenates.
- Becoming richer in thiosulfates (Merox extractive).
- Carbonation (Na_2CO_3).
- Becoming richer in SS (iron oxides and FeS).

The phenol content, present in the form of Na phenolates, of course characterizes sweetening of feeds that are rich in these compounds. The main one is from the FCC despite a reaction temperature of around 500°C . In the SC at a higher temperature (around 800°C) phenol production is theoretically more massive. However the phenols are immediately reextracted by the considerable steam recirculation.

The spent caustic from preliminary scrubbing operations, which represents some 30 to 50% of the discharges, is low in phenols and often richer in Na_2S than in mercaptans.

Spent caustic coming from light gasoline sweetening is rich in highly soluble monohydric phenols. When it comes from heavy gasoline sweetening it may contain large proportions of water-insoluble cresols or thiophenols.

The relative concentration in phenols used to be the basis for dividing spent caustic into two main types: phenolic and sulfidic. This distinction was made for a long time in the U.S. and M.R. Beychok (Aqueous Wastes from Petroleum Plants, John Wiley and Sons) in particular characterized phenolic spent caustic as coming from alkaline scrubbing of cracked gasoline that has been debutanized. It contains mainly thiophenols and mercaptans and very little Na_2S .

Later the definition seems to have been broadened to cover spent caustic whose phenols are extractable (steam or solvent) and marketable. This presupposed a total phenol concentration of around $5\text{--}6\text{ g}\cdot\text{l}^{-1}$.

Since the current market value of reclaimed phenols is almost zero, the treatment of spent caustic is now based first of all on desulfurization and secondly on phenol removal. No attempt is made at reclaiming phenols so the treatment can be destructive.

Having buffer tanks to hold eight to 15 days' worth of stored spent caustic ensures a supply of relatively homogeneous and constant spent caustic for treatment.

By way of an illustration, orders of magnitude of the composition of the two types of spent caustic are given (Table 36).

Table 36
The two types of spent caustic

	Sulfidic spent caustic (SC)	Phenolic spent caustic (FCC)
Initial NaOH	5%	12-18%
S^{2-}	$2\text{--}5\text{ g}\cdot\text{l}^{-1}$	$10\text{--}25\text{ g}\cdot\text{l}^{-1}$
RSH	$5\text{--}10\text{ g}\cdot\text{l}^{-1}$	$10\text{--}30\text{ g}\cdot\text{l}^{-1}$
Phenols	$1\text{--}5\text{ g}\cdot\text{l}^{-1}$	$10\text{--}40\text{ g}\cdot\text{l}^{-1}$

4.1.2.1 Physical composition of spent caustic

Three parameters are to be considered: SS, HC, gums or "polymers".

A. SS

Since the liquors come from gas scrubbing and have been settled for a long time, the SS are almost colloidal and do not interfere with treatment. Solids are not usually measured and the few recorded values range from 0.2 to 0.5 g·l⁻¹ (except when gums are present). In addition, it is not easy to measure them.

B. HC

HC are of course present in three forms:

- Dissolved: light and aromatic HC.
- In fine but unstable emulsions (paraffinic HC) or stable emulsions (asphaltenic HC).
- In a solution of polar compounds (naphthenates) separated only by acid hydrolysis.

Total HC content may vary from 0.05 to 4%. It may therefore be high enough to cause volatile HC to evaporate which is a hazard during air stripping. Anticipated concentrations of less than 0.05 g·l⁻¹ are in fact seldom achieved.

IR analysis of HC often shows a considerable fraction of polar compounds. It is sometimes of the same order of magnitude as the nonpolar HC fraction itself. For example: 12 g·l⁻¹ before Florisil, 7.5 after.

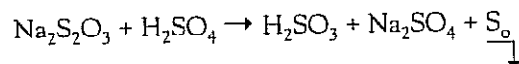
C. Gums or "polymers"

Just one of the drawbacks of these products which can be very troublesome is that they are deposited on pH meter probes and on packing. They can have two origins:

■ Existing before treatment: two causes of gum formation are involved:

- Aging and peptization of heavy HC at pH 14 which initiate slow polymerization due to long residence time in buffer tanks. This may occur in spent caustic from naphtha or especially gas oil steam cracking, cuts that are rich in S and in heavy aromatic fractions.
- Reaction of water and acetylenic HC with formation of polymerizing acetaldehyde in the form of sticky pink products. These products are thought to contain bonded sulfur. A washing pretreatment for SC spent caustic by light or aromatic cuts can keep these products from forming. This problem is believed not to exist for FCC spent caustic which is very rich in phenols. This is because phenols, powerful antioxidants, are thought to slow down gum formation.

■ Formed after the spent caustic oxidation treatment. Direct acidification can then neutralize these alkaline effluents and gives rise to S₂O₃²⁻ disproportionation:



The precipitated sulfur is colloidal and gives a yellowish color to the deposits. The reaction can also occur without air oxidation of spent caustic if the caustic already contains a significant fraction of thiosulfates. This is often the true for SC caustic but is undetected by analysis.

The spent caustic can also be characterized by its density which depends mainly on the average NaOH concentration of new make up caustic and the final Na₂SO₄ and Na₂S₂O₃ concentration in the treated spent caustic. In an industrial context, spent caustic specific gravity may vary from 1.04 to 1.2 for an initial NaOH content of 4 to 20%.

4.1.2.2 Chemical composition of spent caustic

The four basic parameters are: free caustic, total phenols, mercaptans and sulfides. Two secondary parameters must also be taken into consideration: Cl^- and CN^- .

A. Free caustic and total alkalinity

Free caustic content depends on the initial concentration and on the sulfide and phenolate concentration rate.

The initial concentration depends on the type of scrubbing and the degree to which sprung acids are to be reclaimed. High NaOH concentrations lower the spent caustic volume and boost the amount of cresols that can be reclaimed when this is the objective.

Converting to Na_2S and to phenolates in turn defines the following orders of magnitude for caustic consumption:

$$\text{Caustic loss} = \text{phenol input} \times \frac{40}{108} + \text{H}_2\text{S input} \times \frac{40}{34} + \text{mercaptan input} \times \frac{40}{32}$$

Experience has shown that the loss calculated in this way is always lower than the effective measured loss.

For a maximum possible effectiveness of 90% for the initial caustic, actual effectiveness ranges in fact from 40 to 75%. Part of the free alkalinity is in fact carbonated into Na_2CO_3 . It is not usually measured, but may account for 10 to 25% of the total alkalinity. It is advisable to state the total alkalinity of a spent caustic rather than the free caustic, which only represents 75 to 95% of the total alkalinity.

B. Chlorides and cyanides

Chlorides are always present and in variable concentrations (0.25 to $5 \text{ g} \cdot \text{l}^{-1}$).

Alkaline cyanides are not often measured either, but can be present in amounts of a few milligrams per liter. Any alkaline cyanide presence in stripping gases after acidification must be taken into account (HCN is harmful).

C. Phenolic compounds

These compounds are of different types as summarized in Tables 37 and 38. Their characteristics are approximate but useful in understanding spent caustic treatment. Analysis must involve both entrainable and total phenols. In contrast with process condensates, many heavy nonvolatile phenols can predominate in spent caustic (Table 37). On the other hand phenol removal efficiency of acidification alone must be evaluated based on the measurement of total phenols. In this example, entrainable phenols represent 38 to 50% of the total phenols. Whereas volatile phenols represent 70 to 85% of total phenols in coking plants depending on coal type, in refineries the rate depends on intermediate cuts and their treatment before caustic scrubbing. Additionally, the ratio is not as well known as for coking plants.

Nevertheless, a preponderant proportion of cresols and xylenols is acknowledged after FCC cracking of heavy products or SC cracking of phenols. The presence of thiophenols is seldom monitored.

Table 37

Examples of total and entrainable phenols in spent caustic

	FCC Mercox caustic	SC Mercox caustic
Total phenols (by bromination)	$0.2 \text{ g} \cdot \text{l}^{-1}$	$68 \text{ g} \cdot \text{l}^{-1}$
Entrainable phenols (Diaminoantipyrene)	$0.1 \text{ g} \cdot \text{l}^{-1}$	$26 \text{ g} \cdot \text{l}^{-1}$

Table 38
Characterization of the main phenolic compounds

Nomenclature	Name	Specific gravity 4°/18°C	Melting point (°C)	Water solubility (g·l ⁻¹)			COD/BOD ₅ (mg·mg ⁻¹)
				20°C	40°C	100°C	
Monohydric compounds							
Phenols C ₆ H ₅ OH	Phenyllic acid	1.07	41	70	90		2.3/1.8
o-cresol CH ₃ C ₆ H ₄ OH	2-methylphenol	1.04	31		31	56	2.3/1.8
m-cresol	3-methylphenol	1.04	13	20	23	58	2.3/1.8
p-cresol	4-methylphenol	1.03	34	20	24	54	2.3/1.8
2,4-xylene (CH ₃) ₂ C ₆ H ₃ OH	2,4-dimethylphenol	1.036	26	5	8		2.6/1.4
3,4-xylene	3,4-dimethylphenol	1.023	65	5	10		2.6/1.4
3,5-xylene	3,5-dimethylphenol		68				2.6/1.4
α-naphthol C ₁₀ H ₇ OH	1-hydroxynaphthalene	1.22	96				2.5/1.8
β-naphthol	2-hydroxynaphthalene	1.21	122	1		12	2.5/1.8
Dihydric compounds							
Catechol	1,2-benzenediol	1.37	105	450			1.9/1.2
Resorcinol	1,3-benzenediol	1.28	276	V.S.	V.S.		1.9/1.2
Hydroquinone C ₆ H ₄ (OH) ₂	1,4-benzenediol	1.35	172	V.S.	V.S.		1.9/1.2
Sulfur compounds							
Thiophenol C ₆ H ₅ SH	Benzene-thiol (phenyl mercaptan)	1.08					2.7/-
o-thiocresol CH ₃ C ₆ H ₄ SH	2-toluenethiol	1.08	15				2.8/-

Sprung acids

The acidification required to liberate H_2S was used to free the supersaturated "sprung oils and acids". These are mainly made up of cresylic acids and there was an attempt to find a market for them. The low solubility of the acids allows sufficient precipitation, if the initial spent caustic is concentrated enough in them. This use is no longer profitable due to the low cost of synthetic phenols.

Sprung acids can also contain naphthenic acids or paraffinic HC when the paraffinic HC are present in sufficiently significant concentrations.

The oily layer formed after acidification and settling may amount to 1 to 5%, rarely 8%, of the volume of phenolic spent caustic treated. It may contain from 0.5 to 5% of paraffinic HC in dispersion. In fact the layer comprises (Table 39):

- The phenolic fraction (mainly cresols and xylenols).
- Neutral oils (HC).
- Water in direct emulsion, containing the same concentration in Na_2SO_4 and other salts as the acidified spent caustic (around 5 to 20% water depending on separation conditions).
- Mercaptans in shared solubility.

Table 39

Examples of sprung acids composition

	FCC spent caustic	Scrubbing spent caustic
Phenolic oil	60 to 75%	1 to 5%
H_2O	10 to 20%	10 to 25%
Neutral oils	0.5 to 3%	2 to 15%
Inorganic salts	1 to 2%	2 to 3%
Sulfur compounds	5 to 15%	20 to 50%
Naphthenic acids	0 to 5%	0 to 10%

The presence of water-insoluble disulfides is likely, but does not seem to have been looked for.

D. Sulfur compounds

These compounds are of several different types:

- Mercaptans and sulfides make up the majority, with mercaptans fairly often more abundant than sulfides. Removal by scrubbing is a priority since they are foul-smelling and volatile.
- Thiophenols.
- Thiosulfates sometimes in fairly significant concentrations, but seldom measured.

E. Examples of spent caustic analyses (table 40)

Table 40a

I General chemical characteristics of six refineries

Compounds in $\text{g}\cdot\text{l}^{-1}$	Sulfidic spent caustic			Phenolic spent caustic		
	(1)	(2)	(3)	(4)	(5)	(6)
S^{2-}	4-10	4.5-12	4-8	2.5-6	20 (5 to 40)	0.3-0.6
RSH	10-16	6.9-16	8-30		20 (2 to 35)	6-7
$\text{S}(\text{S}_2\text{O}_3^{2-})$	2	3.7	0.5-1			
Total phenols	26-35	0.3-6	2-5	12-20	15 (2 to 30)	30-50
Thiophenols	6-8	—	1	—	—	—
HC	<0.5	0.1-7		<5	0.1-0.7	
Total alkalinity	120-150	15-25	40-70		30-70	
COD		30				(Merox extractive)

Table 40b

II Particular characteristics (Refinery (1))

	General spent caustic	Scrubbing	SC
Specific gravity	1.27	1.14	1.10
Dynamic viscosity at 20° C (cP)	7.5	2.5	1.5
Redox potential/Ag (volt)	-0.83	-0.67	-0.83
S^{2-} ($\text{g}\cdot\text{l}^{-1}$)	4	2	12.9
RSH ($\text{g}\cdot\text{l}^{-1}$)	12	5.7	—
Total alkalinity ($\text{g}\cdot\text{l}^{-1}$)	228	80	34

The corresponding COD is considerable. Refinery (6) processing 6 to 8 Mt/y discharges 1.5 to $2 \text{ m}^3\cdot\text{h}^{-1}$ of spent caustic whose COD varies from 20 to $100 \text{ g}\cdot\text{l}^{-1}$.

4.2 Desulfurization of spent caustic

Two common processes are stripping after acidification and oxidation. Oxidation can be performed in several steps generally confined to the $\text{S}_2\text{O}_3^{2-}$ state and less often reaching the SO_4^{2-} state.

Theoretically, the first process requires reneutralizing the acid effluent after it has been stripped and is more expensive in reagents. Meanwhile the second process is supposed to allow some recycling of the oxidized spent caustic which is still highly alkaline.

In practice however, the first process requires less investment and also performs partial phenol removal from the phenolic spent caustic. As a result, it is being developed more than the second one.

The way the two reactions evolve can be seen on the redox potential versus pH diagram (see Fig. 9a).

4.2.1 Acid hydrolysis and stripping

The process involves phenolic as well as sulfidic spent caustic and includes the following mechanisms:

■ Acidification of spent caustic at pH 4.5 (hydrolysis of sulfides) or at pH 3.5 or even 3 (hydrolysis of mercaptans) which also has the following secondary effects:

- Hydrolysis of phenolates into phenolic acids whose supersaturated fraction can be separated by direct settling.
- Destabilization of paraffinic emulsified HC.
- Hydrolysis of naphthenates into naphthenic acids.
- Precipitation of dense polysulfides sometimes.

As a result, two phases are formed: sprung acids and water, or sometimes three (polysulfides or even precipitates of Na_2SO_4).

■ Stripping by steam or a neutral gas.

4.2.1.1 Prewashing of steam cracking spent caustic

Two solutions are possible to remove the HC in emulsion or prevent gum or polymer formation.

■ Spent caustic is washed by hydrogenated gasolines, BTX or toluene which dissolve the preformed gums and polymers or carry off the heavy HC. Washing is performed at the storage tank outlet in a drum:

- Make up from four to six volumes of solvent per volume of spent caustic.
- Settling time around 30 to 60 min (Fig. 44).

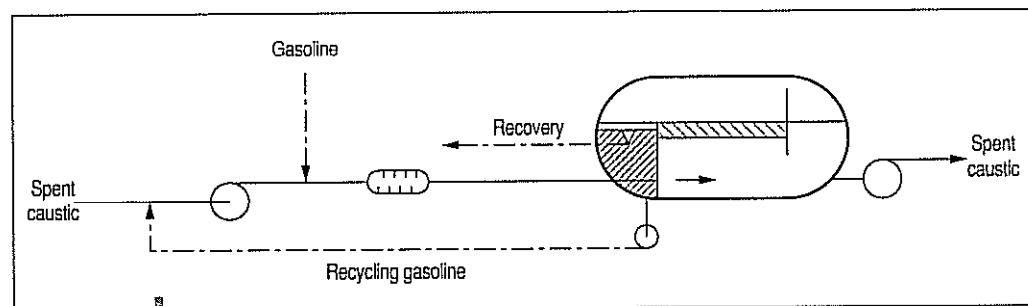


Fig. 44 Pretreatment of steam cracking spent caustic

■ Spent caustic is washed by steam which removes the acetylenic fractions or partially eliminates heavy aromatic fractions. It is effective only as long as it is carried out before the general storage tank, which in itself induces polymerization. This operation is a preliminary stripping process in an alkaline environment:

- Volume load of steam: 20 to 30 volumes per volume per hour.
- Steam consumption from 80 to 100 $\text{kg} \cdot \text{t}^{-1}$ of spent caustic.

4.2.1.2 Acidification

Acidification is characterized by the choice of the reactor and the acid, and the problem of separation by specific gravity.

A. Choosing the reactor

As in any WW neutralization process, the reaction time is very short relatively speaking. Reaction time is mainly defined by the diffusion time of the acid in a viscous environment and by the principle of pH regulation.

It can vary from 6 to 12 min and the reactor must be closed either because harmful gases are released (H_2S and HCN) or because they must be kept in solution by means of high back pressure. The reactor can be:

- Equipped with a blade mixer. Reactor manufacture is constrained by the need to ensure a liquid-tight seal as the shaft passes through a hot corrosive environment.
- Static with internal recirculation by a Turbactor-type hydroinjector. This type of reactor requires an external recirculation pump when flow rates are too low in relation to the internal diameter of the injector (miniaturization). The injector itself must be large enough to prevent plugging. This device recycles from 20 to 25 times the incoming flow.
- An in-line static mixer combined with a residence drum and a recycling pump.

The equipment needs to be protected against the aggressivity of the acid (H_2SO_4 is preferable to HCl), the presence of solvents (BTX) and the temperature (dilution of H_2SO_4 is highly exothermic). The following can be used:

- Hastelloy, Z2CND17-12 or Z1CNDU20-25 in a sulfuric medium.
- Uranus B6 (Z1CNDU20-25), Teflon or furan resin coating in a hydrochloric medium.

The pH regulation should be based on the use of:

- Circulation probes.
- Self-cleaning electrodes (pneumatic or by brush) with a special bridge.

B. Choosing the acid

Generally speaking, concentrated H_2SO_4 is used rather than HCl . H_2SO_4 is more economical in Europe and offers the advantage (although it has other drawbacks) of heating the spent caustic considerably due to its heat of dilution. It can also keep the acidified liquors more concentrated, thereby resulting in more efficient separation of the sprung acids that are released again. It can also be obtained from spent acids from the sulfonation unit, except that they are too dilute.

HCl costs less in North America and is sometimes considered in its 35% commercial form. There is no heating effect but corrosivity is more severe.

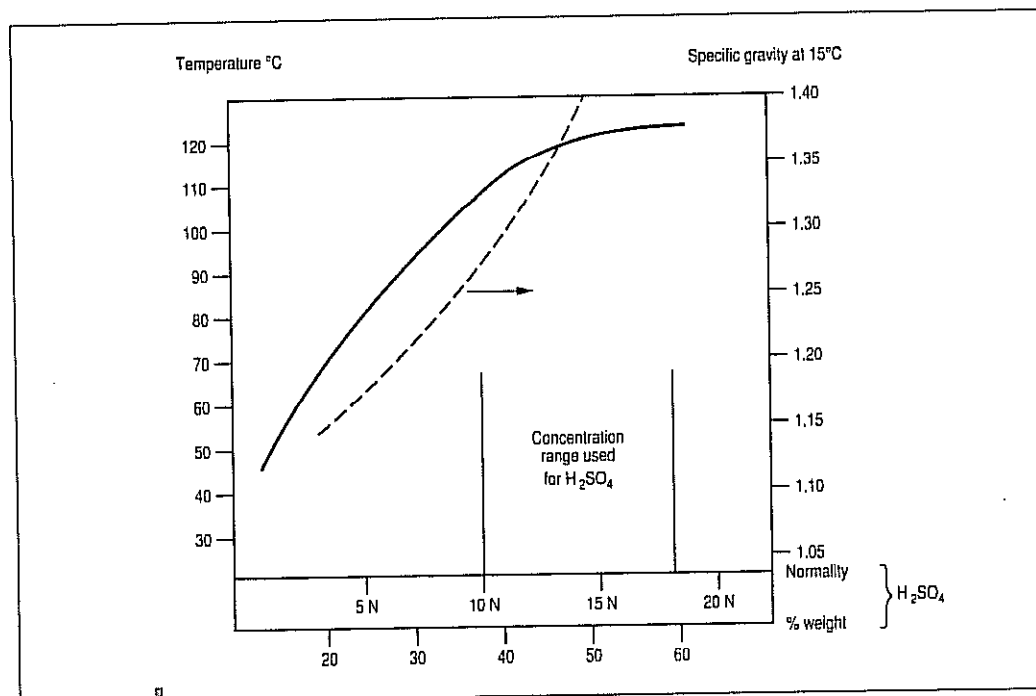
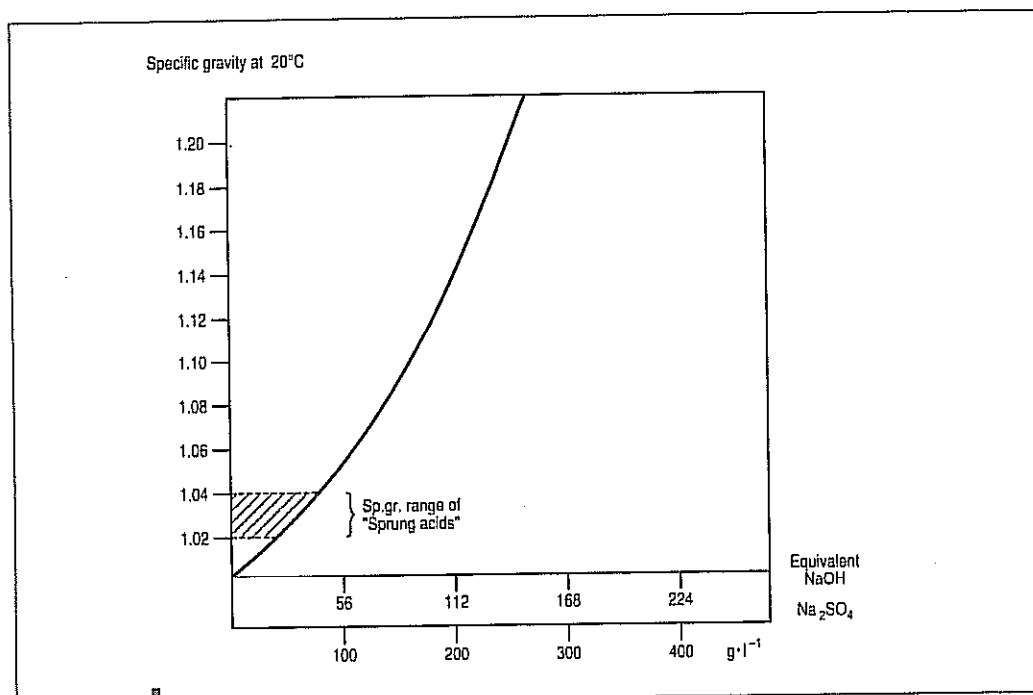
If the choice of the acid arises, it means considering its thermal impact and also the modification in the density of the acidified caustic which becomes a solution of $H_2SO_4 + Na_2SO_4$ or $HCl + NaCl$.

Figure 45 shows the variation in specific gravity of equivalent Na_2SO_4 solutions from 10 N and 18 N sulfuric acid. These extreme concentrations are sometimes used.

As a reminder, spent caustic can contain:

- 1 to 4% of free $NaOH$.
- 10 to 40 $g \cdot l^{-1}$ of total S^{2-} .
- 1 to 30 $g \cdot l^{-1}$ of phenols.

Accordingly 40 to 180 kg of pure H_2SO_4 is required to neutralize a cubic meter of spent caustic. The added sulfuric acid, 10 or 18 N, will therefore dilute the spent caustic by 80-44 liters to 360-200 liters of water.

Fig. 45 Heating and 15°C specific gravity of H_2SO_4 solutionsFig. 46 Specific gravity of Na_2SO_4 solutions

This means that the specific gravity of the acidified spent caustic (Na_2SO_4 solution) will be considerably lowered. It would be lowered even more drastically by a commercial HCl solution.

Acidified spent caustic specific gravity varies from 1.01 to 1.06 whereas sprung acid specific gravity depends on the dominant make up in phenolic acids (sp.gr. from 1.02 to 1.05), in HC (sp.gr. from 0.75 to 0.9) or even in disulfides (sp.gr. from 0.95 to 1.05).

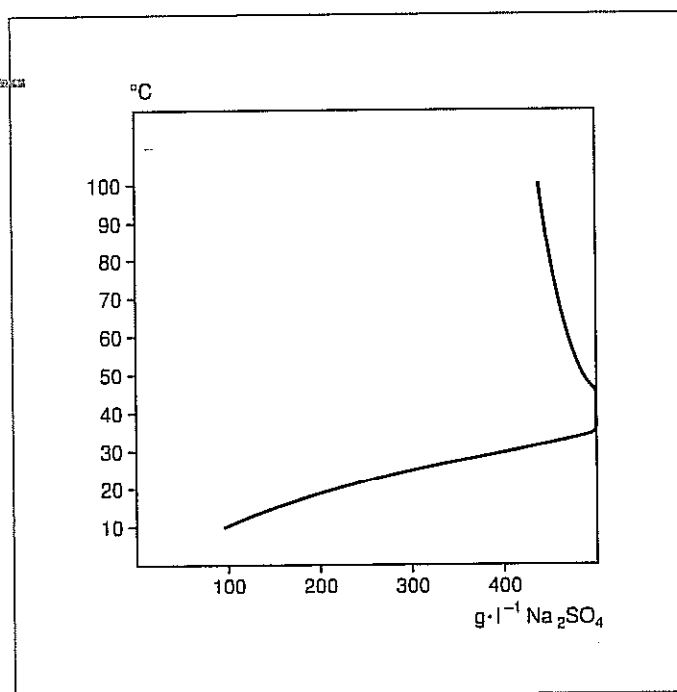
C. Precipitation of Na_2SO_4

Although this risk exists, it is not common. It has occurred during neutralization of very concentrated spent caustic by 20 N acid.

Na_2SO_4 solubility declines with increasing temperature. Above 35°C and according to whether the crystallization form is $7\text{H}_2\text{O}$ or $10\text{H}_2\text{O}$, great differences can be seen in its solubility.

Substantial precipitation can occur, especially in the laboratory if a concentrated acid is used and if it is allowed to cool down (Fig. 47).

Fig. 47
 Na_2SO_4 solubility versus
temperature (Berkeley, 1904)



D. Using spent acids

In sulfonation units, sulfuric acid discharges can in fact be profitably reclaimed if they are relatively concentrated and if they have strong free acidity. However, the fact that they carry considerable associated COD pollution must be remembered. As an illustration, the following example of analysis is presented:

Acidity (H_2SO_4)	47.6%	Thiophenols	0.1%
Phenols	2.7%	Sulfonates (in S)	2.4%

E. Carrying out laboratory tests

Experience shows that the layer of sprung acids forms in 15 min to a few hours and almost always in the upper part of a test tube. This is due to the difference in real specific gravities or to assisted flotation promoted by the amount of H_2S and CO_2 degassing into the atmosphere, something that would not happen in a pressurized vessel.

Sedimentation of viscous black products has been seen (third phase) with very concentrated caustic ($\text{COD } 100 \text{ g}\cdot\text{l}^{-1}$) containing over $10 \text{ g}\cdot\text{l}^{-1}$ of total sulfur. It has been attributed to tars and polymers, but can also be concomitant with the precipitation of Na_2SO_4 , whose saturation is sometimes exceeded (see paragraph 4.2.1.2.D).

Foaming can also be observed. It can be substantial if acidification is fast, but does not hinder the run if acidification is gradual for about fifteen minutes.

Importance of acidification pH

The pH must also be checked during laboratory tests. Though a pH of 4 is sufficient in theory, in fact the lower the pH the better the oil separation (Table 41) and mercaptan hydrolysis (Table 42).

Table 41

Example of the impact of the pH on freeing oils

pH	4	2.5
% of sprung acids	4.5%	6.5%

Table 42

Impact of pH on sulfide and mercaptan stripping

	RSH		S^{2-}
Initial concentrations	$12.4 \text{ g}\cdot\text{l}^{-1}$	$5.7 \text{ g}\cdot\text{l}^{-1}$	$12.9 \text{ g}\cdot\text{l}^{-1}$
Concentration at pH 5 after stripping	$1.7 \text{ g}\cdot\text{l}^{-1}$	$3.8 \text{ g}\cdot\text{l}^{-1}$	$8 \text{ g}\cdot\text{l}^{-1}$
Elimination	84%	34%	92%
Concentration at pH 3 after stripping	$1.2 \text{ g}\cdot\text{l}^{-1}$	$3.3 \text{ g}\cdot\text{l}^{-1}$	$0.5 \text{ g}\cdot\text{l}^{-1}$
Elimination	90%	42%	96%

F. Consumption of sulfuric acid and changes in specific gravity

Consumption corresponds to the following reactions:

- Neutralization of the total free alkalinity, NaOH and Na_2CO_3 .
- Hydrolysis of Na_2S and mercaptans.
- Hydrolysis of phenolic acids.
- Possible liberation of naphthenic acids.

More specifically, it is (as 100% H_2SO_4):

- 1.225 kg of H_2SO_4 per kilogram of free NaOH.
- 3 kg of H_2SO_4 per kilogram of S^{2-} .
- 0.45 kg of H_2SO_4 per kilogram of cresol.

Examples of changing concentrations during neutralization are shown in Table 43 for 10 N acid (sp.gr. = 1.29).

Table 43

Changing concentrations during neutralization of spent caustic

	Example 1	Example 2
Free NaOH	$60 \text{ g}\cdot\text{l}^{-1} = 73.5 \text{ kg } \text{H}_2\text{SO}_4$	$30 \text{ g}\cdot\text{l}^{-1} = 36.75 \text{ kg } \text{H}_2\text{SO}_4$
Total S^{2-}	$20 \text{ g}\cdot\text{l}^{-1} = 60 \text{ kg } \text{H}_2\text{SO}_4$	$5 \text{ g}\cdot\text{l}^{-1} = 15 \text{ kg } \text{H}_2\text{SO}_4$
Equivalent cresol	$5 \text{ g}\cdot\text{l}^{-1} = 2.25 \text{ kg } \text{H}_2\text{SO}_4$	$50 \text{ g}\cdot\text{l}^{-1} = 22.5 \text{ kg } \text{H}_2\text{SO}_4$
Consumption of acid per m^3	135.75	74.25
Kg of Na_2SO_4 formed	196.7	107.6
Sour water input in liters	280	151
Na_2SO_4 concentration	$153 \text{ g}\cdot\text{l}^{-1}$	$93 \text{ g}\cdot\text{l}^{-1}$
Final equivalent specific gravity	1.057	1.028

4.2.1.3 Stripping acidified spent caustic

Stripping is designed to serve two purposes. The first is to remove only H_2S in supersaturation at acidification temperature. The second is to remove almost all the H_2S liberated in order to yield an effluent with a residual S^{2-} value compatible with discharge or with further treatment of the effluent. Depending on the goals, this residual value can vary between 0.05 and $0.5 \text{ g}\cdot\text{l}^{-1}$.

Stripping is located upstream or downstream from the sprung acid separator according to how important efficient separation is.

The carrier gas can be:

- A neutral gas which, after use, is usually flared or redesulfurized.
- Nitrogen in small facilities.
- Air, now being phased out since it requires disposal by controlled combustion and there are explosion risks.

Steam could also be contemplated, but entails a specific combustion unit for condensed vapors.

Stripping is carried out either in compact, packingless flash strippers or in conventional stripping columns. The conventional columns operate with a number of transfer units calculated on the basis of the required efficiency (from 3 to 5 transfer units). When original S^{2-} concentrations are high ($>15 \text{ g}\cdot\text{l}^{-1}$), these two processes are combined.

Figure 48 shows the three possible layouts and typical orders of magnitude of residual concentrations that can be achieved depending on original values.

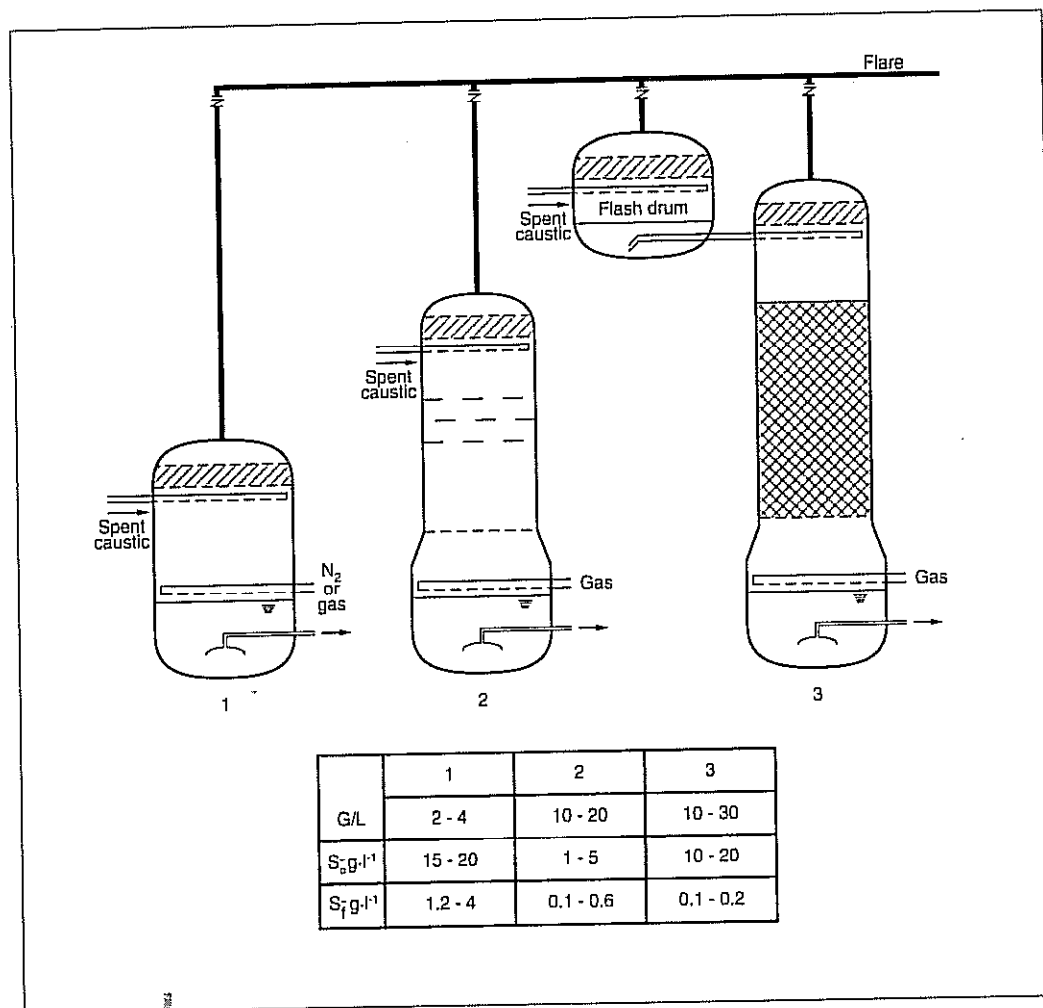


Fig. 48 Spent caustic stripper layout

The flash drum (1) is simply supplied with a "bumper" gas flow for the H_2S in super-saturation.

The stripper (2), equipped with sieve trays or with plastic ring packing (60 mm) and with gas flows of 10 to 20 volumes per volume of spent caustic, can treat most of the spent caustic whose original concentration is lower than 10 g.l^{-1} .

The set-up (3) corresponds to exceptional situations where the total carrier gas flow is deliberately limited.

It should be pointed out that when the technology of the neutralization reactor imposes recycling part of the acidified and degassed spent caustic, the actual flow through the stripper can be one and a half to three times the useful throughput of the facility.

Orders of magnitude for common loads are as follows in relation to the actual spent caustic throughput:

Surface load.....	15 to 40 m ³ ·h ⁻¹
Volume load	10 to 20 space velocity
$\frac{G}{L}$ ratio	10 to 20

4.2.2 Oxidation of spent caustic

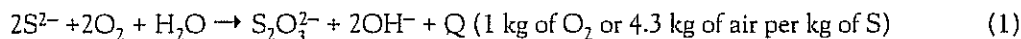
This process involves sulfidic spent caustic more than phenolic spent caustic and comprises the following steps:

- Oxidation with air or oxygen usually limited to the $S_2O_3^{2-}$ stage, seldom extended to the SO_4^{2-} stage.
- Recycling of part of the spent caustic into alkaline scrubbing (preliminary LPG scrubbing) or dilution in the general effluent stream before it goes through physicochemical purification. Another possibility is acidification-neutralization before general biological purification. This process is subject to possible colloidal sulfur precipitation if preventive spent caustic treatments have been incomplete or badly designed and run.

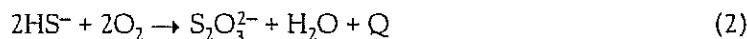
4.2.2.1 Oxidation reactions

The reactions can be as follows:

- Oxidation of S^{2-} into thiosulfates:

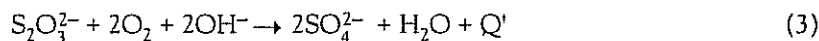


- Oxidation of HS^- :

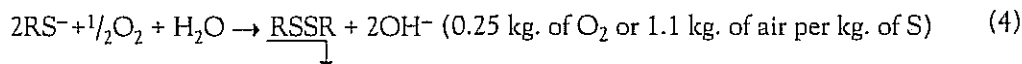


Q, the heat of reaction is 3.4 th·kg⁻¹ of S.

- Oxidation into sulfates:



- Oxidation of mercaptans:



which is balanced by parallel hydrolysis of mercaptans:



Hydrolysis keeps a fairly significant fraction of volatile mercaptans in solution that could otherwise be carried off by the oxidation air. This must be taken into account in the operation of cocurrent oxidation towers.

Almost all the reactions are exothermic and therefore raise the temperature of the spent caustic and of the spent air which is saturated in steam.

Reaction (1) liberates 50% of the caustic bonded to the sulfides and reaction (4) liberates 100%.

The kinetics of reaction (1) are fairly fast and first order according to an example given by API (Fig. 49).

The kinetics of reaction (3) are very slow and under atmospheric pressure it may require almost ten times longer than for oxidation into $S_2O_3^{2-}$. As a result, reactors cost more due to oversized design.

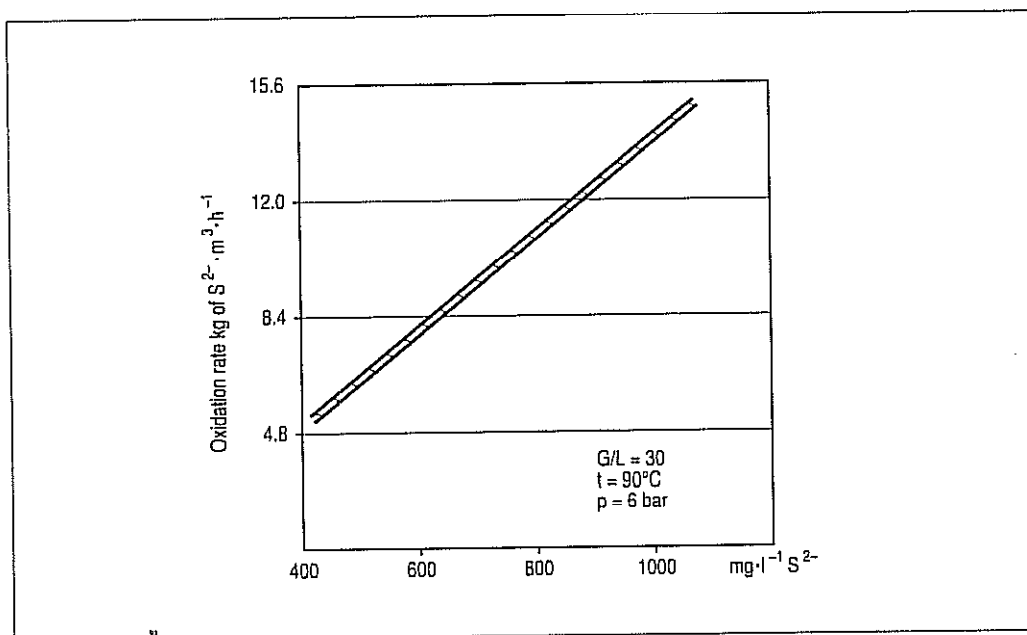


Fig. 49 Oxidation rate of S^{2-} into $S_2O_3^{2-}$ in pressurized reactors (After API, Liquid Waste, Chap. 11, 1969)

4.2.2.2 Impact of the reactions on the COD and the general chemical balance

The COD reduction when oxidation is limited to $S_2O_3^{2-}$ involves 50% of the sulfide-related COD. Only oxidation to SO_4^{2-} would give roughly the same COD reduction as acid hydrolysis followed by stripping, independently of any organic compound volatilization.

Since mercaptan oxidation is not complete, it also limits the COD reduction. This is independent of any possible transfer of a fraction of volatile mercaptans into the air gaseous phase.

Acid consumption in the assumption of a final neutralization step is not insignificant, since it is defined by the initial free caustic plus the released caustic (and initial Na_2CO_3).

Accordingly, in comparison with the direct acidification of $1 m^3 \cdot h^{-1}$ of spent caustic with 6% free NaOH, $5 g \cdot l^{-1}$ of S^{2-} and $12 g \cdot l^{-1}$ of S-RSH, the respective H_2SO_4 consumptions are still 81 kg after oxidation and 106 kg for direct neutralization. This is notwithstanding the overconsumption in order to lower the pH from 7 to 4 in the second case.

This puts the oxidation process at a disadvantage, especially if the expenditures on reagents are compared to the COD reduction achieved. The only thing that makes the oxidation process advantageous is if the oxidized spent caustic can be recycled to preliminary scrubbing or if it can be diluted without neutralizing it with a high general effluent flow rate. In the second hypothesis, however, care must be taken not to develop spontaneous uncontrolled softening of the general effluent with CaCO_3 precipitation and scaling.

Therefore, savings achieved in comparison with neutralization are only 15 to 25% depending on the relative $\text{S}^{2-}/\text{RS}^-$ concentration.

4.2.2.3 Pressurized reactors (oxidizers)

A. With air

These reactors were the first ones used and are still today a fairly common way of carrying out oxidation in refineries. In contrast, replacing air with oxygen is much more recent.

With the $\text{S}_2\text{O}_3^{2-}$ stage as the limit, cocurrent oxidation towers in the United States are often designed for the following conditions:

- 150 to 200% excess air.
- $\frac{G}{L}$ ratios of 30 to 100.
- Residence time of 1 to 2 hours.
- Pressures of 5 to 8 bar and temperatures from 65 to 90°C.
- Oxidation rate of 5 to 8 kg of S^{2-} per hour and per cubic meter of reactor.

There is no addition of catalyst, but steam make up instead to hold the temperature to the required level.

Oxidation to the SO_4^{2-} stage is seldom carried out completely, but when it is the following conditions prevail in pressurized reactors:

- Countercurrent reactors.
- Excess air from 150 to 250%.
- Residence times of three to four hours, but the specific oxidation rate of S^{2-} into SO_4^{2-} per cubic meter of reactor could be much lower: 0.2 to 0.8 kg of S^{2-} .

API (Liquid Waste, 1969, Chapter 11, Section 1.7) gives a design example for a cocurrent column, with the same aim of reaching only $\text{S}_2\text{O}_3^{2-}$ (Fig. 50):

Spent caustic flow rate	40 $\text{m}^3 \cdot \text{h}^{-1}$
Air flow rate	2250 Std $\text{m}^3 \cdot \text{h}^{-1}$
Temperature	92°C
Pressure	6 bar
Reactor volume	53 m^3
Head losses	0.8 bar
Residence time	80 min
Excess air	100%
Initial S^{2-} concentration	8 $\text{g} \cdot \text{l}^{-1}$
S^{2-} oxidation rate per m^3 of reactor	6 $\text{kg} \cdot \text{h}^{-1}$

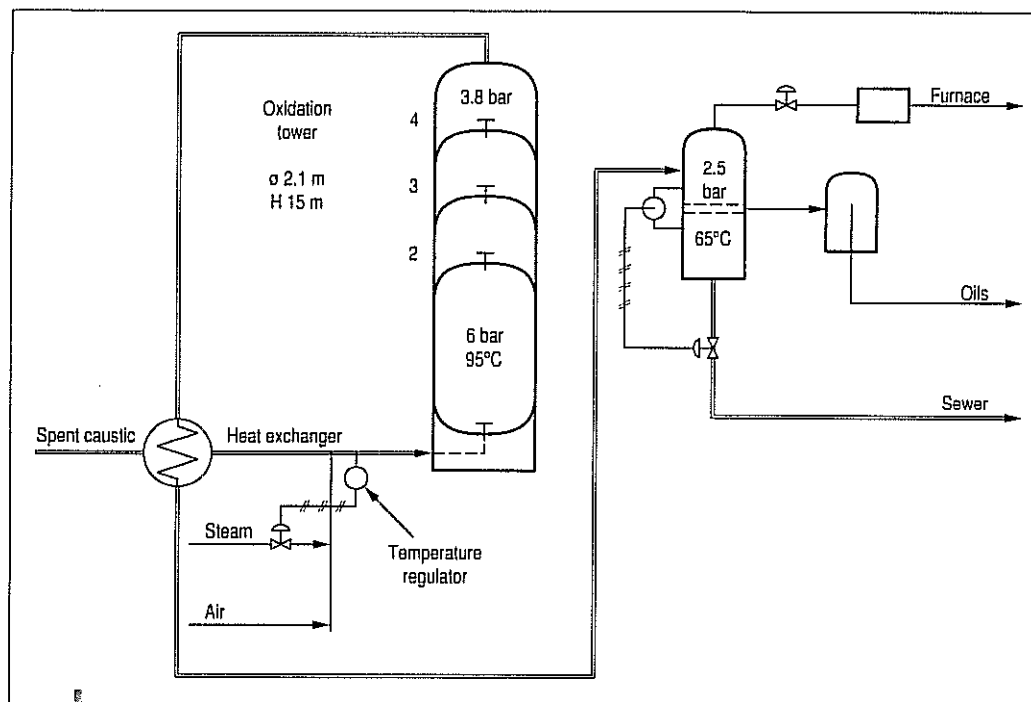


Fig. 50 API example of a layout with a pressurized oxidizer (API -Liquid Waste, 1969)

B. With oxygen

Liquid oxygen conveniently available near the reactor makes it more advantageous to use as an oxidizing agent than air and widens the scope of oxidation under pressure. Spent caustic oxidation units have been set up on the following basis:

- Stripping of aromatic HC by nitrogen and combustion of the residual gas in a burner.
- Oxidation of spent caustic by O_2 in a reactor with a thermostated jacket keeping the temperature at 70°C or 110°C under a pressure of 9 to 10 bar.
- Mixing and dissolution of oxygen by a multibladed mixer.

Depending on temperature and residence time conditions, oxidation can be total for sulfides or partial for phenols as shown in the two examples below (Table 44).

Table 44

Oxidation reactors using pure oxygen

	Sulfidic caustic (FCC)	Phenolic caustic (FCC)
Pressure	10 bar	10 bar
Temperature	70°C	$100-110^\circ\text{C}$
Residence time	1 hour	6 hours
Efficiency:		
S^{2-} ($\text{g}\cdot\text{l}^{-1}$)	$3-5 \rightarrow 0$	$2-3 \rightarrow 0$
RSH ($\text{g}\cdot\text{l}^{-1}$)	$8-20 \rightarrow 0.5-2$	$5-6 \rightarrow 0$
Phenols ($\text{g}\cdot\text{l}^{-1}$)	$1-5 \rightarrow 1-5$	$20-30 \rightarrow 6-8$

4.2.2.4 Atmospheric pressure reactors

This type of reactor has developed more recently. In Europe, the first examples of implementation were designed for tannery and kraft paper pulp water, i.e. less concentrated in S^{2-} than spent caustic. Operation at atmospheric pressure and at the only temperature allowed by the exothermic nature of the reactions naturally defines longer reaction times. However, the oxidation tanks built for this type of process are less sensitive to the maintenance and corrosion problems which may affect reactors working at high temperature and pressure.

Because of the low pressures (0.4 to 0.6 bar) and temperatures (20 to 50°C), oxidation kinetics are slow and limited by the oxygen transfer velocity. The orders of magnitude for operating the tanks, which are limited to a water depth of 5 m and to blowered air flows of 100 Std $m^3 \cdot h^{-1}$ per square meter, are as follows:

- Oxidation rate of 0.3 to 0.6 kg of S^{2-} per cubic meter of tank and per hour for temperatures rising from 20 to 50°C.
- Air make up from 40 to 80 times stoichiometry.
- Residence times of 18 to 85 hours for initial S^{2-} concentrations of 10 to 30 $g \cdot l^{-1}$.

The equipment of these facilities comprises:

- Possible washing with gasoline or BTX if the spent caustic comes from the SC.
- A closed integral mixture tank fitted with:
 - A device to disperse large bubbles of air and a electrically-powered blowered air unit for 0.4 to 0.6 bar.
 - Possibly an outside supply of calories by circulation bubbling of steam to keep the temperature steady.
 - Possibly a mechanical mixing device.
- A drift separator on the polluted air stream to be treated.
- Addition of an antifoaming agent.

As for pressurized reactors, no provision has to be made for adding a catalyst since the spent caustic almost always contains enough metallic oxides of iron, nickel or cobalt to achieve expected oxidation kinetics.

4.3 Removing phenols from spent caustic

Depending on local conditions, phenol removal can be carried out in two main ways:

- Aerobic biological purification, in all cases after H_2S stripping, then dilution in the general refinery effluents, or (seldom) in cooling water. This is the most economical and widespread way.
- Extraction by solvents.

4.3.1 Solvent extraction

This technique has often been used to treat ammonia water from coking processes or even from coal gasification processes. In these processes, phenol production flows are very high and concentrations are at least 3 $g \cdot l^{-1}$. The aim is to reclaim and market cresylic acids. The technique is too expensive because the solvent must necessarily be regenerated (solvent stripping).

As a result, it has been phased out in coking plants, but nevertheless remains feasible in refineries because the solvent, a light fuel oil of the LCO type, is used in much smaller volumes and sent back to the refinery FO network in an open system without regeneration. This cuts investments by two-thirds. Typical LCO flow rates in refineries vary from 1 to 16 m³·h⁻¹, whereas they are at least five times higher in coking plants.

The advantage of the extraction process is that it is compact, does not consume significant amounts of energy or reagents and does not produce sludge. The investment in the extraction system alone has to be considered. The economics are favorable unless there is already a biological purification unit treating a general BOD₅ load on the site, or unless such a unit is necessary to treat other effluents.

4.3.1.1 Principle

Solvent extraction is a physicochemical process whereby dissolved phenolic compounds are distributed into two liquid phases, the solvent (D) and the water (A), according to their relative solubility.

The essential parameter in designing extractions is the distribution coefficient K_D which expresses the ratio:

$$K_D = \frac{\text{Phenols concentration in the liquid solvent phase}}{\text{Phenols concentration in the liquid water phase}}$$

This factor can be defined for slightly ionized phenol dispersions, i.e. at pH values under 8. If the phenols are ionized, an apparent coefficient K_A is measured such that:

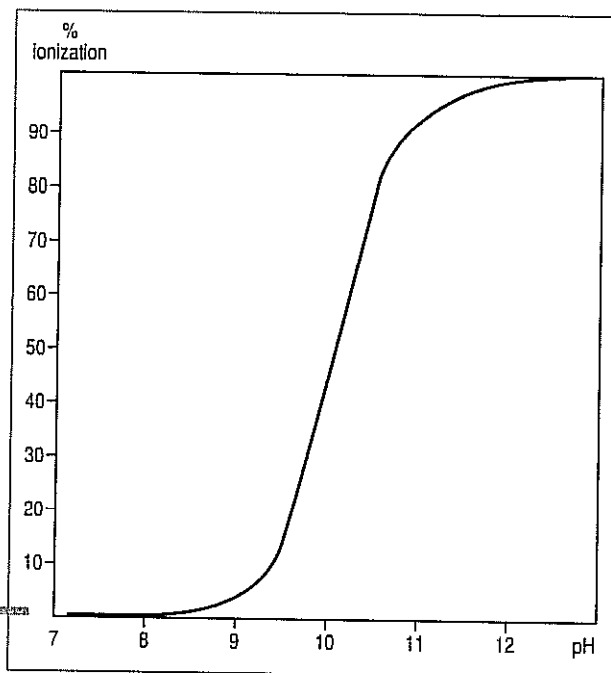
$$K_A = \frac{[\text{Phenols in the solvent}]}{[\text{Phenols in the water}] + [\text{Ionized phenols}]}$$

The relationship between the two coefficients depends on the ionization constant K_i of phenols in water and on the pH as expressed in the equation established by Beychok (Aqueous Wastes from Petroleum Plants, Wiley, 1967):

$$\frac{K_A}{K_D} = \frac{1}{1 + K_i \cdot 10^{\text{pH}}} \quad \text{for monohy-}$$

dric phenols. It shows the need to work at low pH, even more so since the lower the pH the better the separation of sprung acids and naphthenic acids. Prior acidification is, as mentioned before, combined with desulfurization by stripping which should precede any and all extraction (Fig. 51).

Fig. 51
Dissociation of phenolic acid



In practice, depending on the solvent the following K_D can be considered close to neutrality at 40°C:

	Phenols	Cresols	Xylenols
BTX	2.3 to 2.7	4 to 8	6 to 10
LCO	1.3 to 1.5	2 to 4	
Cyclohexane	1 to 3	3 to 5	5 to 8
Paraffins	0.4 to 1	1 to 2	3 to 5

4.3.1.2 Choosing the solvent

Despite their favorable K_D , BTX are not suitable because of their overly high solubility in water, which can also limit their use in removing gums from spent caustic before stripping.

Paraffinic HC have an unfavorable K_D which, however, allows crude desalters to be considered as excellent phenol extractors. This function has been used to remove phenols from spent caustic recycled to the desalter inlet, but has been almost totally phased out. This practice is dangerous for two reasons:

- The extra alkalinity is harmful for desalter and overhead drum anticorrosion properties as the alkalinity level is kept too high.
- The extra Na salts require desalting capacity to be boosted.

Accordingly, recycling $1.5 \text{ t}\cdot\text{h}^{-1}$ of spent caustic containing 6 to $15 \text{ g}\cdot\text{l}^{-1}$ of phenols and salinity of $100 \text{ g}\cdot\text{l}^{-1}$ in a $1\,000 \text{ t}\cdot\text{h}^{-1}$ desalter containing 30 to $50 \text{ mg}\cdot\text{l}^{-1}$ of salts:

- Eliminates 80% of the phenols.
- But increases the desalting capacity by $150 \text{ kg}\cdot\text{h}^{-1}$.

Light cycle oil (LCO) an intermediate cut representing 15 to 20% of FCC production, has the following properties:

- Specific gravity at 15°C: 0.94 to 0.96
- Aromatics content: 50 to 83%
- Dynamic viscosity $\begin{cases} 20^\circ\text{C}: 5 \text{ cP} \\ 40^\circ\text{C}: 2.2 \text{ to } 2.9 \text{ cP} \\ 60^\circ\text{C}: 2.4 \text{ to } 3 \text{ cP} \end{cases}$

- Phenol content: 150 to 175 ppm.

The advantage of LCO is its own low phenol content which is lower than 200 ppm. This is possible because phenols are preferentially carried over to fractionation by the main naphtha stream.

Its surface tension is about $23 \text{ dyn}\cdot\text{cm}^{-1}$ and has the advantage of being constant between 30 and 50°C.

However, recent improvements in FCC efficiency have modified the specific gravity and aromatics content of LCO which may as a result become less favorable for extraction.

4.3.1.3 Impact of pH and temperature

Keeping a sufficient K_D requires a pH lower than 7, but it is necessary to operate at an even lower level to completely desulfurize and decrease the solubility of phenolic oils.

The substantial reduction in COD is due to natural H_2S degassing in supersaturation. Solvent extractions can be carried out at pH values between 6 and 3.

pH	11	5.5	4
Phenols ($\text{g}\cdot\text{l}^{-1}$)	31	10.8	9.8
COD after settling ($\text{g}\cdot\text{l}^{-1}$)	100	49	48
Phenol removal efficiency (%)	—	65	70

Raising the temperature from 40 to 60°C can lower the K_D from 1.35 to 0.9. It is therefore not favorable, in any case, no more so than to the separation of phenolic oils.

Solvent/spent caustic ratio

The ratio depends on extractor design and on the initial phenol concentration in the spent caustic. To achieve the same efficiency of 75% in one stage, it may be necessary to use:

- 1 volume.volume⁻¹ with 40 g·l⁻¹ of phenol.
- 3 volumes.volume⁻¹ with 10 g·l⁻¹ of phenol.
- 6 volumes.volume⁻¹ with 1 g·l⁻¹ of phenol.

Using a four-stage system with parallel solvent currents would require a ratio of 6 to 8 to treat spent caustic with 80 g·l⁻¹ of phenols. However, using a countercurrent can cut this ratio to one (Fig. 52).

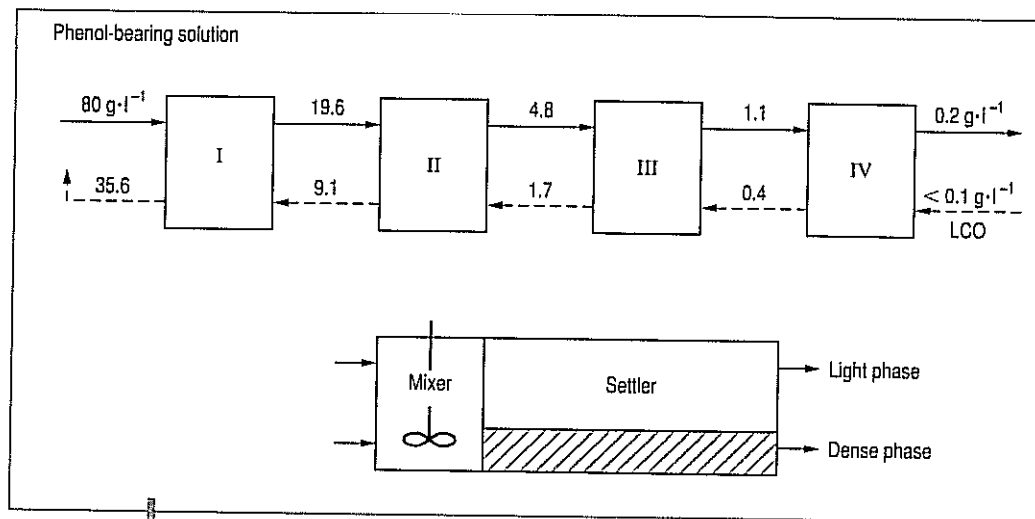


Fig. 52 Extraction of a solution with 80 g·l⁻¹ of phenols by four-stage countercurrent mixer-settlers

4.3.1.4 Implementation

Several techniques can be contemplated.

A. Mixer-settlers

These units comprise a series of extractions. A simple extraction process is made up of two operations:

- Integral mixing of the two liquid phases so that the solute can migrate to its equilibrium concentration from the rich phase to the poor phase.
- Separation of the two phases by settling then draw-off.

The treatment stage therefore includes a mixer and a settler and extracts 50 to 60% of the phenols in spent caustic treatment. To reach the rates of 90 to 96% that may be required, there must be three or four stages with feed input countercurrent to the two phases.

Spent caustic facilities have been built with these units whose negative features are their size, the required electric power and the maintenance of circulating pumps.

The units lend themselves to slow kinetics and phases exhibiting fairly narrow differences in specific gravity (between 0.10 and 0.20). For difficult dispersions, a single unit can correspond to three or four theoretical transfer stages. In the present application the following orders of magnitude can be considered:

- Mixers: 20 to 30 min residence time.
- Settlers: loads of 4 to 5 cubic meters per square meter per hour.

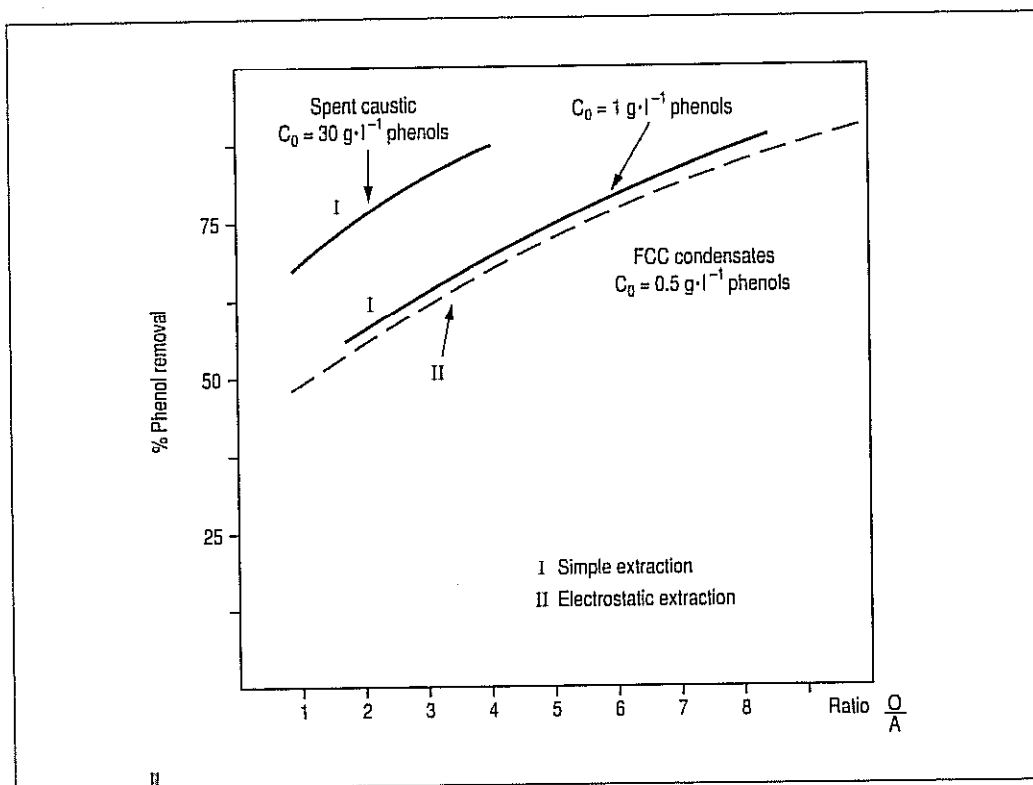


Fig. 53 Impact of the O/A ratio on phenol removal (one stage)

B. Pulsed columns

These columns perform countercurrent circulation by gravity of the two nonmiscible liquid phases of different specific gravity. The heavy phase, which is spent caustic in the beginning, enters in the top and the solvent, in this case LCO, enters in the bottom. The aqueous phase is dispersed in tiny droplets.

Compared to mixer-settlers, pulsed columns offer the following advantages:

- Units are compact and group the n stages necessary inside one single enclosure.
- There is no intermediate pumping and power requirements are four to five times lower.
- Residence time is very short so after shutdown around an hour is needed to bring the system back into equilibrium.
- There are few constraints on shutdown for cleaning.

However, the columns require minimum solute transfer kinetics, which is true for phenols. The difference in specific gravity between the solvent and the aqueous phase must, however, be greater, at least 0.15, because of the high circulating velocities.

The columns comprise (Fig. 54):

- A vertical vessel or shell which serves as the contact zone for the two phases. It is fitted with plates (sieve, disc or fin). Pulsation agitates the zone periodically and keeps the dispersion in tiny droplets.
- An upper settler to separate the light phase and inlet the heavy aqueous phase after agitation has ceased.
- A lower settler to coalesce the dispersed aqueous phase and separate the two phases completely before the aqueous phase is drained off the bottom. The settler is connected to a pulsator leg which accommodates the light phase and is equipped with a compressed air pulsation valve. The pulsation generates the energy needed to disperse the two phases.

Increased retention rate or volume ratio $\frac{A}{O+A}$ increases

the exchange area and thereby the efficiency. However, the rate is limited by the fact that the column gets blocked or that the dispersed phase (here A) accumulates too much in the vessel at the top of the column.

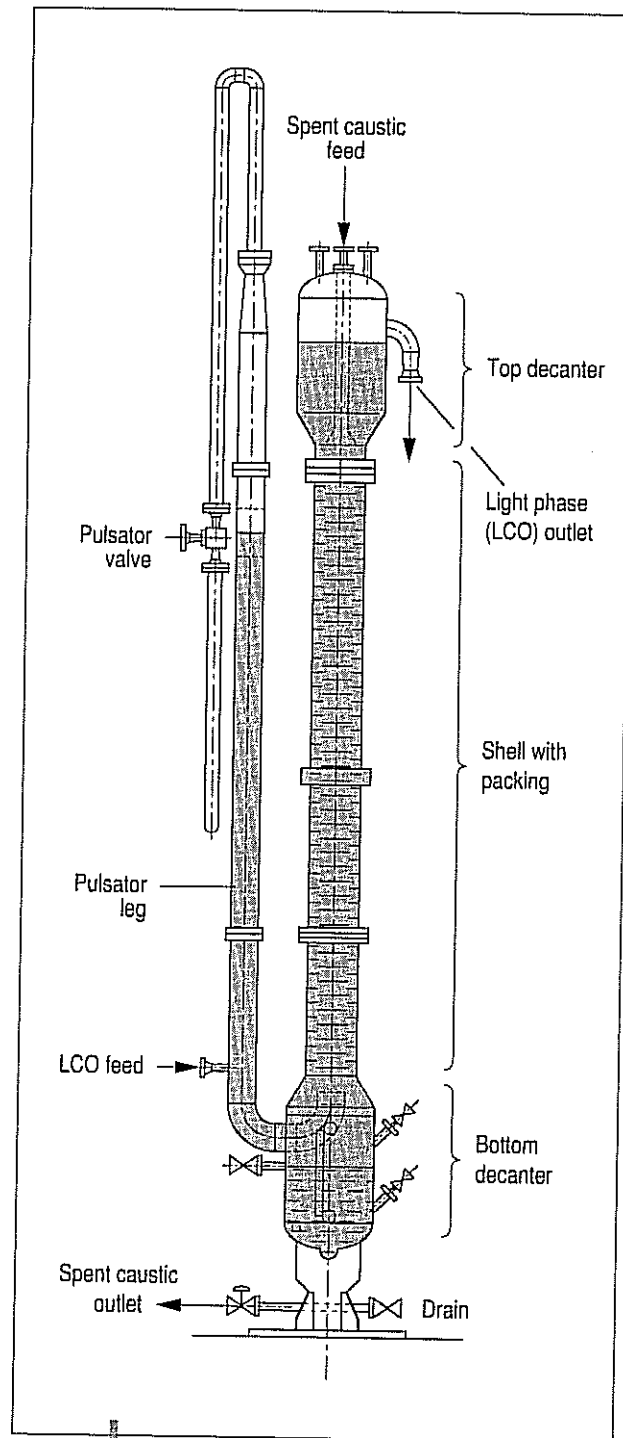


Fig. 54 Eries pulsed column

The sizing parameters are mainly:

- The extraction factor or the product $K_D \cdot \frac{O \text{ (Flow of continuous phase)}}{A \text{ (Flow of the dispersed phase)}}$
- The ratio $\frac{C_o}{C_N} = \frac{\text{Concentration in phenols in the feed}}{\text{Concentration in phenols in the draw-off}}$

The number n of theoretical stages required is dependent on $\frac{O}{A}$ for a given $\frac{C_o}{C_N}$ ratio and a reduction in phenol concentration of 12 to $0.5 \text{ g} \cdot \text{l}^{-1}$:

If $Q = 2 \text{ m}^3 \cdot \text{h}^{-1}$

$\frac{O}{A}$	1	1.5	2
Number of theoretical stages	7.3	3.8	2.9
Column diameter (mm)	480	540	640
Height (m)	10	4.6	3.6

Transfer velocities are calculated on the basis of the "total specific flow rate" which is the sum of the flow rates of the two phases per unit of cross-sectional area. They can vary between 20 and $30 \text{ m}^3 \cdot \text{h}^{-1}$ per square meter in pulsed columns. Fig. 55 shows the phenol removal facility equipped with a Turbactor reactor and an Eries pulsed column for the Lindsey refinery (Great Britain).

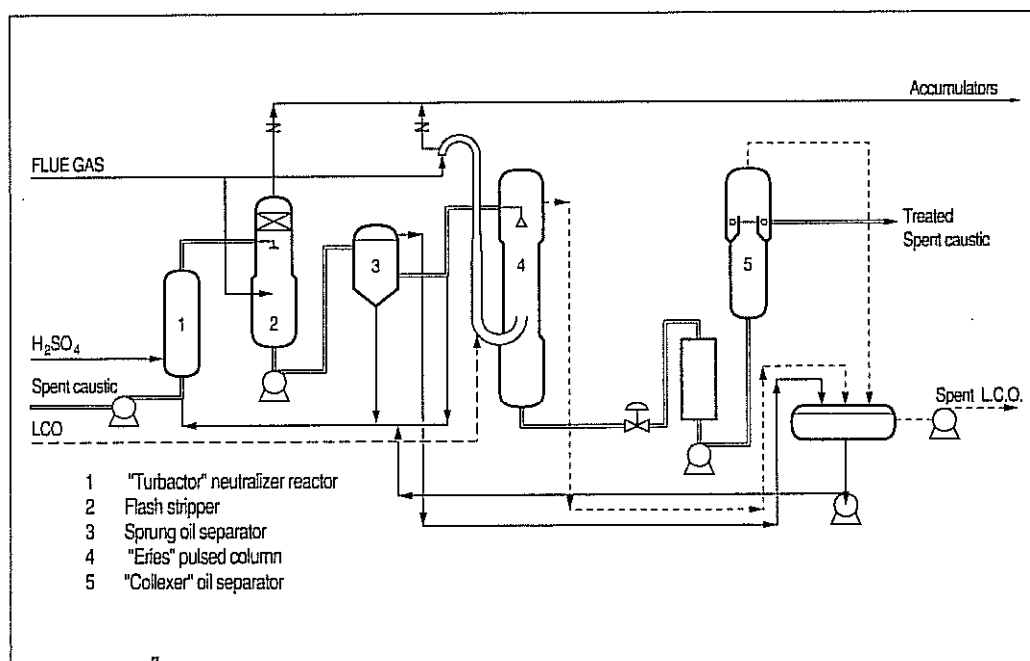


Fig. 55 Flow scheme of the Lindsey refinery (Hydrocarbon Processing, 1987)

The plant treats $0.5 \text{ t}\cdot\text{h}^{-1}$ of spent caustic whose initial phenol content of $12 \text{ g}\cdot\text{l}^{-1}$ is cut to less than $1 \text{ g}\cdot\text{l}^{-1}$ (values obtained from 0.15 to $0.5 \text{ g}\cdot\text{l}^{-1}$). The LCO used in the process has a specific gravity of 0.92 to 0.95 and a dynamic viscosity of 2.1 to 2.9 cP at 40°C .

Operating pulsed columns

Sensitive points can be:

- Irregular LCO quality, e.g. the specific gravity can get too high. This makes separation slower or its temperature cooler, and as a result it is more difficult to emulsify the dispersed phase.
- An increase in the operating temperature decreases the viscosity of the continuous phase and allows tinier droplets to be separated. In other words, their overall area and retention rate are enhanced. Finally, operation at higher temperature can be favorable.
- Too large a difference in temperature between the two phases can create thermal convection currents while lowering the retention rate. This must be prevented by controlling the temperature of LCO which is much more sensitive (temperature and specific gravity) than the aqueous phase stored in huge surge tanks.
- A floc can be precipitated after the spent caustic has been in contact with the solvent. This must be prevented by finer filtration of the spent caustic before acidification.

C. Extractors with electric fields

This technique was developed under the name Phenex (Humble Oil and Refining Co., Baton Rouge) and was designed to deal with catalytic cracking condensates which only contain from 400 to $800 \text{ mg}\cdot\text{l}^{-1}$ of phenols, rather than spent caustic.

In order to extract the phenols with sufficient efficiency despite the low initial concentration, a $20,000$ to $40,000$ volt electrostatic field is applied. This disperses the water droplets after they have been mixed with LCO in a butterfly valve under a head loss of 0.15 to 0.30 bar . The extractor is built somewhat like a desalter.

Figure 53 shows the advantages of simple extraction for spent caustic alone, which is much more concentrated than cracking condensates.

D. Centrifuge extractors

For low flow rates ($<0.5 \text{ m}^3\cdot\text{h}^{-1}$), these compact devices would seem to be more competitive than pulsed columns.

For an $\frac{O}{A}$ ratio of 1.5 , they can correspond to four theoretical stages and remove 95% of the phenols from spent caustic containing $20 \text{ g}\cdot\text{l}^{-1}$.

They can also be adapted to treat difficult dispersions with as many as eight or nine theoretical stages.

4.3.2 Aerobic biological purification

Phenolic compounds are known to be perfectly biodegradable as long as their concentration is not extremely variable and there are no coexisting toxic compounds (particularly S^{2-}).

Spent caustic can therefore be sent to aerobic biological purification after having undergone desulfurization by stripping or by air oxidation and after having been neutralized.

In the first case, S^{2-} and RSH have been sufficiently eliminated.

In the second case, they have been transformed into thiosulfates which means their own potential BOD_5 of 0.57 mg per milligram of $S_2O_3^{2-}$. This BOD_5 must be added to that of the phenols, since in most activated sludge purification processes thiosulfates are oxidized into sulfates.

At the inlet to the biological purification step, the pH must therefore be kept between 6.5 and 9 and the temperature between 15 and 30°C.

A certain degree of dilution must also be provided for two reasons:

- To bring the phenol content down to less than $0.5 \text{ g} \cdot \text{l}^{-1}$ if necessary.
- To keep the total salinity of the environment below 15 to 20 $\text{g} \cdot \text{l}^{-1}$. Above these values the osmotic pressure of the environment may become unfavorable to the quality of the biological floc.

Dilution is generally due simply to mixture with process condensates (among them FCC condensates) which themselves exhibit low BOD_5 and salinity values and are fairly rich in NH_4 .

If dilution occurs by clean water instead of WW, the water can be relatively sterile and an initial seeding step is required before start up. NH_4 and PO_4^{3-} must be added continuously.

The salts ($NaSO_4$) added by the spent caustic are obviously unfavorable to recycling purified water after tertiary treatment.

Treatment of petrochemical plant effluents

Chapter

5

Two main petrochemical plant processes are involved:

- Steam cracking of naphtha or gas oil with production of ethylene, propylene, butadiene, styrene, then polymers and rubbers, etc.
- Catalytic reforming of naphtha for production of aromatics, then phenols, nylons, anionic detergents, etc.

These activities are derived directly from the refining industry. The study of refining effluents already includes steam cracking discharges which are very similar.

But in their diverse and numerous production streams petrochemical plants often generate specific discharges. Their original features will be discussed and a few examples of relevant flow schemes will be given.

5.1 Original features of petrochemical plant effluents

The similarities between refining and petrochemical plant effluents that can justify common aspects in treatment are:

- Primarily organic pollution with HC in the three states of dispersion in water.
- Less commonly, presence of phenols, sulfides or their intermediate oxidation products.

In fact, particular parameters are involved. They can modify the treatability of effluents and require specific preliminary treatments or treatment layouts other than those used in refining.

These parameters can include:

- Irregular discharges coming sporadically from relatively short production runs. These can cause acclimatization hazards for the activated sludge bacterial mass.
- The lack of N and especially P nutrients in the effluents, except for production streams such as urea and acrylonitrile or reactions using amines or NH_4^+ (e.g. alkylation).
- Higher flow rates than in refineries, due to the considerable size of complexes rather than to the diversity of production streams. As a matter of fact, petrochemical plants have already succeeded in making drastic cuts in water consumption.
- Frequent high salinity levels as a result of certain processes (alkylation, latex copolymerization, chlorohydrin process, etc.). Salinity can range from 5 to 25 $\text{g}\cdot\text{l}^{-1}$ of NaCl- base, CaCl_2 -base or less often NH_4Cl -base salts. Salinity is lowered if effluents are mixed 50% with cooling blowdown water (salinity from 0.6 to 3 $\text{g}\cdot\text{l}^{-1}$) ahead of general biological purification.

■ The presence of chlorinated compounds due to certain synthesis processes (PVC, caprolactame, acetone, acetaldehyde).

■ Often high temperatures (40 to 60 °C) that require waste water to be cooled down before biological purification if not before DAF. BOD₅ concentration and exothermic oxidation of some compounds can also cause spontaneous heating of the water in activated sludge tanks. This in turn can even cause a certain slowdown in biological activity. In winter in Central Europe, despite a residence time of over 24 hours, an outside temperature of -15°C only made the apparent temperature fall by less than 10°C in a biological purification unit.

During oxidation of alcohols defining BOD₅ values of around 1.5 mg·mg⁻¹ with a concentration of 1 000 mg·l⁻¹ of BOD₅, the exothermic nature of the oxidation reaction can contribute an input of 4 to 5 thermies per cubic meter.

For such BOD₅ levels, biological purification can be self-limiting in summer, especially if it is carried out in deep tanks with small blowered air bubbles. In contrast, surface aerators (turbines) can provide quite significant cooling effects.

■ The $\frac{\text{COD}}{\text{BOD}_5}$ ratio, measured after physicochemical purification of course and therefore characterizing only dissolved organic pollution, is also more variable than in refineries and more difficult to interpret. A substantial COD fraction may be nonbiodegradable. On the other hand the BOD₅ is often underestimated if measurements are not made with seeding with sufficiently aged and, especially, acclimatized sludge. In refineries, relatively high ratios of three to two for a BOD₅ range of 50 to 300 mg·l⁻¹ can come from subsisting intermediate products generated by the oxidation of sulfides or aromatic HC. In petrochemical plants, when the discharges from a number of units together determine a BOD₅ of more than 400 mg·l⁻¹ in the general effluent after physicochemical purification, the $\frac{\text{COD}}{\text{BOD}_5}$ ratio can range between only 1.4 and 1.75. It becomes five to seven after biological purification, with residual COD values located often between 100 and 200 mg·l⁻¹.

■ Certain petrochemical plant effluents, especially in polymer production, are low in dissolved pollution and loaded with SS and HC. In contrast, when solvent or alcohol processes are involved, or when sophisticated products and additives for the pharmaceutical industry are manufactured, the dissolved BOD₅ becomes the main pollution fraction and can reach 500 to 1500 mg·l⁻¹.

■ The volatility of pollutants must also be taken into account so as to prevent pollution transfer to the atmosphere during biological purification. Whenever there are considerable concentrations in volatile solvents, whether biodegradable (IPA, IPE, MEK) or not (chlorinated solvents), it is advisable to strip the rich effluents at their point of origin or to detect their concentration and send them off to storage and possible recovery treatment.

5.2 The concept of "toxic pollutants"

The wide variety of petrochemical production processes and related intermediate reactions release organic pollutants into water that can have common precursors. In the United States the EPA (Environmental Protection Authority) published a list in Env. Sc. Techn.

Vol. 15, No. 4, in November, 1981, of almost 130 "potentially toxic" compounds in the effluents of 40 petrochemical complexes. Eliminating these "priority pollutants", as they were termed, was the subject of particular recommendations advising the use of the "best available technology". This is one reason why specific pollutant breakdown techniques were developed. They mainly use strong oxidizing agents (H_2O_2), wet air oxidation (often in preliminary treatment) and adsorption on activated carbon in polishing (granular activated carbon, GAC) or associated with activated sludge (powdered activated carbon, PAC).

Table 45 gives a list of common priority pollutants. Some of them must now also be eliminated in a number of European countries (e.g. polyaromatic hydrocarbons in Scandinavia) and may threaten potable water sources.

Table 45

Main "priority pollutants" in petrochemical plant effluents

- Organochlorinated compounds (C_2 to C_5)
- Aromatic compounds (benzene, toluene, ethylbenzene)
- Polyaromatic hydrocarbons (PAH)
 - Benzo-3,4 pyrene
 - Benzo-11,12 fluoranthene
 - Benzo-1,12 perylene
 - Benzo-3,4 fluoranthene
 - Fluorene
 - Acenaphthene
 - Acenaphthylene
 - Anthracene
 - Naphthalene
 - Phenanthrene
- Nitrosamines and nitroaromatics
- Phenols, nitrophenols and chlorophenols
- Heavy metals (Sb, Be, Cd, Cu, Cr, Pb, Hg, Ni, Se, Ag, Th).

These techniques can also be used to remove the nonbiodegradable COD, but are seldom implemented due to operating costs.

5.3 Influence of salinity and of certain compounds

Besides the corrosivity of salty or brackish aerated water, salinity influences biological purification in two ways.

■ Settleability of activated sludge

Increased SS in settled water relatively proportional to salinity have often been attributed to saline water. In fact the deterioration of SS, which is common in the petrochemical and pharmaceutical industries, may have several causes related to poor quality bacterial floc:

- Sporadic but massive leakage from the sludge bed whose level is difficult to control. SS can rise to $300 \text{ mg} \cdot \text{l}^{-1}$ (clear interstitial water).

- Micellization of sludge following excessive agitation during long residence time (extended aeration) with coexisting metallic hydroxides, or due to a high insoluble HC content which determines a tendency to flotation.
- Osmotic pressure increasing with salinity and formation of colloidal sludge (turbid interstitial water). High nonbiodegradable COD often associated with high salinity may have a joint effect whose impact is hard to assess. As a result, SS figures are commonly from 60 to 120 mg·l⁻¹, a level that may require tertiary clarification treatment in order to meet discharge standards.

In contrast, some albeit rare examples show that with precautions in prior treatments and in operating activated sludge, it is possible to settle saline process water (2 to 5 g·l⁻¹) properly with Mohlman index values of 25 to 35 in the mixed liquor and SS of 25 to 30 mg·l⁻¹ in the clarified effluent.

■ Mass loading

Mass loading may be reduced by 40 to 50% when salinity rises from 0.5 to 10 g·l⁻¹. But if the salinity holds fairly steady, i.e. if the sludge can get acclimatized, load degradation is much less significant. Activated sludge purification works as described below in the petrochemical industry:

- One (polystyrene unit) for water with 10 to 12 g·l⁻¹ TDS and a mass loading of 0.1. It is possible to eliminate 98% of the BOD₅ and get only 25 to 30 mg·l⁻¹ SS in the clarified effluent, due to considerable make up sludge from the softening process which "weights up" the activated sludge.
- The other (steam cracker and propylene oxide, etc.) with pure O₂ and mass loading of 0.3 to 0.4 for water with 20 to 25 g·l⁻¹ salinity. It is possible to eliminate 95% of the BOD₅ and 80% of the COD, and get 60 to 100 mg·l⁻¹ SS in the effluent that is probably due to CaCO₃ sludge and a pure O₂ reactor with a high activated sludge concentration.

In the United States, distribution of 15 to 40 mg·l⁻¹ of added PAC to reduce the toxicity index or to cut down on "priority pollutants" can also have a positive effect on the quality of the activated sludge and its settleability.

■ Impact of some organic compounds

By their very nature, some compounds that are being processed subsist in the effluents and exert a floc dispersion action though they themselves are quite difficult to biodegrade. The acrylates and sulfonates can be cited among others. Their remanence will require an extra dose of inorganic coagulant upstream from tertiary treatment. During coagulation, the zeta potential can in fact reach a maximum before being canceled out by a sufficient dose of inorganic coagulant.

5.4 Particular treatments

5.4.1 Use of strong oxidizing agents

The use of severe oxidation other than at atmospheric pressure or by biological process has developed in two different situations:

- Powerful oxidizing agents such H₂O₂, Fenton's reagent, persulfuric acid and ozone are used in Europe and the United States to remove final traces of toxic compounds such as phenols and cyanides. High doses of oxidizing agent are required (4 to 10 times the stoichiometry) due to the competition of other reducing copollutants.

■ Oxidation with air or with oxygen under higher pressure and temperature conditions than those practiced in sulfide oxidizers is sometimes performed in the United States under the name of WAO, wet air oxidation:

- 250 to 320°C.
- 25 to 120 bar.
- Residence time from 20 to 120 min.

The process is expensive in energy consumption and involves metals that can withstand strong corrosivity. It is used for organic liquids that are already relatively concentrated (COD of 20 to 100 g·l⁻¹) so that the reactions are sufficiently exothermic. COD reductions achieved vary from 55 to 75%. WAO is used for liquors that are too dilute to be burned, generate too much excess biological sludge, but that are nevertheless fairly low in chloride content.

5.4.2 Adsorption on granular activated carbon (GAC)

The use of adsorbents can be contemplated especially downstream from biological purification and will then only act on the nonbiodegraded COD. This can curb investments and operation costs.

Specific adsorbent resins are seldom used as they are sensitive to fouling and mean alkaline regeneration eluates that are hard to break down. GAC is more commonly used, especially in North America, and requires less investment while offering two or three alternatives for regeneration.

5.4.2.1 Pretreatment before filtration on GAC

Though GAC can accommodate clarified water that is still colloidal and whose fine particles may not be retained by the granular medium, its adsorption activity is nevertheless curtailed. It is often preferable to carry out a complete tertiary flocculation treatment upstream from GAC.

Flocculation of petrochemical and pharmaceutical industry effluents may entail the use of up to 500 mg·l⁻¹ of commercial inorganic coagulant and an intermediate settler with considerable hydroxide sludge production. In contrast, the reduction in COD achieved in this way may go up to 80 or 100, even 130 mg·l⁻¹.

5.4.2.2 Scope of adsorption

Two types of compounds are eliminated that can be biodegraded only slightly or not at all:

- Relatively volatile and well adsorbed aromatic compounds, provided that the water temperature is far below their boiling point.
- Compounds with high molecular weight, chlorinated, phosphorated or even nitrated addition compounds and polyaromatic hydrocarbons.

5.4.2.3 Implementation

Because of slow kinetics, space velocities must allow residence times of 20 to 120 min and are therefore around two to three volumes per volume per hour, in two or three in-line columns, two to three meters high. This set up allows bed permutation and maximum saturation in the first column (bed specific gravity of 0.42 to 0.46).

Fixation efficiency varies according to the compound, the pH and the temperature from 75 to 95% of the COD.

At ambient temperature, adsorption capacity depends on the initial concentration and can vary from 100 mg·g⁻¹ (benzene) to 180 (nitrobenzene) for water that is saturated in these compounds (process condensates). However, at the reduced concentrations achieved after biological purification, adsorption capacity becomes four to six times less. GAC can then fix only 0.05 to 0.1 kg of COD per kilogram.

Prior treatment by O₃ can cut up certain molecules by ozonolysis and make them more readily adsorbable (as well as more readily biodegradable). While ozonolysis of humic matter is optimum at pH values of 4 to 5.5, some addition compounds in petrochemical plants are more easily broken down between pH 8.5 and 9.5, a range that is unfavorable to the stability of ozone solutions.

5.4.2.4 Regenerating GAC

GAC is usually regenerated thermally in a reducing environment. The furnace is generally located outside the plant often on a fairly remote site common to several users. Seventy to 85% of the initial capacity can be restored.

However, on-the-spot partial regeneration can be performed, thereby allowing longer running time between thermal regeneration operations. In-situ regeneration may be done by:

- Steam countercurrent washing to strip adsorbed volatile compounds (chlorinated compounds or BTX); or
- Extractions with caustic and/or isopropanol that can desorb a fraction of macromolecular compounds (chemical regeneration).

However, it is more difficult to dispose of the regeneration liquor in the second method than to incinerate the vapors in the first one.

5.5 Styrene production

5.5.1 Conventional process

- Liquid phase ethylene alkylation of benzene in the presence of AlCl₃ in a dispersed phase (Lewis acids).
- Dehydrogenation of ethylbenzene by the oxygen in the air.

5.5.2 Main discharges

- Highly acid primary rinsing water that is rich in AlCl₃ and HCl.
- Countercurrent washing alkaline water saturated in benzene and ethylbenzene and loaded with HC, NaCl, AlO₂Na, with a pH of 11 to 12.
- Possibly dinitrocresol baths (polymerization inhibitor) in small volumes daily.
- Miscellaneous storm and run-off water.
- Al³⁺ discharge.

5.5.3 Pollution

Besides emulsified HC, pollution is composed primarily of aromatic HC in high concentrations in alkaline effluents. Miscellaneous oxygenated compounds and phenols constitute secondary pollution.

	Boiling point (°C)	Solubility 20°C (mg·l ⁻¹)
Benzene	78	600-1000
Ethylbenzene	130	150-200
Styrene	140	200-300

5.5.4 Treatments

- Acid and very salty discharge liquors are concentrated to 25% AlCl_3 by evaporation. The resulting solution may have some market value (WW coagulant).
- Dinitrocresol baths, a toxic product, can be broken down by extended ozonization or, after dilution with other liquors, by incineration.
- Aromatic HC in alkaline water are steam stripped to residual values lower than 20 $\text{mg}\cdot\text{l}^{-1}$.
- Residual Al^{3+} (less than 0.1 $\text{kg}\cdot\text{t}^{-1}$ of styrene) is precipitated by neutralization and separated by settling or flotation. Even in the absence of dissolved Al (processes on a catalyst carrier with BF_3), the DAF unit is recommended to enhance oil separation before the biological unit.
- Biological purification is carried out by extended aeration with an attempt made to keep the activated sludge at an advanced age. This is necessary to break down the fraction of the COD made up of aromatic compounds.

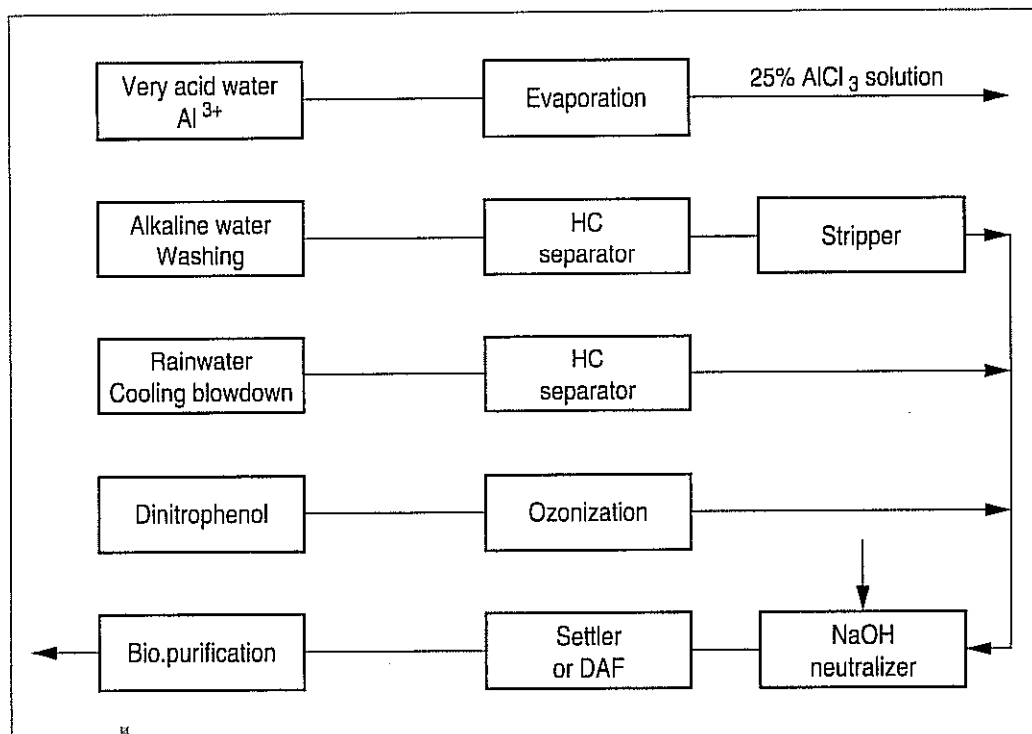


Fig. 56 Treatment of styrene production effluents (ethylbenzene process with Al suspension)

5.6 Propylene oxide production

5.6.1 Lime and epichlorhydrin process

Propylene is oxidized by HClO yielding chlorohydrin, which is in turn saponified by a lime solution to give propylene oxide.

Recently, a NaOH solution has replaced lime and has cut out a good part of the inorganic pollution due to lime.

5.6.2 Discharges and pollutants

For one ton of oxide when lime is used, there are 40 to 60 m^3 of hot alkaline water that can contain considerable inorganic pollution:

- 2 to 2.3 t of CaCl_2 .
- 0.2 t of lime impurities and precipitated CaCO_3 .

Dissolved lime itself may amount to 0.5 to 0.7 $\text{g}\cdot\text{l}^{-1}$.

Soluble organic pollution includes propylene oxide, propyleneglycol, acetophenone and chloroketone.

The equivalent COD may amount to 0.25 t with a considerable biodegradable fraction and a $\frac{\text{COD}}{\text{BOD}_5}$ ratio after clarification of 1.4 to 1.7.

5.6.3 Treatment

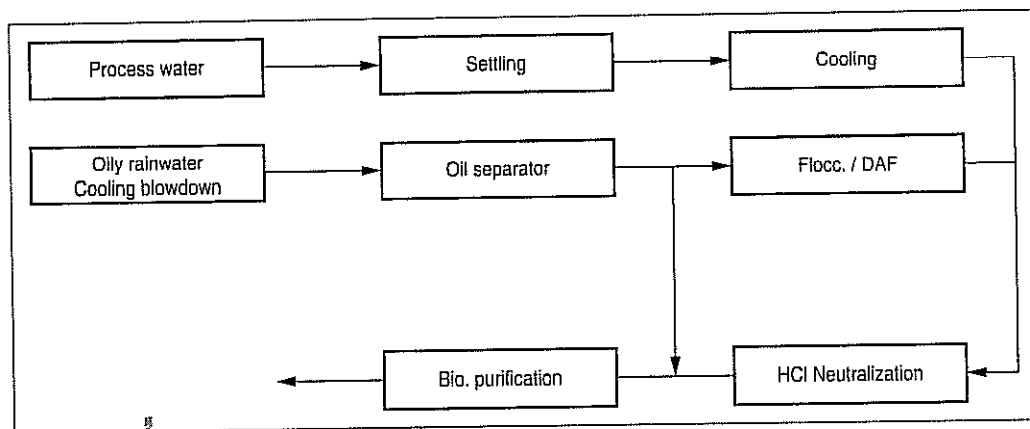


Fig. 57 Treatment of propylene oxide production effluents

The process water, heavily loaded with SS (3 to 5 $\text{g}\cdot\text{l}^{-1}$), undergoes settling which generates CaCO_3 sludge. Then it is cooled and neutralized by HCl or by mixing with the other dilute residual water. After N and P nutrients are added, the water lends itself to high load biological purification. The excess biological sludge can be mixed with the inorganic sludge produced in one and a half to two times greater amounts. This makes it easier to dewater on filter presses and achieves dryness of 35 to 40%.

After clarification, low levels of COD and BOD₅ warrant biological treatment in a one-step trickling filter.

For finishing wash effluents, an increased dissolved BOD₅ load and mainly the frequent requirement of achieving low final nonionic detergent concentrations mean biological treatment by medium load activated sludge. Even extended aeration can be used, whereas a trickling filter would suffice for final treatment of the first two effluents.

The dry process with propylene put into solution in hexane generates much less pollution. It is confined to washing and dust removal water which chiefly contains SS: PP dust, traces of catalysts and separable oils.

5.8 Polystyrene production

5.8.1 Process

Polymerization of styrene in inorganic dispersion in water (H₃PO₄) and HCl washing.

5.8.2 Discharges and pollutants

Very acid process water can amount to 4 to 5 m³ per ton of PS. For example:

- pH 0.7 to 1
- SSA = 160 to 200 meq·l⁻¹ (HCl mainly)
- PO₄³⁻ = 20 to 50 mg·l⁻¹
- Nonionic detergents = 8 to 12 mg·l⁻¹
- Anionic detergents = 30 to 40 mg·l⁻¹
- SS = 0.5 to 3 g·l⁻¹
- Dissolved BOD₅ = 40 to 60 mg·l⁻¹.

It can be diluted by cooling water.

5.8.3 Treatment

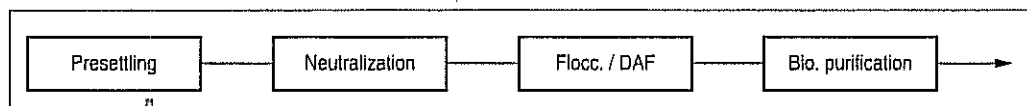


Fig. 59 Treatment of PS effluents

An example of how concentrations change during treatment is given below (in mg·l⁻¹):

	After DAF	After activated sludge
BOD ₅	35	15
PO ₄ ³⁻	8-10	5-6
Anionic detergents	5-6	0.5
Nonionic detergents	6-7	5

Though trickling filters can provide proper elimination of BOD₅, activated sludge yields better removal of PO₄³⁻ and detergents.

5.9 Nylon-6 production

5.9.1 Process

Nylon-6 is produced by polymerization of ϵ -caprolactame, a monomer which is synthesized from hydroxylamine sulfate and cyclohexanone.

5.9.2 Discharges and pollutants

Process discharges mainly contain caprolactam, ammonium sulfate and amines. But they are generally associated with discharges of other production streams such as polyesters and epoxy resins.

For production of $120 \text{ t} \cdot \text{d}^{-1}$ of nylon-6, total discharge amounts to 20 t of COD, 8 t of BOD_5 and 2 to 2.3 t of nitrogen, one-third of which in organic form and the rest in the form of ammonia. Depending on the dilution rate by other discharges, the BOD_5 can vary from 400 to $1\,200 \text{ mg} \cdot \text{l}^{-1}$.

5.9.3 Treatment

Treatment may include:

- Neutralization of residual acidity.
- Addition of P.
- Activated sludge in extended aeration with nitrification.
- Intermediate anoxia tank allowing partial denitrification of the nitrates.

During treatment, there is ammonification of organic nitrogen and a tendency to foam and produce sludge with a high Mohlman index. A number of precautions must be taken (deaeration chamber, flocculation before secondary settler, etc.). The aim is to ensure proper settling and advanced sludge age so that the sludge is better adapted to complete degradation of caprolactame.

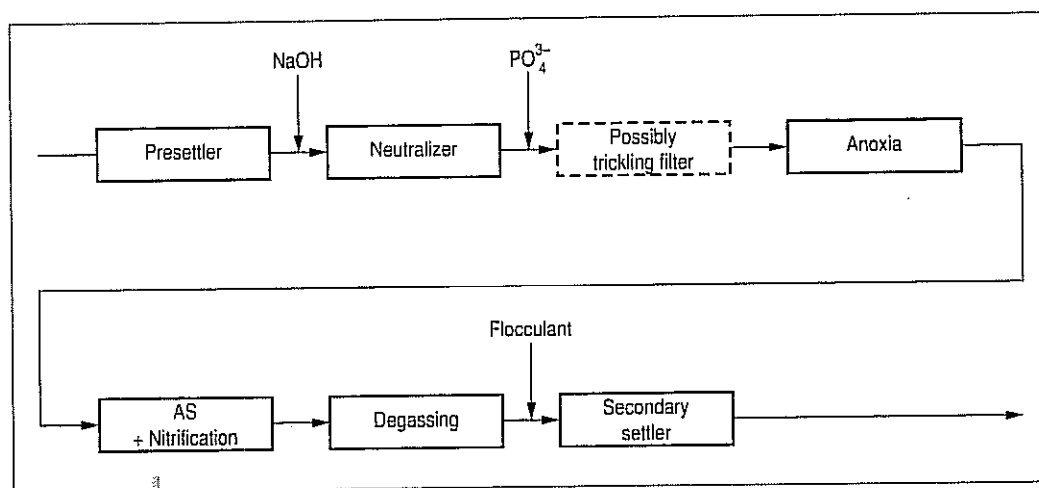


Fig. 60 Treatment of nylon-6 effluents.

Treatment case studies Purification monitoring and sludge disposal

Chapter

6

In the preceding chapters the most widely used pretreatment and treatment processes were discussed. In practice these processes are chosen and designed in different circumstances:

- If there is an existing plant, the choice must be made according to a given sewer segregation set up and existing treatment components that often include large API oil separator tanks.
- If a grassroots plant is to be built, there is complete freedom as to effluent stream segregation and the choice of pretreatments. However, there is some uncertainty about the scale of pollution, especially the dissolved fraction which may be inaccurately assessed. Good reliability can be expected from primary and physicochemical purification operations. Meanwhile, a certain leeway must remain to extend or modify biological purification, in particular by adding surge tanks.

Construction of complete treatment systems, which increasingly include a tertiary stage, sometimes stretches out over several decades. As a result, the authors have decided to discuss the treatment set up in five chosen French plants. The examples illustrate a growing degree of complexity from simple hydroskimming refineries up to petrochemical complexes.

Despite the common legal framework for discharges, the plants' background and growth, local government decrees and bye-laws, water authority requirements, and new regulations (odor, noise, NH_4) have all led to original developments specific to each plant. Recycling waste water into cooling water systems is sometimes at the basis of tertiary water treatment. It may mean that open recirculating systems must be operated differently depending on whether they are partially or exclusively supplied with waste water.

Each discussion includes three points involving the operation of treatment stations:

- **Disposal of sludge.** It is often dewatered by centrifuging (bottom sludge from API tanks) in an outside facility and disposed of by incineration or controlled discharge depending on its nature. Controlled discharge is now often regulated.
- **Nearly-continuous monitoring.** Certain parameters are involved (TOC, theoretical oxygen demand, HC, etc.) and are monitored by sensors that function as alarms. Sensors can cut down on expenditures for analysis in treatment stations that are increasingly run from the refinery's central control room.
- **Reagent consumption.** It can vary widely depending on the complexity of treatment stations and the end result expected from purification.

6.1 French Mobil Oil Gravenchon refinery

The refinery has a processing capacity of $3.1 \text{ Mt} \cdot \text{y}^{-1}$ and includes topping, vacuum distillation, an inorganic lube oil plant ($185,000 \text{ t} \cdot \text{y}^{-1}$) and a recent synthetic PAO (polyalpha olefins) lube oil plant ($15,000 \text{ t} \cdot \text{y}^{-1}$).

It is supplied with Seine river water clarified in an outside plant (Norville), the 1989 volume was $2.3 \text{ Mm}^3 \cdot \text{y}^{-1}$. It also consumed $1.13 \text{ Mm}^3 \cdot \text{y}^{-1}$ of water from the water table in 1989.

The two types of water have the following main characteristics.

However, with the dramatically reduced low-water flow rates in the Seine river in 1990, the salinity of the water has risen. In particular, the Cl^- content has reached maximum values of 191 to 440 ppm and has become more sensitive to the influence of the tides.

	Clarified river water	Well water
Hardn. $\text{meq} \cdot \text{l}^{-1}$	4.4 to 6.4	4 to 6
M alk. $\text{meq} \cdot \text{l}^{-1}$	3.6 to 4.6	3.2 to 4.2
Cl^- ppm	50	28 to 35
SO_4^{2-} ppm	65	38
NO_3^- ppm	21	21

6.1.1 Treatment of waste water

6.1.1.1 Deballasting water

Saline water accounts for a yearly volume of some $80,000 \text{ m}^3$ and is purified separately before it is discharged into the Seine river. The purification system has three storage tanks, an API oil separator and a sand filter. The maximum throughput is around $50 \text{ m}^3 \cdot \text{h}^{-1}$. The treated water is characterized by:

- $\text{SS} < 10 \text{ mg} \cdot \text{l}^{-1}$
- $\text{HC} < 5 \text{ mg} \cdot \text{l}^{-1}$
- $\text{COD} < 150 \text{ mg} \cdot \text{l}^{-1}$.

6.1.1.2 Oily water

All waste water except for deballasting water is collected in a single network and undergoes complete physicochemical and biological treatment (see Fig. 61).

The water is made up of:

- Neutralized eluates from ion exchange regeneration.
- Nonreclaimed heating steam condensates.
- Cooling and tank bottom blowdown.
- Economizer washings.
- Rainwater.

It amounts to an average flow rate of around $500 \text{ m}^3 \cdot \text{h}^{-1}$. After treatment, 50% is discharged and around 50% recycled as make up to cooling towers.

Primary oil separation is carried out in two in-line API-type oil separator stages. The separators are very large and are equipped for skimming off surface oil alone. Bottom sludge is removed periodically (once every three years for a compartment).

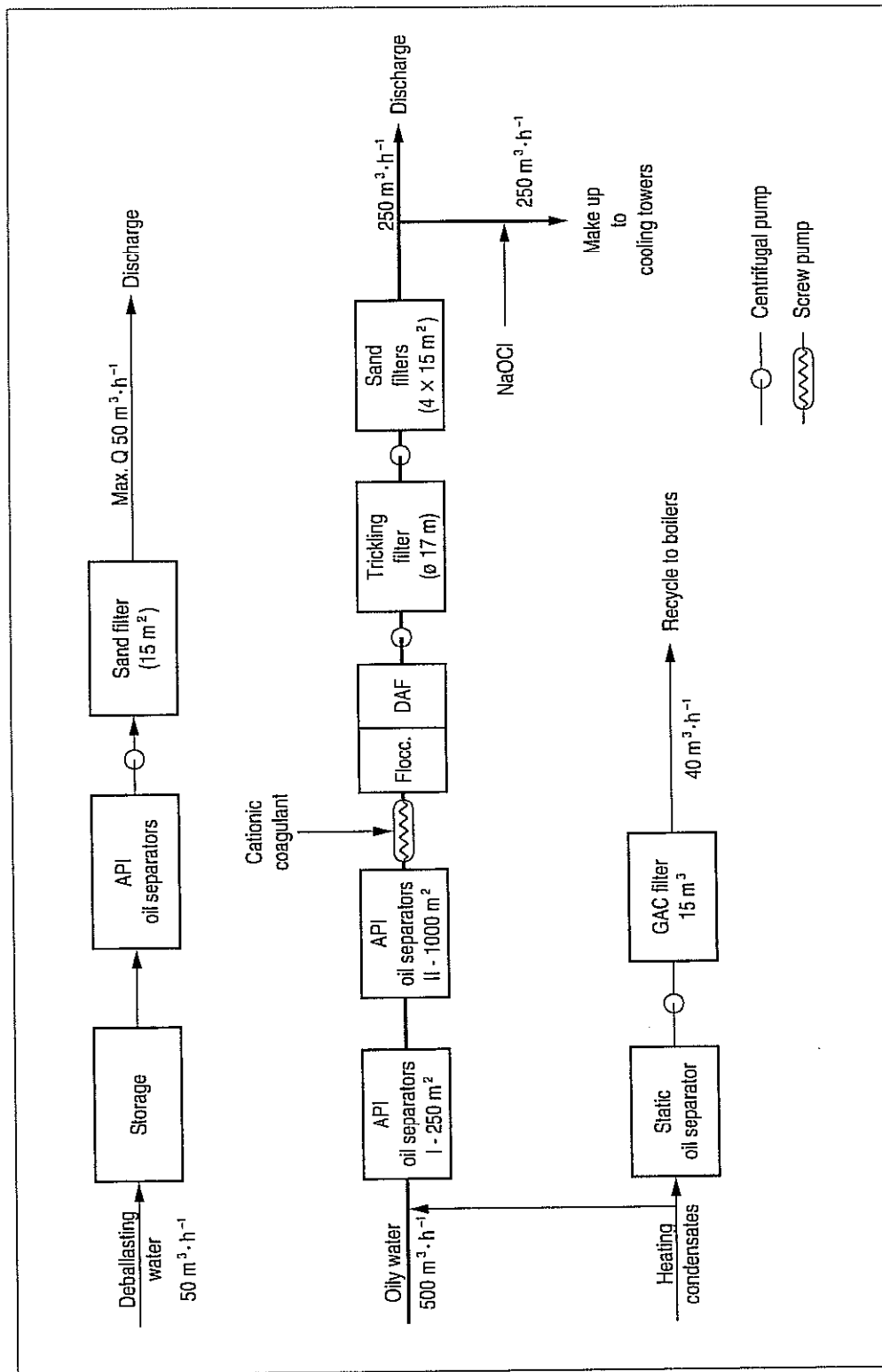


Fig. 61 French Mobil Oil's Gravenchon refinery: IWV treatment flow scheme.

Flocculation in the DAF is performed by an organic cationic coagulant.

The trickling filter is made up of random plastic materials and has an original feature. It is fitted with a sampling basket that runs down to the bottom and is weighed once a month. In this way the fouling of the bed is measured and a decision can be made as to when it should be washed (alkaline washing one or twice a year).

Sand filters perform final SS elimination. An example of efficiency is given below.

Total salinity of treated water is lower than $2 \text{ g} \cdot \text{l}^{-1}$ thereby allowing it to be recycled to cooling.

Reusing 50% of the water in cooling makes it possible to achieve an exceptionally small specific volume of discharges, e.g. 1.28 m^3 per ton of crude in 1989.

	Before DAF	After filters
COD	$430 \text{ mg} \cdot \text{l}^{-1}$	$70 \text{ mg} \cdot \text{l}^{-1}$
BOD ₅	75	15
HC*	115	<2
SS	30	1-3
Dissolved salts		$0.8-1.5 \text{ g} \cdot \text{l}^{-1}$

* HC content before DAF is around 50 to $60 \text{ mg} \cdot \text{l}^{-1}$ on effective average.

6.1.1.3 Heating condensates

These condensates amount to a flow rate of around $100 \text{ m}^3 \cdot \text{h}^{-1}$, with 60 discharged into the IWW network described above and 40 recycled after the following particular treatment at 80°C :

- Gravity oil separation in a closed drum.
- Filtration on granular activated carbon.

The treated condensates are characterized by $\text{SS} < 1 \text{ mg} \cdot \text{l}^{-1}$ and $\text{HC} < 3 \text{ mg} \cdot \text{l}^{-1}$ (1 on average).

6.1.2 Eliminating purification sludge

The sludge from API oil separator bottoms is dealt with directly by incineration in an outside facility. Amounts represent about 500 t/year at a concentration of 150 to $250 \text{ g} \cdot \text{l}^{-1}$. The oil collected at the API surface with flotation sludge (20% of the total) in slop tanks comes to $2500 \text{ m}^3 \cdot \text{y}^{-1}$, with humidity under 10%. It is reused in the refinery's industrial fuel network.

6.1.3 Cooling systems

There are seven systems, six of which are run in a similar way and one (system No. 2) operated differently because stainless steel predominates (Table 46). Circulating flow rates vary from 1 to $300 \text{ m}^3 \cdot \text{h}^{-1}$ per system. Total make up amounts to:

- $250 \text{ m}^3 \cdot \text{h}^{-1}$ of industrial water from the Seine.
- $250 \text{ m}^3 \cdot \text{h}^{-1}$ of purified recycled IWW.

The concentration ratios are held at 1.4 to 1.95 for normal systems (leakage control should raise this figure to 2). The ratio is 1.2 for system No. 2, where an attempt is made not to exceed a Cl^- content of $50 \text{ mg} \cdot \text{l}^{-1}$.

Conditioning is done:

- On the basis of phosphonates for the first systems.
- On the basis of phosphonates and acrylates for system No. 2.

Continuous chlorination treatment and a biocide plus dispersing agent shock treatment are used on make up water to prevent biological growth.

Table 46
Operating the cooling systems

Operating the cooling systems					
Parameters	Stainless system		Other systems		
	Make up	System	Make up		System
			Seine	Recycled IWW	
Make up water	Seine or well	1.17 8.1 to 8.4	—	—	1.4 to 1.9 8.1 to 8.4
Concentration ratio	—				
pH			6 to 6.4	4 to 7	5 to 6.6
Hardness (meq·l ⁻¹)			4 to 4.4	3.4 to 7.6	
M alk (meq·l ⁻¹)			50 to 90	200 to 500	
Cl (mg·l ⁻¹)			75 to 100		
SO ₄ (mg·l ⁻¹)				800 to 1500	
Salinity (mg·l ⁻¹)				0.5 to 2.2	2.5 to 5
Total germs (10 ⁶ ·ml ⁻¹)					

6.2 Elf Grandpuits refinery

This refinery is equipped with a 4.5 Mt·y⁻¹ topping unit plus the following units:

- A 1.5 Mt·y⁻¹ FCC (with LPG and gasoline sweetening).
- A reformer and two HDS.
- A visbreaker and an alkylation unit.

6.2.1 Particular treatments

Some pretreatments are carried out in the units on sour condensates and spent caustic.

6.2.1.1 Process condensates

Flow rates are 15 to 18 t·h⁻¹ and the condensates come from three main sources:

	Flow rate	Main pollutants
FCC	8 to 9 t·h ⁻¹	S ²⁻ , NH ₄ ⁺ , RS ⁻ , phenols
Visbreaker	3 to 4 t·h ⁻¹	H ₂ S
HDS	5 t·h ⁻¹	S ²⁻ , NH ₄ ⁺

The total effluent undergoes steam stripping with the following orders of magnitude for efficiency:

	Stripper inlet	Outlet
S ²⁻ (mg·l ⁻¹)	500 to 3 500	<20
NH ₄ ⁺ (mg·l ⁻¹)	300 to 600	20 to 50
Phenols (mg·l ⁻¹)	50 to 60	40 to 45
CN ⁻ (mg·l ⁻¹)	100 to 120	<20

6.2.1.2 Spent caustic

It is acidified (H_2SO_4) and the H_2S is removed by steam stripping and sent to the flare.

6.2.2 Treatment of general waste water stream

IWW is collected in two separate networks involving:

- Process water, the more saline and discharged after purification.
- Oily water that is chiefly recycled to cooling systems after purification.

The large size of intermediate storage tanks should be noted (storm water, purified oily water, fire-fighting water).

6.2.2.1 Process water system

In particular, it accommodates desalting water, drainings from crude tanks and neutralization water from alkylation tanks. Boiler blowdown and sweetening brines are discharged downstream from the process water system, whose average throughput is 30 to $60 \text{ m}^3 \cdot \text{h}^{-1}$.

Treatment (see Fig. 62) comprises three main steps after some effluents are cooled down:

- Oil separation by gravity with oil collector drum.
- Physicochemical purification.
- Biological purification by trickling filter.

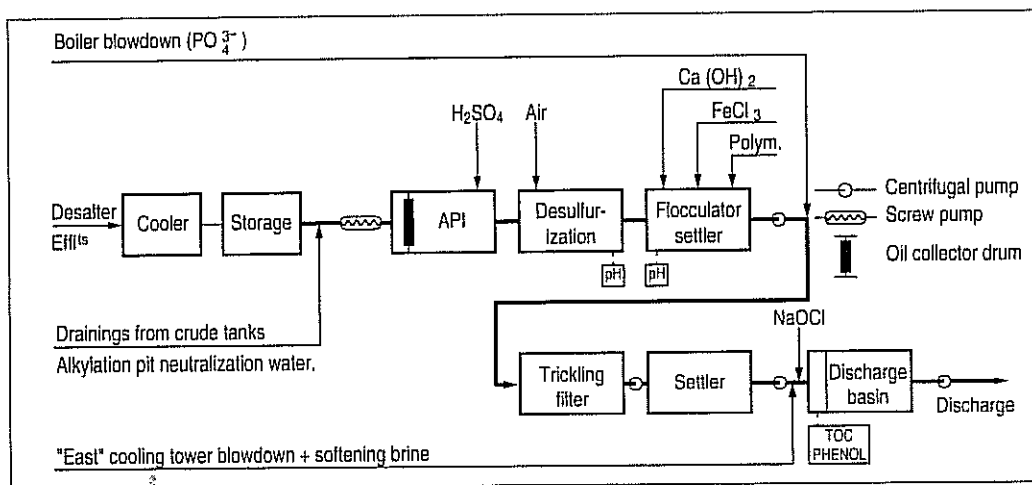


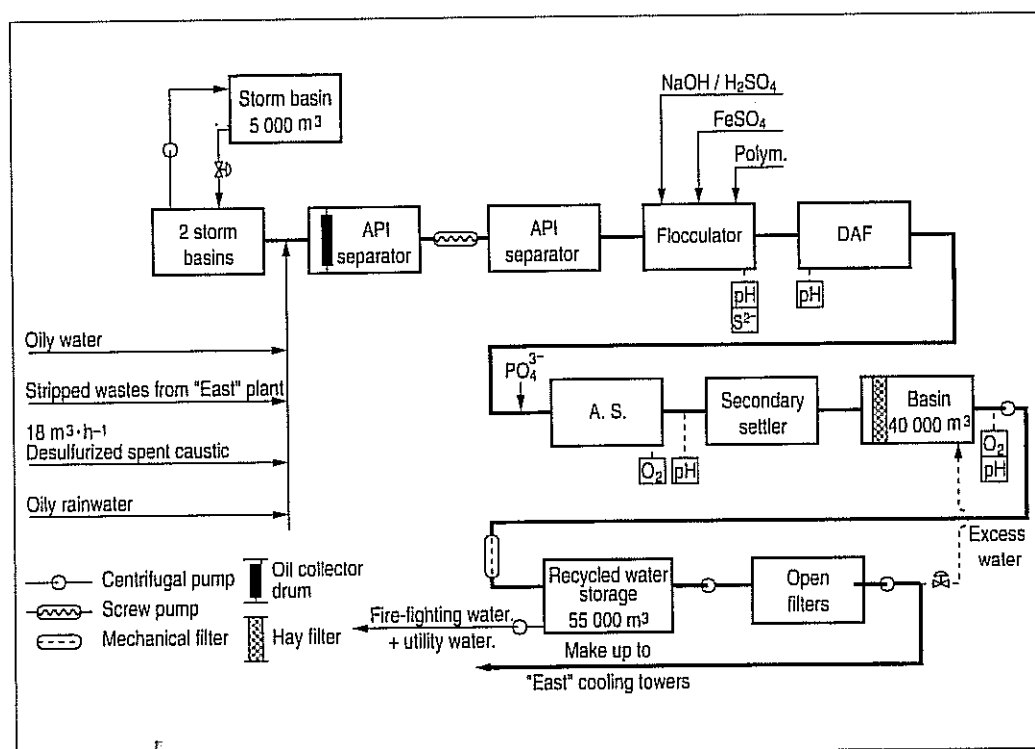
Fig. 62 Process water system (average flow: 30 to $60 \text{ m}^3 \cdot \text{h}^{-1}$)

6.2.2.2 Oily water system

Here is where the oily water from paved areas, oily rainwater, desulfurized spent caustic and stripped condensates from the "East" unit (FCC, alkylation, visbreaker) are channeled. Downstream from this system the blowdown from "West" cooling towers is added. The total average flow is 120 to $130 \text{ m}^3 \cdot \text{h}^{-1}$.

Treatment (see Fig. 63) comprises four steps:

- Oil separation by gravity with an oil collecting drum.
- Neutralization with possible precipitation of sulfides (FeSO_4).
- Biological purification by activated sludge.
- "Tertiary" filtration.

Fig. 63 Oily water system (average flow: $120\text{--}130\text{ m}^3\cdot\text{h}^{-1}$)

Orders of magnitude for the major process water and oily water concentrations at different treatment steps are as follows:

Table 47

Grandpuits refinery: purification efficiency

Parameters	Process water			Oily water		
	Downstream oil separator	Downstream physico-chemical	Downstream trickling filter	Downstream oil separator	Downstream DAF	Downstream biological and tertiary filters
COD ($\text{mg}\cdot\text{l}^{-1}$)	350-400	150-200	70-90	300-800 and more	150-400	110-160
Phenols ($\text{mg}\cdot\text{l}^{-1}$)		2-4	0.1-0.2		25-30	0.1-0.3
BOD ₅ ($\text{mg}\cdot\text{l}^{-1}$)			<25			<20
SS ($\text{mg}\cdot\text{l}^{-1}$)			<30			<5
HC ($\text{mg}\cdot\text{l}^{-1}$)			<5			<1
pH		8.5-8.8	7.5-7.8		7-7.5	7.3-7.8
Salinity ($\mu\cdot\text{l}^{-1}$)			3-5			0.9-1.6

6.2.2.3 Eliminating purification sludge

The sludge produced is separated into two categories:

- **Nonoily sludge**, chiefly made up of sludge from well water softening and in second place of excess activated sludge. It is dewatered to 50-65% of DS by centrifuging in the plant and contains 90% CaCO_3 . Production of about $1200 \text{ t} \cdot \text{y}^{-1}$ and elimination by the land farming process.
- **Oily sludge**, chiefly made up of physicochemical purification sludge. It is thickened on drying beds to about 30% of DS and contains less than 10% HC. Production of around 1300 to 1500 $\text{t} \cdot \text{y}^{-1}$. The sludge is dumped.

6.2.2.4 Cooling systems

An original feature is the way the two open recirculating cooling systems are run (see Fig. 64). The "West" system is supplied with softened slightly mineralized well water. The other, the "East" system, is supplied with oily water after it has undergone tertiary treatment. In both cases, blowdown undergoes water conductivity measurements.

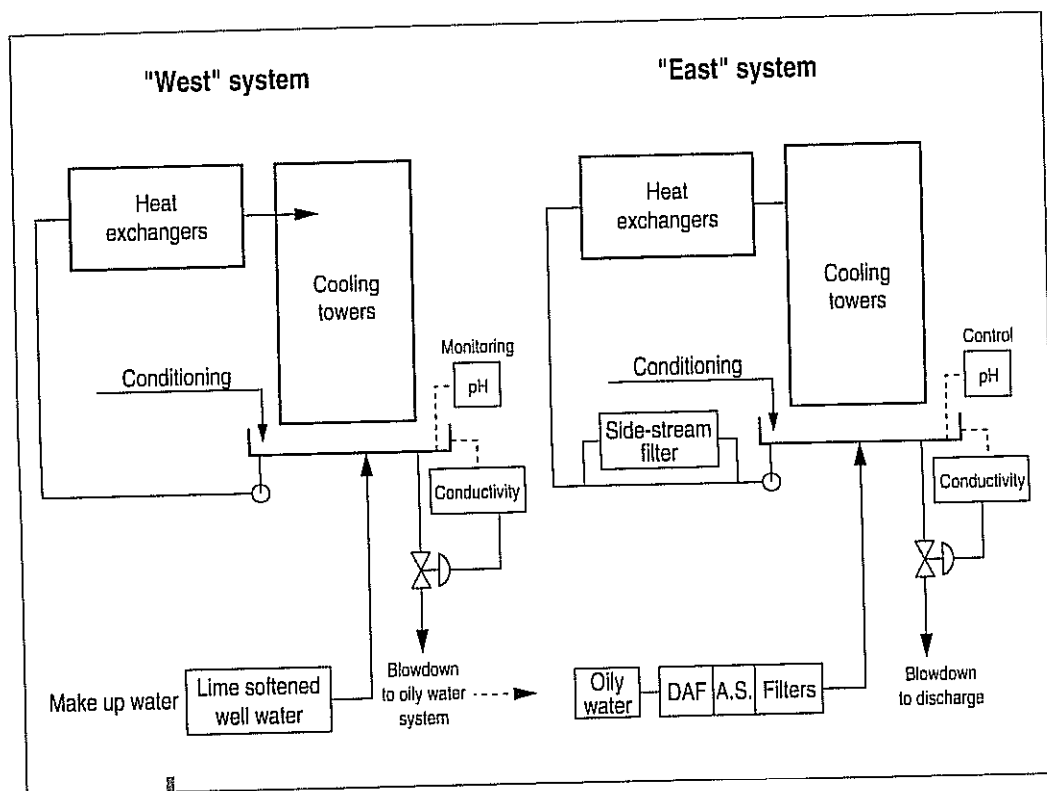


Fig. 64 Elf's Grandpuits refinery. Cooling systems.

Table 48

Operating characteristics

Systems	West		East	
Parameters	Make up	System	Make up before vaccination	System
Circulating flow rate ($\text{m}^3 \cdot \text{h}^{-1}$)	Softened well water	2600-3500	Purified oily WW	3 800-4 400
Temperature gradient ($^{\circ}\text{C}$)		6-8 $^{\circ}\text{C}$		7 $^{\circ}\text{C}$
Make up type				
Make up flow ($\text{m}^3 \cdot \text{h}^{-1}$)		40-50		70-80
Concentration rate		4-4.5		2.5-2.8
pH	9-9.5	8-8.5	7.3-7.8	6.7-7
M alk ($\text{meq} \cdot \text{l}^{-1}$)	0.2-0.4	1-2	3-5	0.3-0.6
Hardness ($\text{meq} \cdot \text{l}^{-1}$)	1.8-2.4	7-8	4-5	<8
Conductivity ($\mu\text{S} \cdot \text{cm}^{-1}$)		800-1400	1400-2000	3000-4200
Cl^- ($\text{mg} \cdot \text{l}^{-1}$)	33-45	150-250	100-250	<600
SO_4^{2-} ($\text{mg} \cdot \text{l}^{-1}$)			400-600	<1 500
Conditioning		$\text{PO}_4^{3-} - \text{Zn}^{2+}$		$\text{PO}_4^{3-} - \text{Zn}^{2+}$

6.3 Shell Oil Company Petit-Couronne refinery

This is a complex refinery, with a light crude capacity of $8 \text{ Mt} \cdot \text{y}^{-1}$ and a heavy crude capacity of 1.2 million. It includes an FCC, a catalytic reformer, a visbreaker, a gas oil hydrosulfurization unit, a naphthenic bitumen unit and a paraffinic oil unit. It is supplied by the water table for boiler make up ($3.3 \cdot 10^6 \text{ m}^3 \cdot \text{y}^{-1}$) and by Seine river water for industrial and cooling water. Cooling is partly once-through and partly open recirculating.

6.3.1 Effluent and pretreatment set up

Usual discharge standards applied to French refineries are supplemented here by a local government decree dating back to 1988. It lays down daily or monthly average figures for a number of parameters.

Phenolic spent caustic amounting to about $1500 \text{ m}^3 \cdot \text{y}^{-1}$ is redistributed in the crude downstream from the desalter depending on further treatment of the crude (visbreaker). Refinery sulfidic spent caustic of a similar volume is disposed of outside the refinery.

	Daily average	Monthly average
HC ($\text{mg} \cdot \text{l}^{-1}$)	7	3.5
SS ($\text{mg} \cdot \text{l}^{-1}$)	30	25
BOD ₅ ($\text{mg} \cdot \text{l}^{-1}$)		25
COD ($\text{mg} \cdot \text{l}^{-1}$)	195	125
Phenols ($\text{mg} \cdot \text{l}^{-1}$)	0.6	0.35
NH_4^+ ($\text{mg} \cdot \text{l}^{-1}$)	45	30
TKN ($\text{mg} \cdot \text{l}^{-1}$)	50	35

Process water (topping, FCC, etc. condensates) undergoes steam stripping. Efficiency has been enhanced so that NH_4 elimination has reached $50 \text{ mg}\cdot\text{l}^{-1}$.

The sour hot effluents for the "naphthenic acids" unit are cooled down by being mixed with other condensates and industrial water and then deoiled still at an acid pH. Then they are collected together and self-neutralized with the general stream which is slightly alkaline (pH 9).

The effluents from the north of the plant (FCC, paved areas, etc.) and from the lube oil complex undergo preliminary two-stage oil removal (CPI and API) before they are pumped to the general storage tank.

6.3.2 General treatment of effluents (Fig. 65)

The oil separators located in the water treatment unit are equipped with oil collector drums. However, since there are no devices to scrape the bottoms, the sludge must periodically be removed. It may be centrifuged before it is disposed of outside the refinery.

The flows to be treated collect in a $20,000 \text{ m}^3$ tank kept only 50% full so it can serve as a surge tank. Then they are redistributed to purification at an average flow rate of 600 to $650 \text{ m}^3\cdot\text{h}^{-1}$.

Physicochemical purification includes flocculation (iron chlorosulfate and cationic polyelectrolyte) followed by flotation.

Biological purification is performed in a trickling filter whose bed is filled with random plastic material (polypropylene rings measuring about 15 cm in a maximum volume of 2200 m^3). SS separation is pursued in a secondary longitudinal settler.

The facility is run based on in-line measurement of the TOC (on $100 \mu\text{m}$ filtered water) and turbidity at the DAF outlet. This gives a rapid assessment of trends. A common level for the TOC is 15 to $30 \text{ mg}\cdot\text{l}^{-1}$ and it can rise to 50 to 80 for short periods.

Table 49

Trickling filter and secondary settler efficiency

Parameters	DAF outlet (approx.)	Secondary settler outlet (in 1989, $649 \text{ m}^3\cdot\text{h}^{-1}$)	
HC ($\text{mg}\cdot\text{l}^{-1}$)	3-10	3.8	$60 \text{ kg}\cdot\text{j}^{-1}$
SS ($\text{mg}\cdot\text{l}^{-1}$)	10-18	18.2	$285 \text{ kg}\cdot\text{j}^{-1}$
COD ($\text{mg}\cdot\text{l}^{-1}$)	200	102	$1587 \text{ kg}\cdot\text{j}^{-1}$
BOD ₅ ($\text{mg}\cdot\text{l}^{-1}$)		25	
Phenols ($\text{mg}\cdot\text{l}^{-1}$)	5-6	0.29	$4.5 \text{ kg}\cdot\text{j}^{-1}$
NH_4^+ ($\text{mg}\cdot\text{l}^{-1}$)	20-21	19	$292 \text{ kg}\cdot\text{j}^{-1}$
pH	7.9	7.9	

The sludge concentration in the trickling filter is assessed by a neutron probe and determines how often the bed will be cleaned or whether to modify the throughput rate (load limits of 800 to 1000 kg of sludge per cubic meter of bed).

Reagent consumption:

- Iron chlorosulfate (Clairtan) = 150 to $250 \text{ t}\cdot\text{y}^{-1}$.
- Cationic polyelectrolyte = 15 to $20 \text{ t}\cdot\text{y}^{-1}$.

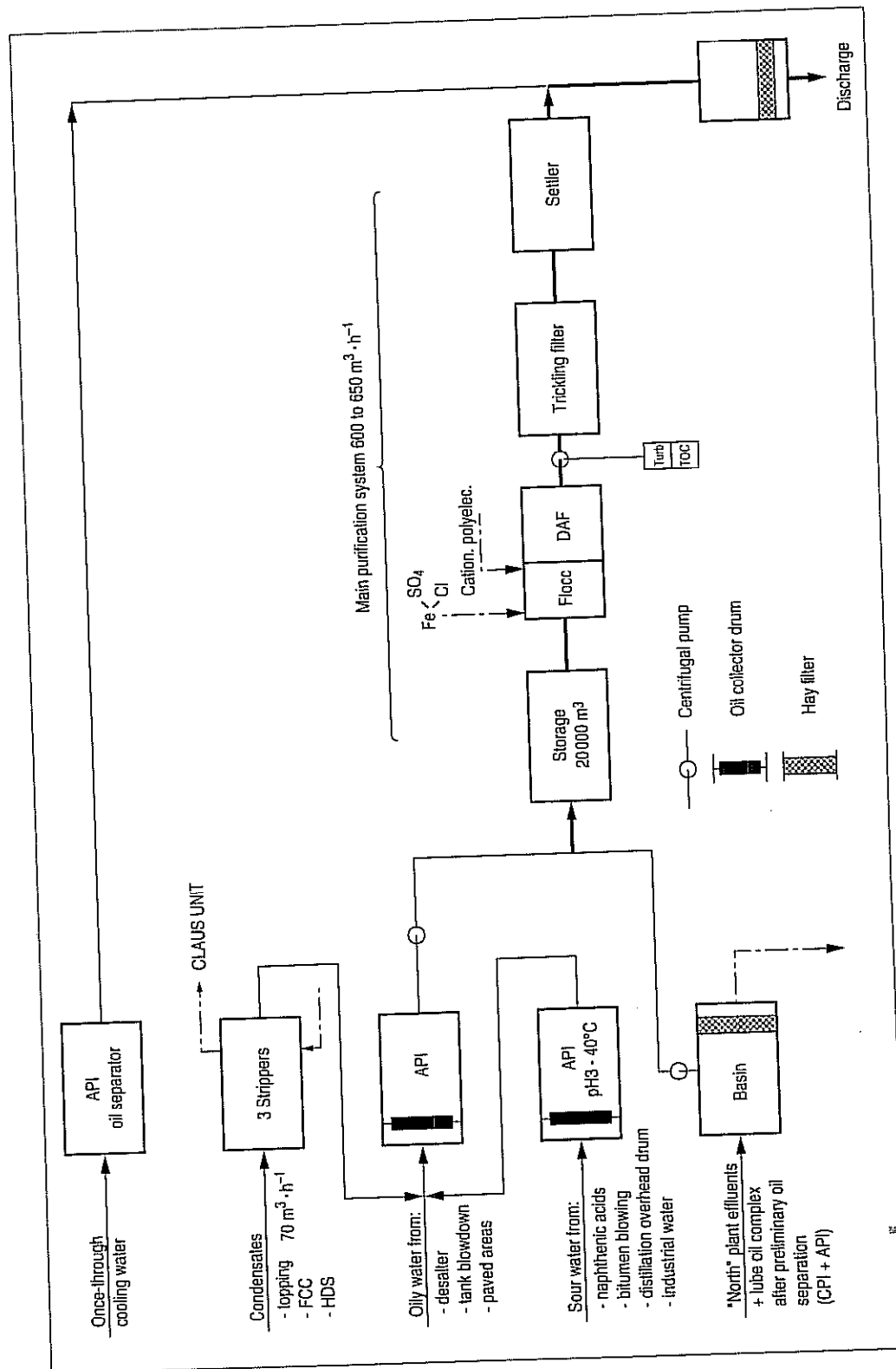


Fig. 65 Shell Oil Company. Petit-Couronne refinery. Effluent treatment system

6.3.3 Eliminating purification sludge

The nature of the naphthenic crudes that are processed generates stable emulsions. Depending on how extensive these emulsions are and how much inorganic coagulant is required, daily production of an average 3 to 4 m³ of flotation sludge may rise to 15 to 20 m³. The sludge is disposed of outside the refinery directly by incineration. Sludge from tank and API oil separator bottoms amounts to 600 to 1300 t·y⁻¹.

Oil collected on the surface of API, CPI, etc. water is a water-in-oil emulsion, of around 20%. It is hard to dewater and may amount to 2000 to 3000 t·y⁻¹.

6.4 Esso-SAF: Port-Jerome

This complex includes the Esso Port-Jerome refinery and the Exxon Chemical Gravenchon petrochemical plant.

The complex refinery has 8 Mt·y⁻¹ distillation capacity. It comprises an FCC, a catalytic reforming unit, a lube oil plant (NMP solvent, MEK dewaxing) and a bitumen plant among others.

The petrochemical plant, built around a steam cracker with a capacity of 0.38 Mt of ethylene per year, comprises two propylene polymerization units, one heavy polymer alkylation unit and several additive units (sulfonic acids, sulfonates, etc.)

The water used for needs other than steam production comes chiefly from the Seine river. The water is clarified and filtered in an outside facility (see Mobil Oil).

6.4.1 Treatment of waste water

The IWW is collected in three segregated networks that involve:

- Process water, or sour water that includes dissolved pollution primarily (phenols, sulfides, etc.).
- Oily water with emulsified hydrocarbons as the main pollution.
- Boiler water demineralization eluates or "clear" water mainly including mineral salts.

6.4.1.1 Process water

This water comes from a number of sources:

- Spent caustic and alkaline washing water: flow rate = 3 to 4 m³·h⁻¹; COD = 3 to 5.3 g·l⁻¹; storage 24 to 48 hours.
- Process condensates (FCC, SC): flow rate = 170 to 180 m³·h⁻¹; storage four hours.
- Product blowdown (MEA, DEA, etc) and tank bottoms: flow rate around 2 m³·h⁻¹; COD = 12 to 15 g·l⁻¹.

The total flow rate reaches 210 m³·h⁻¹ and is treated in three steps (Fig. 66):

- Acidification at pH 4 and desulfurization by air stripping.
- Medium load biological purification.
- "Tertiary" clarification.

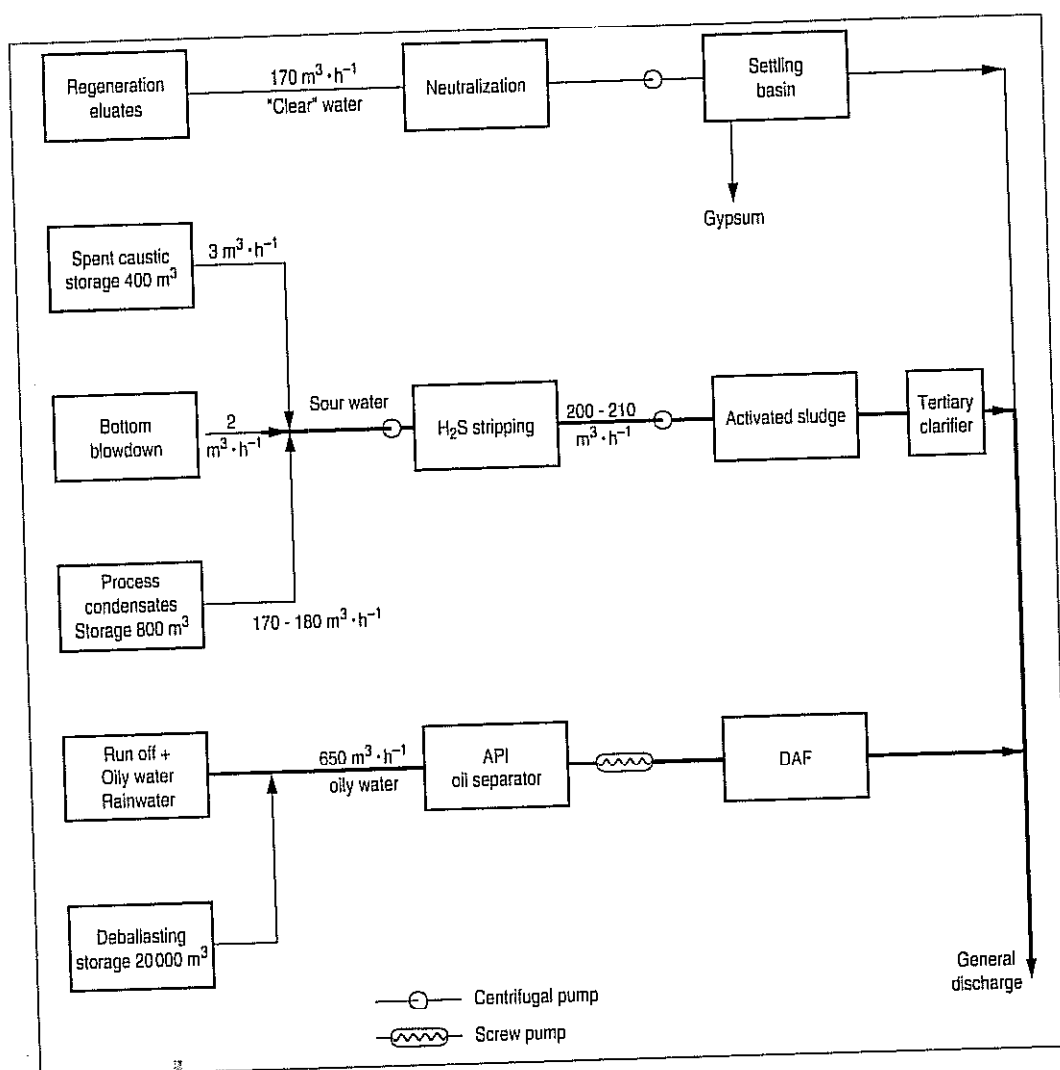


Fig. 66 Esso-SAF in Gravenchon. General effluent layout

Table 50
 Esso-SAF Gravenchon.
 Examples of sour water purification
 efficiency

Table 50 gives an example of sour water purification efficiency.

At the secondary settler outlet, the water undergoes further clarification. Twenty per cent of the flow goes into the flocculator-settler (Al^{3+} and polymer) and 80% goes into the oily water flotation cell. The main reagent consumed is H_2SO_4 (98%): $5500 \text{ t} \cdot \text{y}^{-1}$.

	Upstream from stripper	Downstream from biological purification
Sulfides	$750 \text{ mg} \cdot \text{l}^{-1}$	$<1 \text{ mg} \cdot \text{l}^{-1}$
RSH	$350 \text{ mg} \cdot \text{l}^{-1}$	—
HC	$10 \text{ mg} \cdot \text{l}^{-1}$	$<1 \text{ mg} \cdot \text{l}^{-1}$
COD	1100 max 1600	$315 \text{ mg} \cdot \text{l}^{-1}$
BOD_5	430	$<50 \text{ mg} \cdot \text{l}^{-1}$
Phenols	60	$<0.5 \text{ mg} \cdot \text{l}^{-1}$
SS	—	$60-70 \text{ mg} \cdot \text{l}^{-1}$
TOD	—	$700-800 \text{ mg} \cdot \text{l}^{-1}$

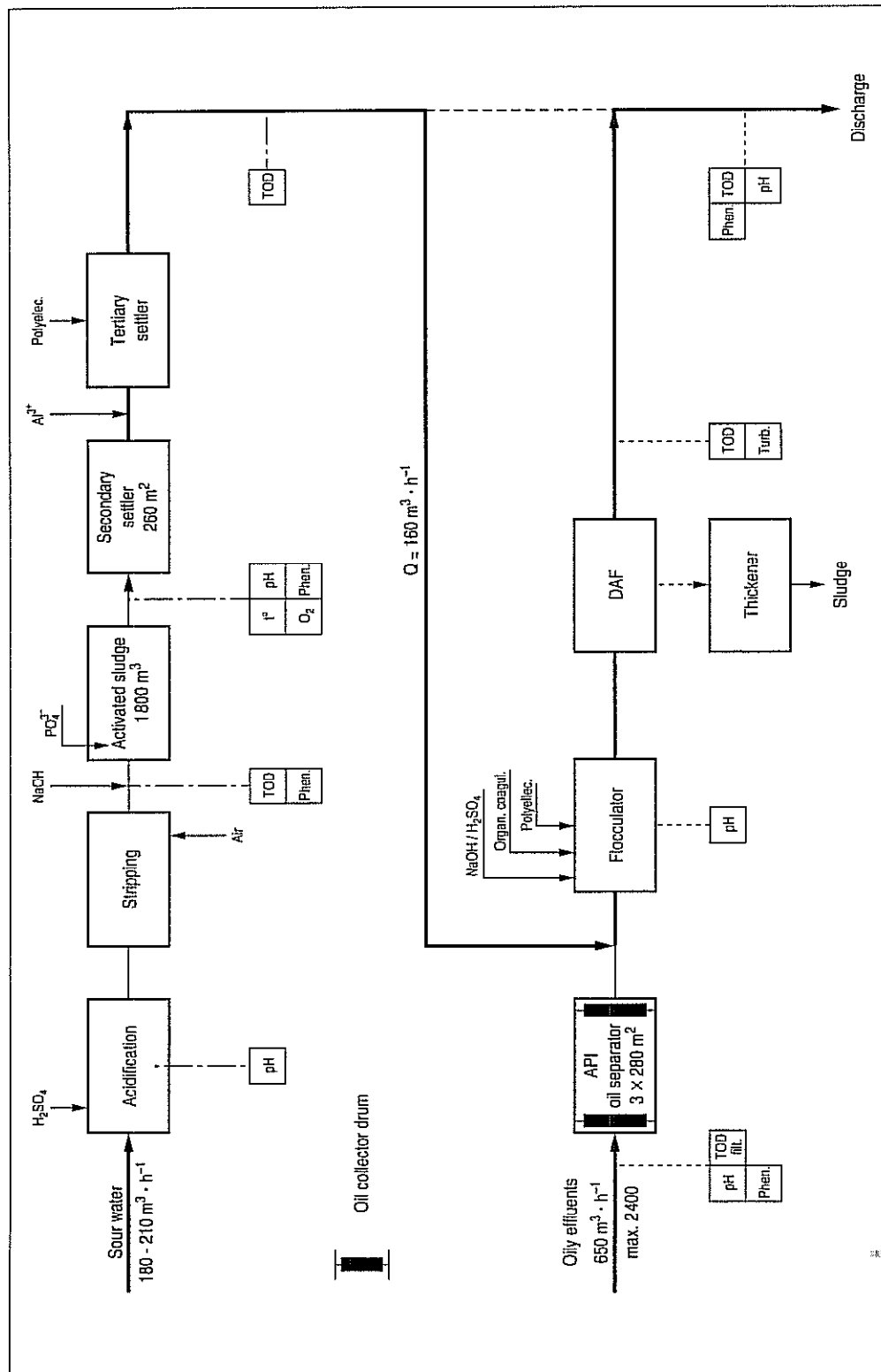


Fig. 67 Esso-SAF in Gravenchon. IWW treatment flow scheme

6.4.1.2 Oily water

Oily water includes:

- Paved area run-off water.
- Deballasting water, very low flow rate, after storage in a 2000 m³ tank.
- Rainwater, after storage in a 20,000 m³ tank.
- Cooling system blowdown.

The normal flow rate is 650 m³·h⁻¹ but it can rise to 2400 m³·h⁻¹ during periods of heavy rainfall.

It is treated in two steps:

- Oil removal by gravity in an API separator with three compartments (860 m³).
- Flocculation pH regulation (cationic coagulant) and dissolved air flotation (2 × 100 m²).

Table 51 gives an example of the efficiency of the flotation operation. Flotation also treats about 180 m³·h⁻¹ of the effluent from sour water biological purification.

Table 51

Esso Port-Jerome. Oily water flotation efficiency

Parameters	Upstream from DAF	Downstream from DAF
pH	6 to 8	7-7.5
HC	100 mg·l ⁻¹	<10 mg·l ⁻¹
COD	300-350 mg·l ⁻¹	180-150 mg·l ⁻¹
NH ₄ ⁺	<15 mg·l ⁻¹	—
Cl ⁻	<1 000 mg·l ⁻¹	
TOD (soluble)		200 mg·l ⁻¹

6.4.1.3 Treatment of "clear" water

Regeneration eluates are neutralized as soon as they come out of the ion exchanger by addition of caustic. They are then sent to a settling tank (24 hours' residence time) where the supersaturated gypsum can be deposited.

6.4.2 Eliminating purification sludge

The bottom sludge from API oil separators amounts to around 1000 to 2000 m³·y⁻¹ and is of low concentration. It is thickened by centrifuging and incinerated outside the refinery.

Surface oil amounts to 1500 to 1600 m³ per month and has about 20% water. It is sent to the refinery's slop tanks.

Flotation sludge, which comprises a very small proportion of excess biological sludge, amounts to some 15 m³ per day with 7 to 10% dry matter. It is incinerated directly outside the refinery.

6.4.3 Cooling systems

Heat exchangers are chiefly made of steel but may have units made of stainless steel, brass, carbon steel and bronze-copper alloys. Four open recirculating cooling systems are operated independently.

Together they exhibit the following characteristics:

- Volume of systems $14,000 \text{ m}^3$
- Overall circulating flow $11,900 \text{ m}^3 \cdot \text{h}^{-1}$
- Average temperature gradient $8 \text{ to } 10^\circ\text{C}$
- Concentration rate $1.7 \text{ to } 1.8$
- Total make up flow rate $430 \text{ m}^3 \cdot \text{h}^{-1}$.

Make up is from clarified, chlorinated Seine river water. Conditioning is performed by a phosphate, phosphonate and dispersing agent combination. Acidification of the make up water keeps the M alk at $2 \text{ to } 2.4 \text{ meq} \cdot \text{l}^{-1}$ in the system in summer and $2.4 \text{ to } 2.8 \text{ meq} \cdot \text{l}^{-1}$ in winter.

The biocide treatment includes shock chlorination of the make up water. Additionally, in hot weather a biocide agent is also distributed once or twice a week.

6.5 Shell complex in Berre

The complex is divided up into four production centers:

- The refining part, with a capacity of $6.3 \text{ Mt} \cdot \text{y}^{-1}$, equipped with two FCC, a visbreaker and a catalytic reformer.
- The steam cracking part, with a capacity of $420,000 \text{ t} \cdot \text{y}^{-1}$ of ethylene (Aubette plant).
- The polymer production center (rubbers, plastics).
- The "specialty" center (solvents, detergents, butadiene, additives, etc.).

It is supplied with water mainly from the Provence canal for boiler and cooling tower make up. Seawater is used for the fire-fighting network and water from the Arc river for the industrial water network.

The water from the Provence canal offers the advantage of low Cl^- and impurity concentrations:

- Hardness $3.6 \text{ to } 4.6 \text{ meq} \cdot \text{l}^{-1}$
- M alk $2.2 \text{ to } 3.4 \text{ meq} \cdot \text{l}^{-1}$
- Cl^- $3 \text{ to } 4 \text{ mg} \cdot \text{l}^{-1}$
- SO_4^{2-} $9 \text{ to } 10 \text{ mg} \cdot \text{l}^{-1}$.

It is softened by lime at a flow rate of $800 \text{ to } 900 \text{ m}^3 \cdot \text{h}^{-1}$ on the site.

Discharge standards laid down by the water authority are as follows for the overall effluent (including rainwater) at the outlet of the complex: pH 6 to 9:

SS	$\leq 30 \text{ mg} \cdot \text{l}^{-1}$	HC	$\leq 20 \text{ mg} \cdot \text{l}^{-1}$
Phenols	$\leq 0.2 \text{ mg} \cdot \text{l}^{-1}$	N	$\leq 30 \text{ mg} \cdot \text{l}^{-1}$
PO_4^{3-}	$\leq 2 \text{ mg} \cdot \text{l}^{-1}$	Cr^{6+}	$< 0.1 \text{ mg} \cdot \text{l}^{-1}$
COD	$\leq 3 \text{ t} \cdot \text{d}^{-1}$	BOD_5	$\leq 1 \text{ t} \cdot \text{d}^{-1}$.

6.5.1 Effluent and pretreatment set up

The central water treatment station for the three chemical production centers receives three effluents (Fig. 68):

- The "North" effluent comes from the "plastics and polymers" center. An elementary stream (expandable PS, $8 \text{ m}^3 \cdot \text{h}^{-1}$) has already undergone physicochemical purification.

- The "South" effluent comes mainly from the "specialty" center, but can contain some discharge from the refinery, which has its own complete purification system (oil separators, DAF, in-line trickling filters).
- The Aubette plant effluent (flows from 80 to 100 m³·h⁻¹) which has also already undergone physicochemical purification (Flocc + DAF).

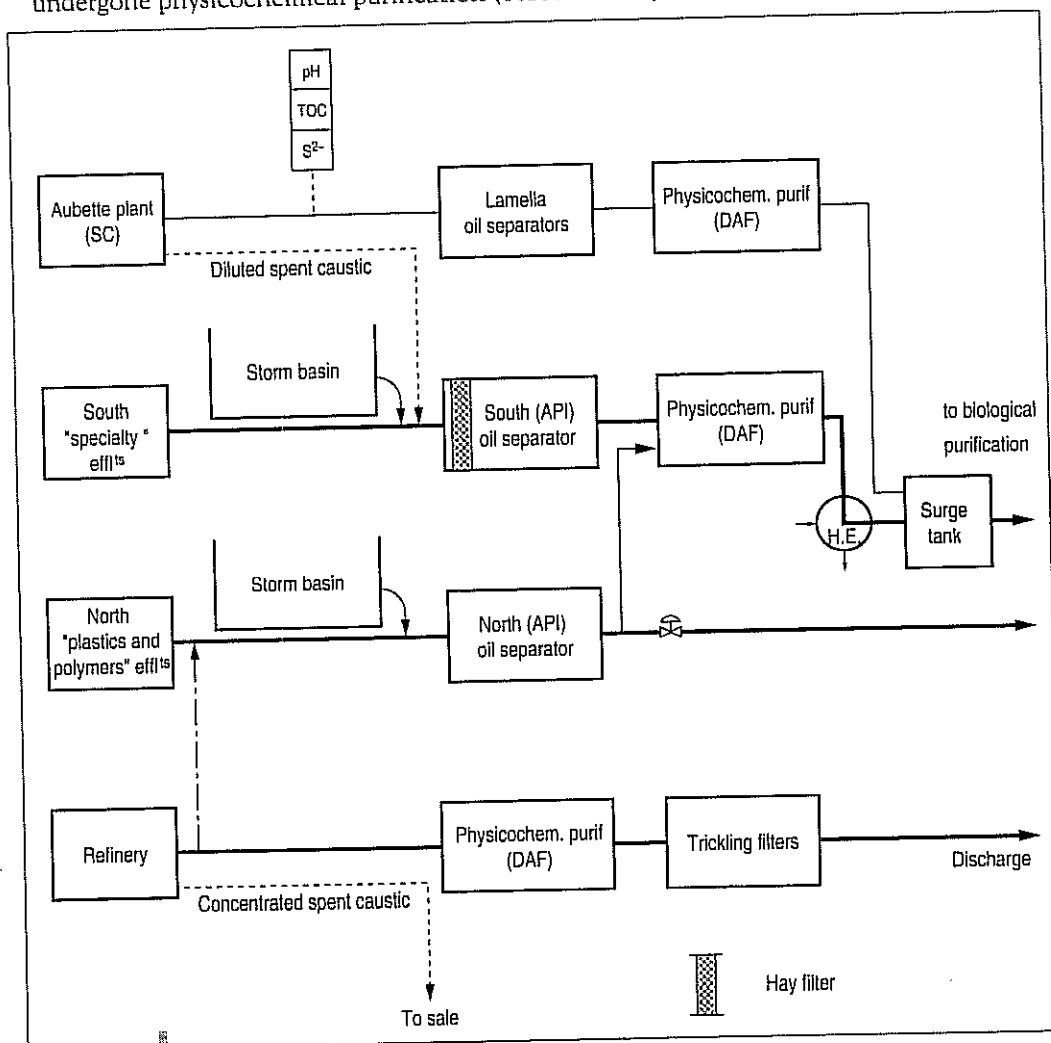


Fig. 68 Shell complex in Berre. General effluent layout.

The "North" effluent goes through an API oil separator and is sent partly to physicochemical purification (DAF). The rest is sent directly to general biological treatment except if there is an accident, it is sent to the site's physicochemical purification process.

The "South" effluent goes through an API oil separator and is sent to the primary DAF (flocculation by FeCl₃) before it is cooled down by a heat exchanger and sent to a 6500 m³ surge tank.

The effluent from the Aubette plant (pH 7 to 8, COD 200 to 300 mg·l⁻¹, SS < 10 and HC < 20) is sent directly to the same surge tank.

The "North" and "South" effluents exhibit the following specific characteristics:

	"South" effluent	"North" effluent
Flow rate ($\text{m}^3 \cdot \text{h}^{-1}$)	400	200
pH	1.5 to 6	10 to 10.5
SS ($\text{mg} \cdot \text{l}^{-1}$)	159 to 45	234 to 385
COD ($\text{mg} \cdot \text{l}^{-1}$)	1411 to 1580	560 to 460
Cl^- ($\text{mg} \cdot \text{l}^{-1}$)	350	

The steam cracker spent caustic (1 to $1.5 \text{ t} \cdot \text{h}^{-1}$) is reused to neutralize acids after pressurized air oxidation. It finally comes back with the Aubette effluent.

The refinery spent caustic is more concentrated in caustic (around $0.3 \text{ t} \cdot \text{h}^{-1}$ at 20%).

6.5.2 General biological treatment

The treatment includes (Fig. 69):

- The general surge tank mentioned earlier.
- A neutralization tank (acid/caustic).
- A 8500 m^3 activated sludge tank with ten $70/50 \text{ kW}$ surface aerators.
- A secondary sucked clarifier 37 m in diameter.
- Tertiary treatment with WAC (aluminum chlorosulfate) flocculation, and separation of the floc by DAF.

The COD load in general biological purification is reduced on the average from 11 to 1.5 t per day, i.e. an efficiency of around 88%.

With a $\frac{\text{COD}}{\text{BOD}_5}$ ratio of about 1.75 and a substantial isopropyl alcohol content, the effluents are readily biodegradable.

Table 52

Average efficiency of biological purification

$\text{mg} \cdot \text{l}^{-1}$	Biological purification inlet	Tertiary treatment outlet
HC	8.5	<0.2
BOD_5	520	16
COD	906	116
Total N	14.8	4.3
SS	130	26

Reagent consumption

- Aluminum chlorosulfate ($10\% \text{ Al}_2\text{O}_3$): 23.5 t per month.
- FeCl_3 ($600 \text{ g} \cdot \text{l}^{-1}$): 43.5 t per month.
- Coagulating polyelectrolyte: 370 kg per month (DAF).
- Anionic polyelectrolyte: 440 kg per month (tertiary treatment).
- Cationic polyelectrolyte: 1590 kg per month (sludge centrifuging).
- Sulfuric acid 66°Bé : 191 t per month (neutralization).

These values are given for purposes of illustration and comparison and represent averages over nine months.

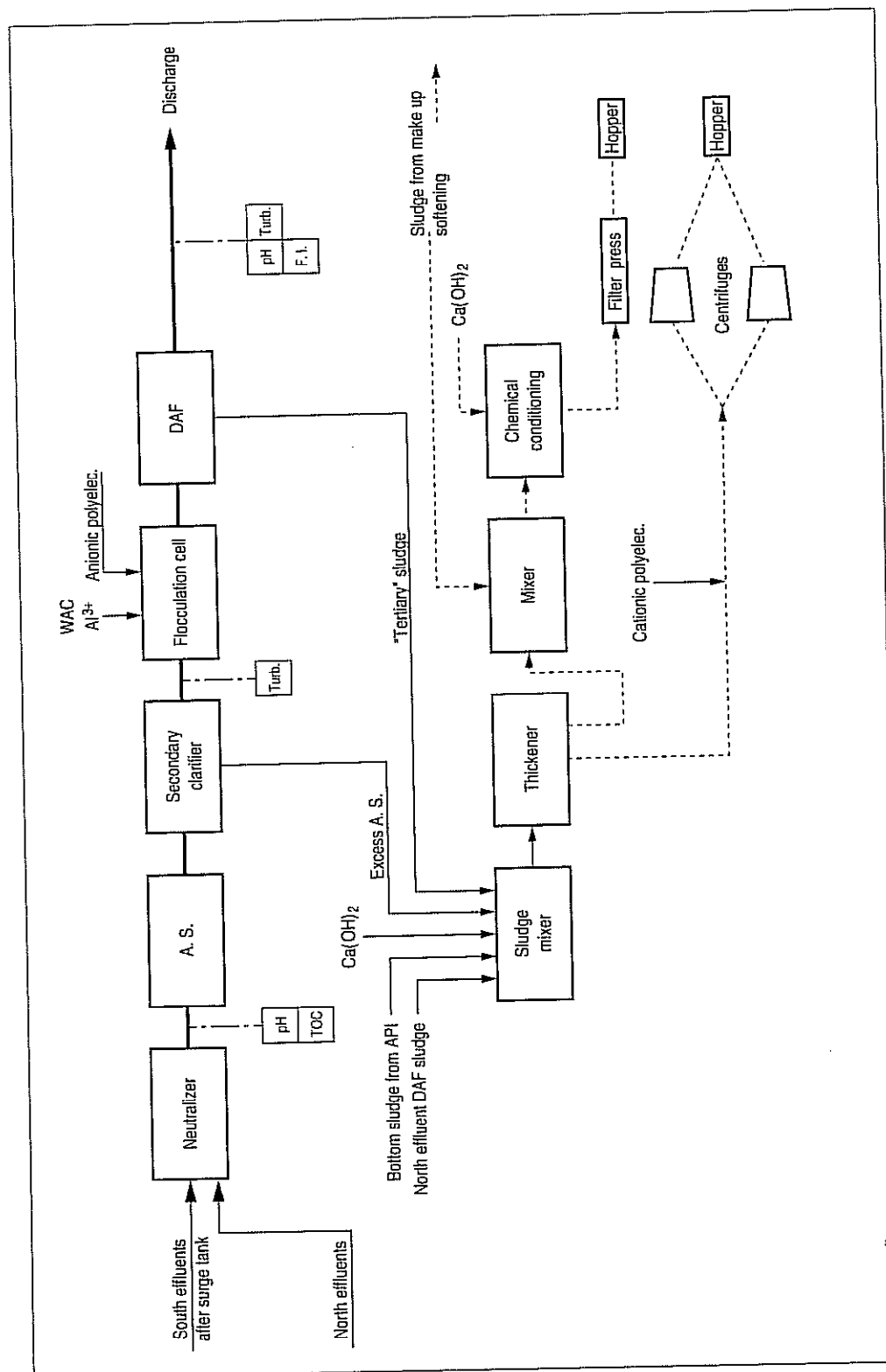


Fig. 69 Shell complex in Berre (petrochemical part). Biological treatment and dewatering of sludge.

6.5.3 Sludge treatment

Excess organic sludge and flocculation sludge from the two DAF on site go directly to a general thickening tank. Lime conditioning is used to vaccinate against foul-smelling biological growth and is conducive to sludge flocculation. Most of the sludge is mixed with make up water softening sludge, it undergoes further lime treatment and is fed into a filter press operated during the day. Sludge from the filter press amounts to 10 to 12,000 t·y⁻¹ with 50% dryness.

Under continuous operating conditions, the rest of the sludge is dewatered by two continuous centrifuges. They treat only sludge from the thickener after it has undergone specific polyelectrolyte conditioning.

Centrifugation sludge amounts to 3 to 4000 t·y⁻¹ with 20% dryness.

The sludge removed from the filter press and the centrifuges is dumped.

The oil skimmed off on the surface of the API separator is partly reprocessed in the refinery and the rest is incinerated.

6.5.4 Cooling systems

The Aubette plant system (steam cracking and hydrotreating) is used as an example (Fig. 70). Its heat exchangers are made of stainless steel and the Cl⁻ content can be kept lower than 4 meq·l⁻¹ by make up water from the canal, despite a concentration rate of 4.5 to 5.

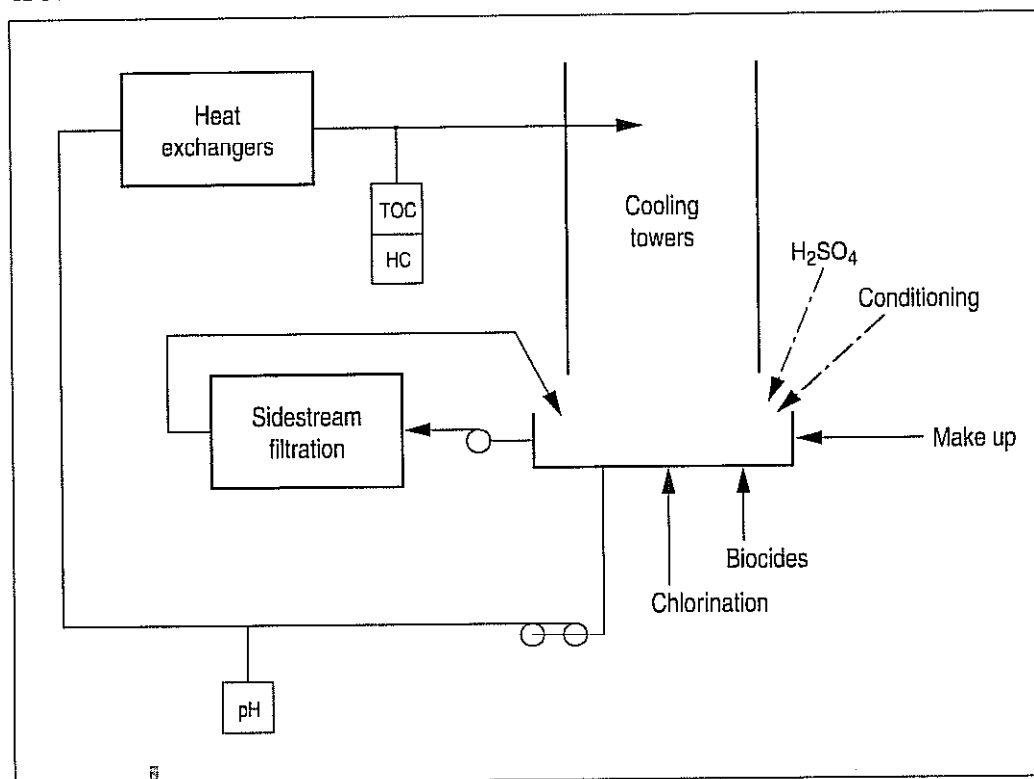


Fig. 70 Cooling systems in the Aubette plant

Chemical conditioning is based on acid vaccination of the canal water which is used without being softened. The chemicals utilized are a combination of phosphonate, zinc and acrylic dispersing agent.

In this as well as the other systems in the complex, biological growth is controlled in a number of ways. These include algicide treatment, periodical chlorination, addition of biocides, detection of leaks (certain products, e.g. propylene), and in-system measurement of HC by a sensor.

The system is of course equipped with side-stream filtration. The flow rate is about 5% of the circulating flow, i.e. $1350 \text{ m}^3 \cdot \text{h}^{-1}$.

Table 53

Operating characteristics

Parameters	Make up before vaccination	System
System volume (m^3)	—	13,000
Flow rate ($\text{m}^3 \cdot \text{h}^{-1}$)	400	27,000
Type of make up	Clarified canal water	
Concentration rate	—	4.5 to 5
pH	7.8 to 8.4	8.2
M alk ($\text{meq} \cdot \text{l}^{-1}$)		2.7 0.3 to 0.6
Hardness ($\text{meq} \cdot \text{l}^{-1}$)	4.3	18 to 20
Cl^- (ppm)	21.3 to 24.8	<142
SO_4^{2-} (ppm)	76.8 to 86	480 to 672
SS ($\text{mg} \cdot \text{l}^{-1}$)	<10	5 to 10
Conditioning	Acid vaccination	Phosphonate + zinc + dispersing agent

6.6 Disposal of sludge

As far back as the 1960s, sludge disposal was already regulated by a number of constraints. This prompted the construction of many on-site incineration units in refineries.

Then high investment and operating costs for these units made operators look into other solutions such as controlled discharges, incineration along with garbage and applications in landfill or land farming. All these solutions were also influenced by growing costs and tougher regulations. Finally, segregation of the sludge into different categories was often required, because each one could have its own disposal method.

6.6.1 Categories of sludge

The sludge produced by a refinery varies widely and can even include dense liquors or nonoily wastes, in addition to the sludge coming from make up water treatment.

The following breakdown can be made:

■ **Oily "floating" sludge from effluent treatments**

- Slops from gravity separators.
- Flotation sludge.
- Excess biological sludge, when it represents a small fraction of this category or when it is slightly oily.

■ **Dense oily sludge often loaded with sand or silt**

- Tank and vessel bottoms.
- API separator and drain pit bottoms.
- Sediments from desalters.

■ **Nonoily sludge**

- Make up water clarification or lime softening (CaCO_3 , hydroxides).
- Alkylation residues.
- Spent catalysts.
- Bleaching earth.
- Excess activated sludge, when its proportion is predominant.

6.6.2 Amounts discharged

Depending on whether the type of sludge involved is insufficiently thickened or dewatered in a filter press, humidity can vary from 95 to 50%. The corresponding volume is also extremely variable as illustrated by the sludge production listed for the five refineries discussed earlier. For partly centrifuged sludge, production nevertheless generally ranges from 0.6 to 2.5 liters per cubic meter of crude entering the refinery.

It may be of interest to focus on some data from the CONCAWE study in 1989 as summarized below. The study (CONCAWE Report 5189-5/1989. Oil Refinery Wastes Survey) involved 75 European refineries processing a total of 400 million tons of crude with 2 kg of sludge produced per ton of crude in 1986.

Sludge humidity was high and variable and the mass breakdown was as follows:

• Separators and flotation cells	44%
• Activated sludge	18.5%
• Tank bottoms	8.2%
• Make up water treatment	20%
• Alkylation residues	0.2%
• Oil leaks	2.2%
• Miscellaneous	5.1%

Of this total, 83% presumably underwent a dewatering treatment enabling concentration by 4.5 times. This factor was achieved by the following three processes each with its corresponding factor:

- Simple thickening by gravity: 1.6 times.
- Centrifuging: 5.9 times.
- Filter press: 7.3 times.

Of course the choice of these techniques is limited by the presence of and concentration in oil. It depends on the ultimate use to be made of the sludge and transportation costs. Transportation is often a determining factor and may require filter press dewatering, if it is possible, whereas simple thickening would otherwise be suitable.

6.6.3 Ultimate sludge disposal

There are two main types of methods:

Nondestructive

- Open controlled discharge (landfill).
- Burial (Canada) which requires more severe dewatering.
- "Land farming" of oily sludge (in North America and Northern Europe) on abandoned land. After the sludge is spread, it must be plowed under periodically to promote aerobic digestion (250 to 350 m³ of sludge per hectare for one or two eight-month periods).
- Spreading oily sludge as an organic soil-improver for farmland. This is allowed for some crops and requires limited concentrations in heavy metals or even polyaromatic hydrocarbons. This is also true for some of the previously-mentioned processes (see AFNOR standard U 44-041).

Destructive

- In situ incineration or incineration along with household refuse. This may require dewatering the sludge until self-combustion conditions are achieved. This is the most common process.
- Injection in wet-process cement factories.
- Anaerobic digestion which can only involve excess biological sludge in large volumes.

6.6.4 Dewatering equipment

The equipment is well known and so only a few of its features for refining industry use will be pointed out.

The equipment includes:

- Dissolved air flotation cells.
- Continuous centrifuges.
- Filter presses.
- Possibly, belt filters.

6.6.4.1 Dynamic thickening by dissolved air flotation

Static thickening by simple settling is used for fairly dense nonoily sludge. It is effective for softening sludge, but much less so for activated sludge, where concentrations of 25 to 35 g·l⁻¹ can be achieved. Thickening oily sludge in a static thickener is unreliable because of the three-phase separation that occurs.

The use of DAF for dynamic activated sludge thickening has only recently become common. It allows concentrations of 40 to 70 g·l⁻¹ under direct pressurization at a mass load four to five times higher (120 to 180 kg of DS per m²·d⁻¹) than by gravity settling.

The construction of a DAF thickening unit is often not justified in refineries, but is more advantageous in petrochemical plants.

6.6.4.2 Continuous centrifuges

This continuous technique requires very little labor. It is the most economical and common way of dewatering oily sludge, despite poorer cake dryness performance.

The equipment has a horizontal cyliandroconical bowl and for this application it usually works with countercurrent circulation of the sediment and the centrate. A relative velocity of the bowl and the extraction screw of 3 to 30 rpm regulates the sediment compaction time. Accelerations vary between 1000 and 1500 G.

Treatment includes the following steps:

- Screening through strainers with openings designed according to centrifuge characteristics.
- Possibly desanding (cyclone). This is because centrifuging the sludge from softening, which is too rich in abrasive or plugging sand, is to be avoided.
- Conditioning by a polyelectrolyte is imperative. It is distributed in a very dilute form with ionic capability opposed to that of the sludge. The dose is from 1 to 3 kg per ton of dry solids.

Feasible percentage recovery is:

- With coexisting metallic hydroxides (DAF):
 - Dry solids 90 to 95%
 - Oils 50 to 70%.
- In the absence of hydroxides (bottom sludge):
 - Dry solids 85 to 90%
 - Oils 40 to 60%.

The dryness achieved also depends on the sludge:

- Nonoily sludge with Al or Fe flocculation 20 to 26%
- Oily sludge from API separator bottoms 30 to 40%
- Mixed biological sludge 18 to 25%
- Oily sludge with flocculation by polymer alone 25 to 40%.

In the last example, a well-designed and well-run DAF unit can deliver scum with a dryness figure of 15 to 25% directly. This makes centrifuging unnecessary later on.

Discontinuous vertical centrifuges can be used in some countries. They are more expensive and troublesome to operate (may become unbalanced). Without the use of polymers, they can give a three-phase separation of sediments with lowered oil content and oils emulsified in the centrate. The centrate must then be settled statically.

6.6.4.3 Filter presses

Filter presses give maximum cake dryness and lend themselves readily to different types of sludge. However, they usually require some manpower for operation and this may hinder continuous use and increase the costs.

When substantial amounts of oil are present (over 15% dry solids), the cloth may quickly become fouled. Despite prior lime conditioning, a considerable fraction of the oil can migrate into the filtrate and require recycling.

The cloth is cleaned by steam in a few hours or by detergent solutions.

Chemical conditioning of the sludge depends on its composition:

	Conditioning		Dryness
	Fe/DS	Ca (OH) ₂ /DS	%
Activated sludge	3-5%	20-30%	30-36
Hydroxide sludge (Oils < 15% DS)	No	6-12%	45-50
Softening sludge	No	No	50-60

6.6.4.4 Gravity-fed belt filters

These filters are widely used with biological sludge. They need only polyelectrolyte conditioning (3 to $5 \text{ kg} \cdot \text{t}^{-1}$ of DS) and lend themselves to **continuous** operation. They have few manpower requirements but yield a cake with only moderate dryness:

- Activated sludge 16 to 22%
- Hydroxide sludge 17 to 20%
- CaCO_3 45 to 55% .

For oily sludge (5 to 10% oils measured on DS), i.e. in refineries, there are references but they are few and far between. This is because operation is based on the need for continuous dual body feeding:

- Granular, hydrophobic material (fly ash, diatoms, catalysts), from 25 to 30% on DS + oils.
- Inorganic coagulant, from 1 to 2% Fe or Al on DS + oils.

Added polymer remains from 1.5 to $3 \text{ kg} \cdot \text{t}^{-1}$ of DS + oils.

Under these conditions, cake dryness may reach 40 to 45% .

The lifetime of the cloth can be short (abrasion, plugging, etc.) ranging from 2000 to 4000 hours.

6.6.4.5 Producing less sludge

Sludge production generates increasing direct dewatering, transportation and disposal costs. It also means indirect costs related to the disposal of the sludge when it is segregated and stored.

Cutting down on sludge production entails acting either on the mass of DS generated, or especially on the initial concentration, which is often too low.

Reductions in DS can be achieved by replacing Al or Fe by an organic coagulant in flocculation, if the treatment allows. Another possibility is not to discharge and dilute spent caustic in hard cooling water, where it precipitates carbonate hardness massively.

Boosting the concentration is easier to plan and more feasible:

- Collect oils with 5 to 10% humidity with oil collector drums rather than with adjustable troughs.
- Decrease light sludge recycling (filter washings, DAF, scum, emulsions from slop tanks) upstream from gravity separators, as sludge hampers their efficiency.
- Keep sludge from falling when it is let into tanks in order to prevent oxygenation and emulsion.
- Eliminate alkaline discharges (spent caustic) that promote emulsions.

There is often an intermediate layer made up of a water-in-oil emulsion in slop tanks. It is at the root of serious problems and may have a number of causes:

- Emulsion build up by recycling and pumping insufficiently concentrated surface oil too often.
- Recycling filter washing water that is rich in fine, aerated SS. It should be sent to a DAF unit beforehand.
- Aging and polymerization by oxidation of olefinic HC.

The slop tanks can be heated to 40 - 45°C or a little higher (60°C), except when regulated for safety reasons, and the intermediate emulsion layer can be recycled upflow through a granular coalescer if the layer is not rich in SS. An attempt should also be made to keep naphthenic

and asphaltenic HC in specific slop systems, since they tend to generate emulsions. The use of continuous centrifuges, in series with disk centrifuges can also improve emulsion separation down to 30-15% H₂O.

6.7 **Monitoring purification plants**

Cuts have had to be made in operating personnel and in the cost of sampling and laboratory analysis. As a result, there has been wider use of a variety of sensors and analyzers. Despite enhanced reliability, they are better suited to monitoring by alarms and indications of trends than to regulating. Regulating still remains the domain of pH-meters (neutralization) or redox-meters (oxidation).

Sensors located on final effluent discharges usually deal with a parameter and a protocol imposed by regulations governing discharges (COD, HC, TOC, etc.). Meanwhile, at intermediate steps in the system, there can be other parameters that are more readily utilized in operations and/or simpler measurements (turbidity, TOC, etc.).

The choice of sensors therefore depends on a number of considerations and operating costs are certainly not the least important. Costs may stem from cleaning the probes, but chiefly from maintenance of sampling loops (filters) and analyzers involving several reagents.

Depending on the complexity of loops and equipment, yearly maintenance time per sensor can range from 24 to 250 hours and should not be disregarded.

Some analyzers must be located after 100 to 150 micrometer filtration and a fraction of the pollution in suspension, or even colloidal pollution is consequently separated.

Reliability studies and even lists of available sensors depend on companies or countries. As a result, it seems advisable to point out only the scope of some of the commonly used devices and discuss how their applications interact in dealing with IWW.

6.7.1 **Measuring hydrocarbons**

■ HC detection by IR spectrophotometry

- HC extraction by a solvent (CCl₄, freon).
- Polar compound removal (Florisil).
- 3.42 micrometer IR measurement (AFNOR T 90-203).
- Cycles lasting some ten minutes.
- Applied to refinery WW in a regulatory context.

■ Heavy HC measurement by UV fluorescence

The sensor measures the fluorescent light that is produced by certain HC and reflected at an angle of 90°.

This measurement usually detects heavy HC (>C₆) present in an emulsion or dissolved. It is continuous, but is based on prior calibration using discharged oils. It is particularly used on heating condensate systems for which there is no interfering foreign turbidity (SS), and which generally contain fairly heavy HC.

■ HC measurement by turbidimetry (UV absorption)

The technique involves in fact all the particles that produce diffusion of light, e.g. colloids and HC in emulsion that can not be dissociated. The measurement must be immediate and is continuous.

Light HC ($<C_6$) are chiefly measured. This simple sensor can serve as an alarm or as a trend indicator at the outlet of a DAF unit for example.

6.7.2 Measuring organic matter

■ Chemical oxygen demand COD

- OM oxidation by dichromate and concentrated H_2SO_4 at $100^\circ C$ with a reflux according to protocols that may comply with an AFNOR, ASTM or other standard.
- Possible loss of a certain fraction of very volatile compounds.
- Utilization of several reagents.
- Cycles lasting 10 to 15 minutes.
- Prior 125-150 micrometer sieving of the sample.

■ Total oxygen demand TOD

- Oxidation not only of OM but of Kjeldahl nitrogen as well, at high temperatures in an O_2 current in air. The reduction in concentration is measured by detecting probes.
- Cycles lasting seven to eight or 3 to 4 minutes with or without dilution.
- Prior 125-150 micrometer sieving of the sample.

Some recent developments should be pointed out. They perform oxidation by a ozonized air current whose O_3 concentration is measured by a specific probe (the sample is sieved at 0.5 mm).

■ Total organic carbon TOC

- Oxidation, either chemically and with UV or in a furnace at $900^\circ C$, then the CO_2 produced is measured by IR.
- Cycles lasting 5 to 12 minutes depending on the device.
- Possible loss of volatile compounds when inorganic CO_2 is stripped.
- Prior sieving of the sample (125 micrometers).

■ "Volatile organic solvent" measurement

Here the aim is to assess the presence of volatile HC (BTX, paraffins up to C_7 , etc.), halogenated HC, alcohols (isopropanol) or ethers that may be dissolved and in large concentrations.

The automatic system air strips these volatile compounds which are then detected by a specific analytic probe.

The advantage is that the device rapidly detects significant leakage of these compounds in condensates or process water.

6.7.3 pH-meters

Antimony or antimony oxide electrodes with continuous cleaning by corundum blades may be used for slightly oily water (outlet of API oil separator or DAF). However, they are sensitive to overly wide variations in redox potential. In this case, a probe with a glass electrode and ultrasound cleaning may be preferred but it is more sensitive to greases.

6.7.4 Miscellaneous devices

■ Sulfide meters

There may be a potentiometric discontinuous titration measurement, with a Ag-Ag Cl probe, in two or three way automatic systems (measurements every 10 or 15 minutes).

■ Conductivity

- For clean water, such as boiler condensates, conventional two-electrode probes.
- With saline or accidentally salty and oily water, there is a risk of rapid electrode polarization. An inductive measurement, without electrodes, is required (deconcentration of cooling systems).

■ Phenol meters

Analyzers with DAAP and photocolorimetry, as per AFNOR standards.

Conditioning of cooling system water

Chapter

7

7.1 Different types of systems

7.1.1 Once-through system (Fig.71)

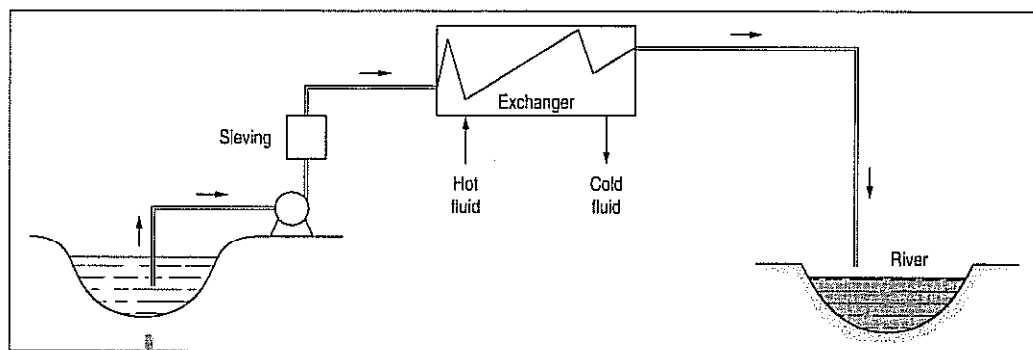


Fig. 71 Once-through system

Cold water is pumped from a river, a well or the distribution network. It flows through the hot point (exchangers, apparatus requiring cooling, etc.) and is then discharged into the river or the sewer.

7.1.2 Closed recirculating system (Fig.72)

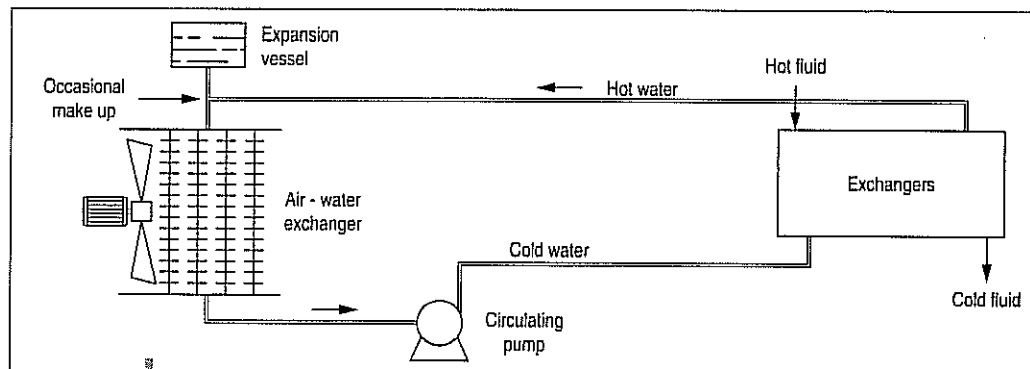


Fig. 72 Closed system

The cooling water circulates in a totally closed system. The system loop is equipped with a cooling point, e.g. a second water-water or water-air heat exchanger.

The most typical example is water-cooled thermal engines.

Water losses should be minimal (leaks, etc.).

Theoretically, there is no contact with the air

7.1.3 Open recirculating system (Fig.73)

The water is recirculated, but it is cooled by evaporation and convection when it comes into contact with the air in a natural or forced-air draft cooling tower.

This type of system is becoming increasingly common.

Specific case: the closed system may be cooled by the recycled pressurized coolant being sprayed from the outside.

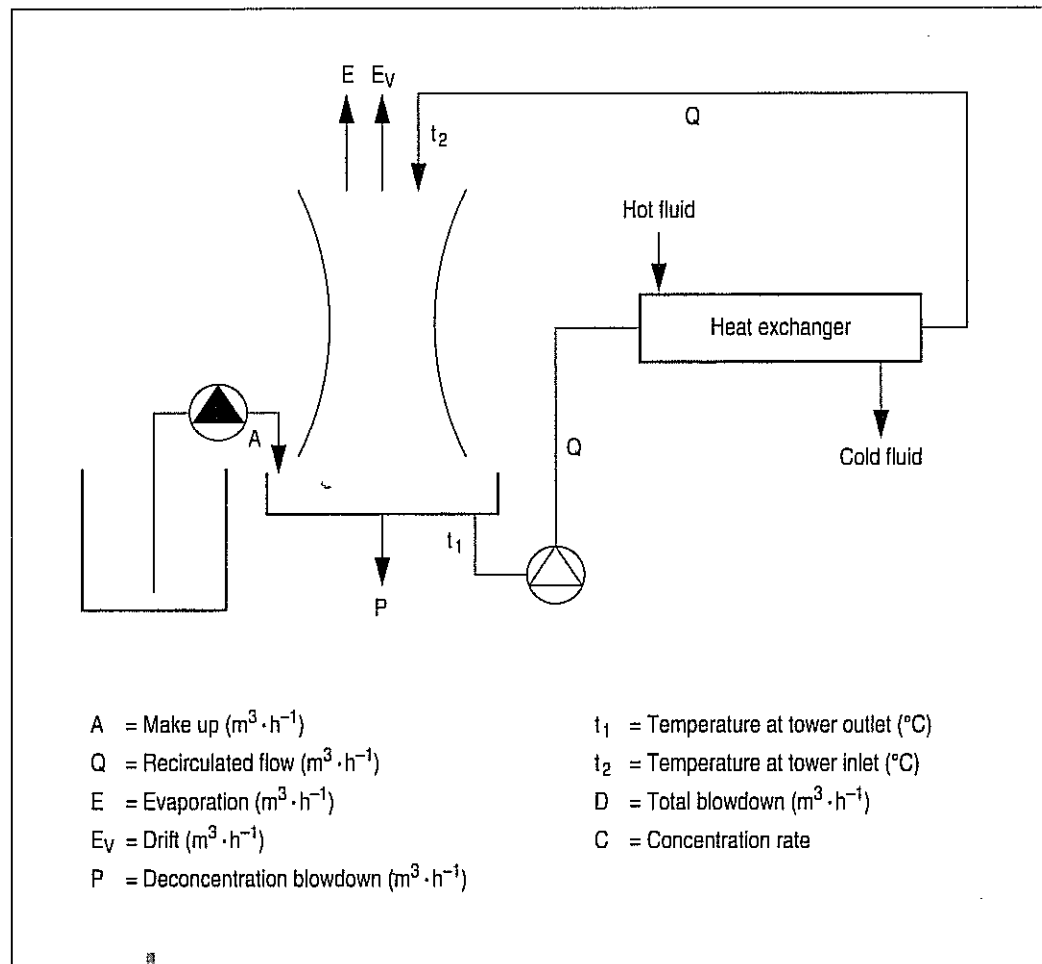


Fig. 73 Open recirculating system with cooling tower

7.2 Main characteristics of an open recirculating system with a cooling tower

All systems are characterized by a number of parameters that need to be known before a treatment or conditioning process is chosen for application to the water.

The parameters are as follows:

■ **System volume:** $V(\text{m}^3)$

The total amount of water contained in the system (basins, piping, exchangers, etc.).

■ **Circulation flow rate:** $Q (\text{m}^3 \cdot \text{h}^{-1})$.

■ **Difference in temperature:** $\Delta t = t_2 - t_1$

The difference between the temperature of the water at the inlet and at the outlet of the cooling tower.

■ **Cooling tower power:** $W (\text{kcal} \cdot \text{h}^{-1})$

This parameter is expressed by the product: $W = 1000 Q \Delta t$.

■ **Maximum temperature:** ($^{\circ}\text{C}$)

The temperature of the film of water ("skin" temperature) in contact with the hottest wall in the system.

■ **Evaporation flow rate:** $E (\text{m}^3 \cdot \text{h}^{-1})$

The flow rate of the water that evaporates in the tower to cool the water in the system. The evaporation flow rate is pure water that has entrained no dissolved salt. It is estimated by the approximate equation:

$$E = \frac{Q}{560} \Delta t$$

with 560 kcal.kg corresponding to the generally acknowledged value of the latent heat of vaporization of water (which is often brought down to 500 in estimates).

■ **Drift loss flow rate:** $E_v (\text{m}^3 \cdot \text{h}^{-1})$

The flow rate of water entrained into the atmosphere in the form of finely divided droplets.

Unlike evaporated water, this water has the same chemical composition as the water in the system. As a result, it is taken into account in calculating blowdowns.

E_v varies depending on the design of the cooling tower.

When towers are designed, there are increasing efforts to keep drift losses to a minimum. The equation $E_v = Q/1000$ is generally used with values that can range from 0.1 to 0.001% of Q depending on the efficiency of the droplet recovery system.

■ **Deconcentration blowdown flow:** $P (\text{m}^3 \cdot \text{h}^{-1})$

Evaporation brings about an increased concentration of dissolved salts in the water circulating in the system. So as to stop this concentration from becoming too high which could thus result in various sorts of deposits, some of the water in the system must be drawn off and sent to the sewer. This is the deliberate blowdown P .

■ **Total deconcentration flow: D ($\text{m}^3 \cdot \text{h}^{-1}$)**

The sum of flows from drift loss E_v , from blowdown P and from a variety of water losses P' that can exist in the system. Some examples are secondary or uncontrolled leaks, windage, supply to sensors and samplers, etc:

$$D = E_v + P + P'.$$

■ **Make up flow: A ($\text{m}^3 \cdot \text{h}^{-1}$)**

This flow compensates for all of the water losses from the system, i.e. evaporation + total deconcentration:

$$A = E + D.$$

■ **Residence time: T**

This parameter corresponds to the period of time elapsed when the concentration of a product injected at an initial time T_0 has decreased by half:

$$T = \frac{V}{D} \times \text{Log}2 \approx 0.7 \frac{V}{D}.$$

■ **Concentration rate: C**

The ratio of the dissolved salt concentration in the system water and in the make up water:

$$C = \frac{\text{System salinity}}{\text{Make up salinity}}.$$

The concentration rate is usually determined by measuring the chlorides, which are easy to analyze and are the most stable in the system because of their solubility. Of course, all products containing chlorides that are added to the system must be taken into account. They could influence the measurements and throw off interpretations. Extra chlorides could come from HCl, chlorine bleach, etc.

A material balance can be set up:

- Salinity of the make up water: S ($\text{g} \cdot \text{m}^{-3}$).
- Salinity of the system water: $C \times S$.
- Input amount of dissolved salts: $S \times A$.
- Output amount of dissolved salts: $C \times S \times D$.

The last two amounts should be equal:

$$S \times A = C \times S \times D$$

hence:

$$C = \frac{A}{D}$$

and, since $A = E + D$:

$$D = \frac{E}{C-1}.$$

■ **Types of heat exchangers:**

- Design: tubular, plate, etc.
- Water circulation: internal, external, velocity.

■ **Materials in contact with the water**

Steel, stainless steel, copper and its alloys, aluminum, concrete, wood, etc.

7.3 Problems and their causes

The operator of a cooling system has to deal with three types of problem:

- Fouling and biological growth.
- Scale formation.
- Corrosion.

The situation is often compounded by interaction among the three. They have a direct impact on heat exchange efficiency, on the operation of the apparatus requiring cooling and on the lifetime of the system.

7.3.1 Fouling and biological growth

What is involved here are compounds that may readily form deposits in cooling systems, excluding scale as such, and corrosion products. The following can be mentioned:

■ Suspended solids

Dust, clay, sand, etc. can form deposits in zones where the flow slows down or where the cross-sectional area is small.

■ Colloidal matter

Colloids coagulate as the temperature rises. As a result, they tend to form a layer on heat exchanger surfaces and hinder proper heat transfer.

They are often the main cause of system fouling, whether they come from the make up water or from the air in the cooling tower.

The most detrimental colloids are the wastes from the metabolism of living organisms. Algae and bacteria produce fatty acids that are very sticky and adsorb suspended particles.

These colloids have large unstable molecules. A mere increase in temperature is enough for them to coagulate in a viscous, gelatinous mass. This explains the accumulations that are found especially on heat exchangers, i.e. where the water is the hottest.

The color may vary from gray to black or reddish-brown, depending on the nature of adsorbed matter.

■ Organic matter

This serves as nutrients for algae and bacteria.

■ Algae

They find a favorable environment for growth in the basins under cooling towers (O_2 , CO_2 , temperature, sunshine, etc.). Their presence can be noted by greenish, often filamentous, masses attached to the walls of the basins.

They can plug up the system when they are carried off by circulating water. The main types are:

- Green algae (Chlorophyceae).
- Brown algae (Cyanophyceae).
- Diatoms, which often produce silica deposits.

■ Bacteria

These are living organisms which, depending on the species, develop in:

- Aerobiosis (e.g. ferruginous bacteria).
- Anaerobiosis (e.g. sulfate-reducing bacteria).
- Mixed environments.

Under the influence of nutrients, they can often multiply at a great rate.

They can produce deposits which, when viewed under a microscope, are characterized by masses with moving microorganisms in the shape of spheres, rods, chains and vibrios, etc. They may produce slime, deposits of iron oxides, corrosion and acidification (H_2SO_4 , HNO_3 , etc.).

The most common bacteria are of the aerobic type. They are less detrimental per se than by their secondary effects:

- They create an environment that promotes the growth of sulfate-reducing bacteria (source of corrosion). Though these are of the anaerobic type, they can develop in symbiosis with aerobic bacteria.
- The waste products from their metabolism loads the water with colloidal matter that coagulates on hot walls and provides nutrients for other living organisms.

■ Filamentous fungi and yeasts

They have the same effect as agglomerating bacteria (gelatinous deposits) and in addition attack wood (cooling tower). They form a gelatinous blackish layer on wet surfaces.

Fungi are nonchlorophyllic, aerobic plants whose optimum pH for growth is between 2 and 7.

■ Hydrocarbon leaks

Leaks come from the process line and are nutrients for some bacteria.

As to the origin of fouling, three main sources of pollution are involved:

- The make up water depending on where it comes from. For example, surface water will often contain suspended solids, colloids and microorganisms. Well water can be loaded with iron which can promote the growth of ferruginous bacteria in the system.
- Air from the atmosphere. The cooling tower functions like an air scrubber where around 500 to 1000 m^3 of air circulates per cubic meter of water. Depending on the environment of the site, the pollution removed from the air can be made up of mineral and organic dust, sand, smoke, gases and microorganisms.
- The processes. As the water cools the various types of apparatus, it may become loaded in material of widely variable nature depending on the process. For example, hydrocarbons in petrochemical plants, scales in the iron and steel industry, calcium salts in cement factories, silicates in glass works and fibers in paper mills.

In actual fact, the different types of mineral and organic fouling are usually associated or adsorbed mutually and form viscous-looking sludge or slime that is often found in heat exchangers.

The resulting drawbacks are:

- Heat exchanger, piping and cooling towers become fouled and consequently the water flow rate and cooling efficiency decline.
- Deposits are produced with corrosion risks underneath due to "differential aeration".
- Biological-type corrosion is possible.

Figure 74 helps situate and compare the size of the different particles found in water.

Table 54 recapitulates the problems created by different types of fouling.

Table 55 summarizes the problems encountered with biological growth and the action it exerts.

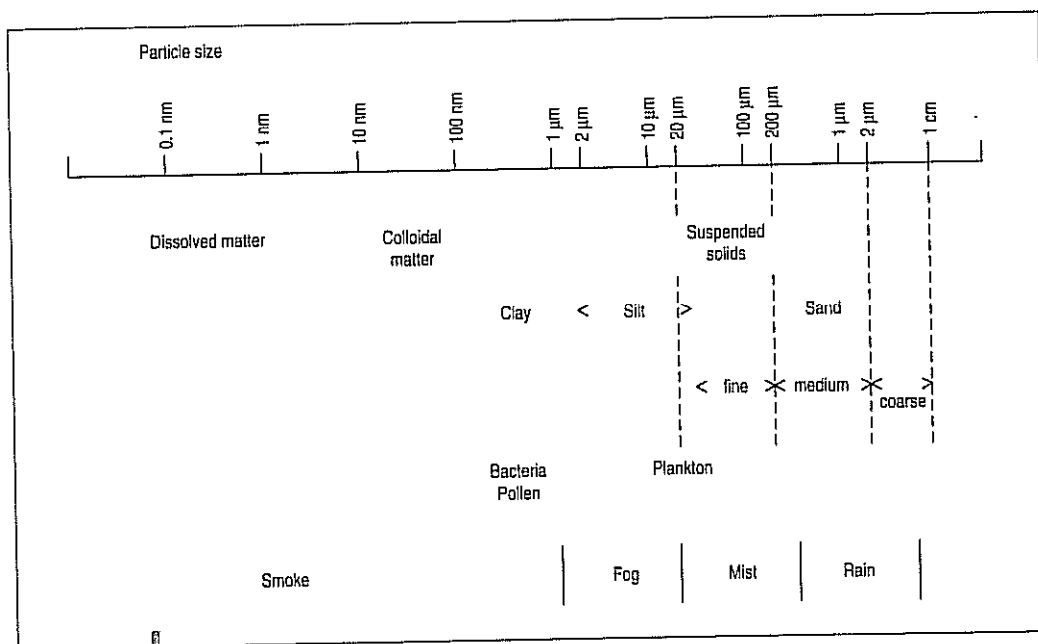


Fig. 74 Sizes of various particles

Table 54
Fouling

Types	Problems
Suspended solids Dust Clay Sand Iron oxides, scales	Deposits Erosion Excess inhibitor consumption Corrosion under deposits
Colloidal matter	Fouling (thermally insulating film)
Organic matter	Nutrients for algae and bacteria
Algae	Plugging
Bacteria	Fouling (slime) Corrosion Acidification Colloids
Filamentous fungi and yeasts	Gelatinous deposits Attack wood
Hydrocarbon leaks	Fouling Nutrients for microorganisms
Origins: • Make up water • Surrounding air • Corrosion	• Microorganisms • Processes (hydrocarbons)

Table 55

Problems created by biological growth

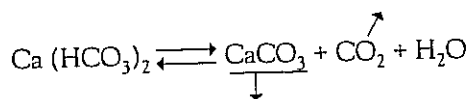
Organisms	Action exerted		Problems encountered
Algae	→ Trap SS and colloids	→ Slime (sludge)	→ Coloring Deposits Plugging Clogging Corrosion under deposits
Fungi			→ Gelatinous deposits Attack wood
Bacteria	→ Masses	→ Slime	→ Corrosion under deposits
Ferruginous bacteria (aerobic)	→ Promote (anodic depolarization)	→ $Fe^{2+} \rightarrow Fe^{3+}$	→ Deposits Corrosion under deposits
Sulfur bacteria	→ Acidification (	→ H_2SO_4)	→ Sludge/odors Acidification Corrosion
Sulfate-reducing bacteria (anaerobic)	→ Reduce sulfates (cathodic depolarization)	→ H_2S	→ Electrochemical corrosion
	→ Promote (anodic depolarization)	→ $Fe^{2+} + S^{2-} \rightarrow FeS$	→ Deposits Corrosion under deposits
Nitrosobacteria (aerobic)	→ Promote	→ $NH_4 \rightarrow NO_2 \rightarrow HNO_2$	→ Acidification Corrosion
Nitrobacteria	→ Promote	→ $NO_2 \rightarrow NO_3 \rightarrow HNO_3$	→ Degrade nitrite-base inhibitors

7.3.2 Scale build up

Scale results from crystalline precipitation on metal surfaces with the formation of a hard bonded crust.

Calcium carbonate

This is the first salt likely to precipitate out in water, according to the following reaction:



The shift in equilibrium to the right with formation and crystallization of calcium carbonate is influenced by:

- A rise in temperature which has a dual action.
- The elimination of CO_2 in the cooling tower due to the low CO_2 partial pressure in air.
- The concentration in dissolved salts (especially the effect of Ca and M alk).

Calcium sulfate

The solubility of this salt increases as the temperature rises, reaches a maximum at $40^\circ C$ and then decreases.

Fig. 75
Solubility product SP of calcium sulfate
in pure water versus temperature.
(Water Treatment Handbook, Degremont, 1989)

Figure 75 shows precipitation curves for calcium sulfate versus temperature and the three corresponding crystalline forms.

Generally speaking, it can be said that in a cooling system with extreme temperatures lying between 10°C and 80°C there is no risk of calcium sulfate precipitation if:

$$\text{Ca meq} \cdot \text{l}^{-1} \times \text{SO}_4 \text{ meq} \cdot \text{l}^{-1} < 600$$

(in $\text{meq}^2 \cdot \text{l}^{-2}$)

However, it should not be forgotten that the "skin" temperatures of the heat exchangers (i.e. the temperatures prevailing right at the metal-water

contact point) must be taken into account. It is easy to understand the difficulties caused by deposits that form local hot spots in furnace cooling systems, with accelerated precipitation of calcium sulfate (from 130°C on, its solubility product can drop to lower than 40).

In natural water, the calcium sulfate content is generally fairly low. In contrast, in recirculating cooling water, the SO_4^{2-} and Ca^{2+} ion content can become such that the solubility product is exceeded. This is due to the concentration of dissolved salts and any injection of sulfuric acid (to prevent formation of calcium carbonate).

Once it has formed, calcium sulfate redissolves only very slowly in the circulating water.

Silica

Silica is found in water in several forms:

- Ionized SiO_2 , as measured by routine chemical methods.
- Colloidal SiO_2 which escapes detection by conventional analysis methods.
- Calcium or magnesium silicoaluminates (clayey water).

At low pH values and high temperature silica solubility is very low. Silica scale is very hard, strongly bonded and insulating.

In cooling systems operating at a low pH (6.4/7), the total SiO_2 concentration is kept down to $150 \text{ mg} \cdot \text{l}^{-1}$ to prevent scale formation.

The presence of alumina also promotes the formation of highly insulating Ca and Mg silicoaluminate-based scale.

Whatever the origin, scale is conducive to the formation of deposits which affect heat exchanges and efficiency in the unit. In addition, corrosion can develop under the deposits.

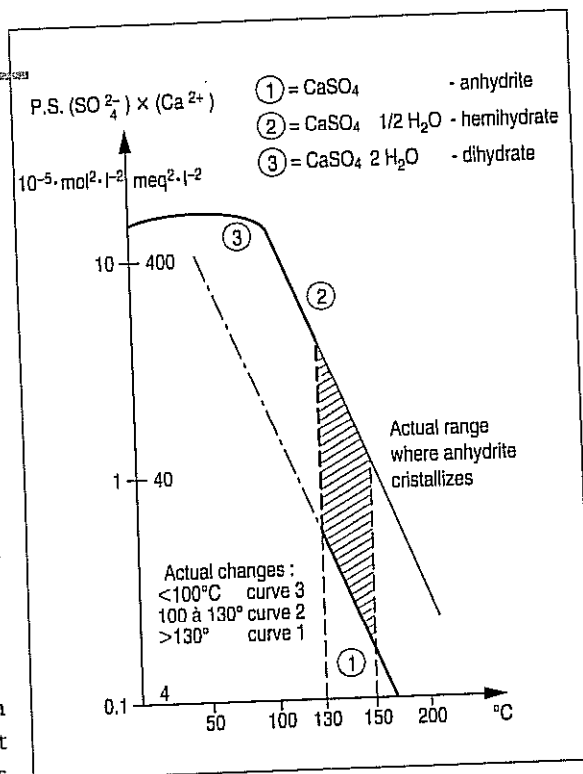
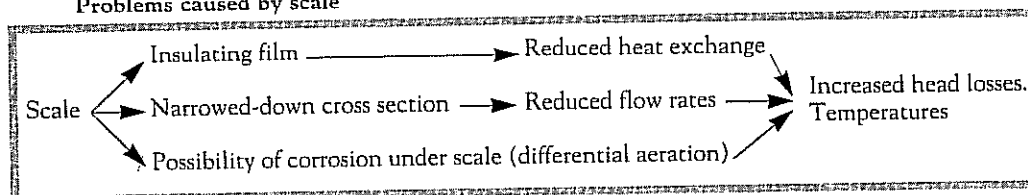


Table 56 summarizes the main problems caused by scale.

Table 56

Problems caused by scale



7.3.3 Corrosion of steel

Corrosion means a degradation of metal as a result of a reaction with the surrounding medium.

It is always related to an electrochemical phenomenon.

7.3.3.1 Note on electrochemical corrosion in water

Iron is thermodynamically unstable in water and is only too ready to dissolve in it.

The slightest heterogeneity is enough to induce iron to go from the Fe state to the Fe^{2+} state, thereby initiating an electrochemical corrosion process.

The energy of iron ions is greater in the metal's crystalline network than in water. All systems tend to evolve toward a state of minimum energy as specified in the second principle of thermodynamics. The iron ions therefore tend to pass into the liquid phase.

When iron is in contact with an aerated solution (as is the case in systems with cooling towers), "microbatteries" are created giving rise to the following oxidation-reduction reactions:

- At the anode: $\text{Fe} \rightarrow \text{Fe}^{2+} + 2e$.
- At the cathode: $2e + \frac{1}{2}\text{O}_2 + \text{H}_2\text{O} \rightarrow 2\text{OH}^-$.

This mechanism of electrochemical corrosion is summarized in Fig. 76. The corroded metal functions as an electron supplier and serves as an anode. The oxygen captures the electrons and serves as a cathode.

The metal dissolves at the anode, while the cathode is protected.

7.3.3.2 Main influencing parameters

The various parameters listed below can not really be considered individually since they seldom change in an unrelated way. Additionally, they may have opposing effects on corrosion. However, an attempt has been made to isolate the major trends for each parameter.

■ Oxygen

As mentioned earlier, oxygen can serve as a cathode in receiving electrons. It can therefore be an important factor in the electrochemical process.

■ pH (and CO_2)

In cooling systems, the pH must be taken into consideration at the same time as the other parameters such as M alk and Ca. It is one of the bases of calcium carbonate stability.

In the presence of oxygen, it does not directly control corrosion especially since the water has a pH close to neutral in the system.

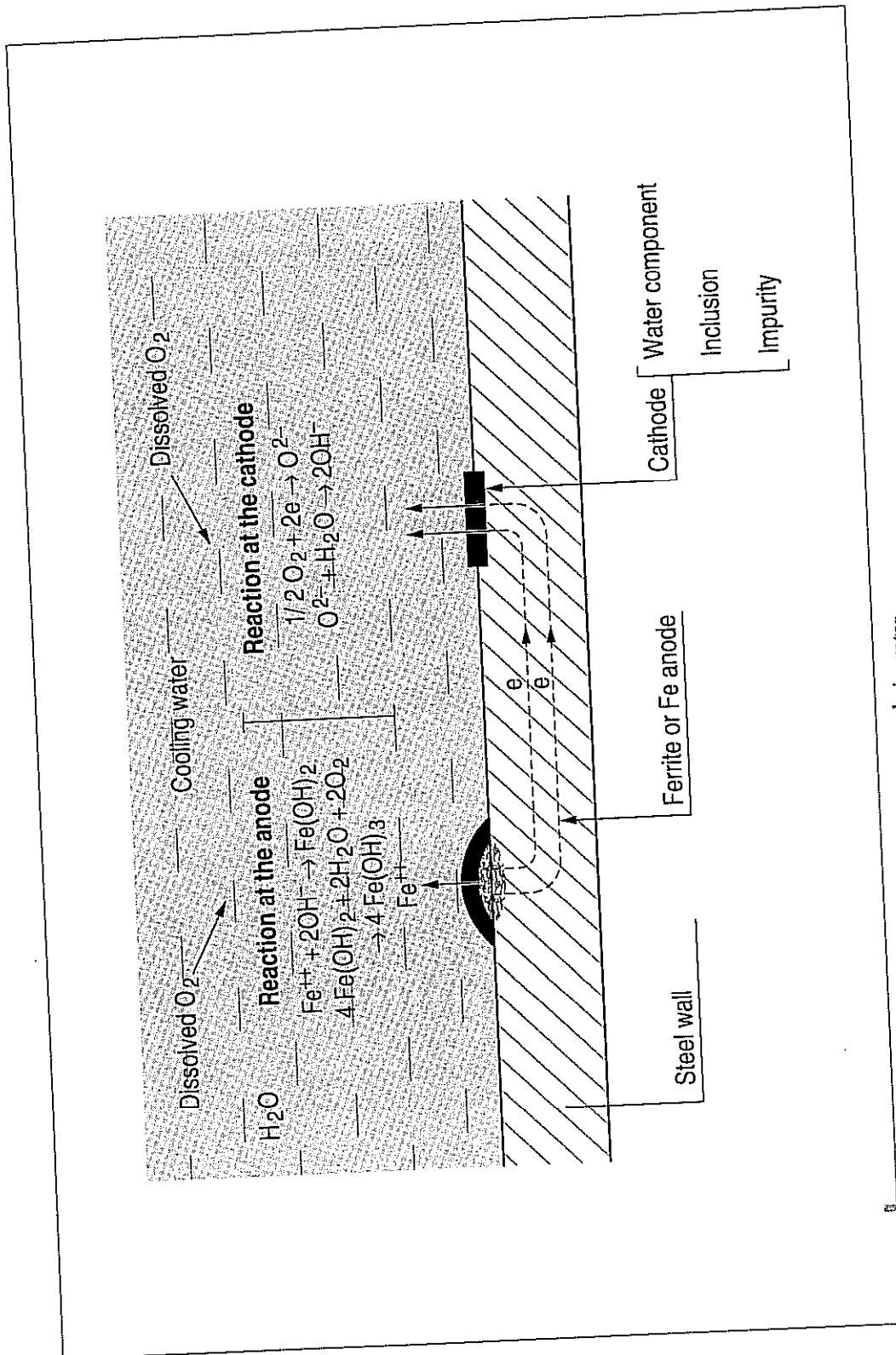
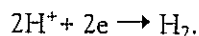


Fig. 76 Mechanism of electrochemical corrosion: steel-air-water

In contrast, for acidic water with a $\text{pH} < 4.5$ approximately, the risk of corrosion is much higher. The hydrogen cathode acts as illustrated by the following reaction:



Of course, in the absence of oxygen, the concentration in H^+ ions (and therefore the pH) becomes the determining factor.

■ Salinity

Generally speaking, the presence of dissolved salts in the water promotes corrosion as conductivity of the water is enhanced.

The type of ions present affects the process. It is the anions representing fixed salinity, SSA, in water that have the greatest influence (sulfates, nitrates and often chlorides).

■ Temperature

An increase in temperature will intrinsically accelerate the corrosion process, mainly by increasing ion mobility and hence the corrosion current.

In practice, the effect in systems is far more complex because the temperature also affects the calcium carbonate equilibrium. Temperature can shift the equilibrium toward increased scale formation.

■ Circulation rate

Generally speaking, the recommended rate in piping and exchangers is about $1 \text{ m} \cdot \text{s}^{-1}$ (0.5 to $1.5 \text{ m} \cdot \text{s}^{-1}$).

Excess water velocity can accentuate the corrosion current in different ways:

- Disturb protective layers.
- Erosion-abrasion if there are suspended solids.
- Cavitation.

Too slow a velocity can:

- Make fouling and corrosion under deposits easier (by differential aeration, etc.).
- Prevent diffusion of corrosion inhibitors at the metal-water interface.

■ State of surfaces

Since the corrosion process involves the creation of batteries, any heterogeneity will be conducive to the formation of anodes and cathodes. The following influences should be pointed out:

- Thermal treatments and mechanical stresses when the metal is worked (strain hardening, oxide formation, modification in crystalline texture, etc.).
- The start-up phase of a cooling system when cleaning and detergent treatments must be scheduled to prevent unwanted deposits.

■ Contact between different metals

Electrochemical couples are formed, the least noble metal will be the anode and will be liable to be corroded (e.g. copper-iron couple).

This is galvanic corrosion. It is particularly significant in high salinity ($> 1 \text{ g} \cdot \text{l}^{-1}$ of NaCl) and therefore more conductive environments. The greater the more noble/less noble contact surface is, the more the resulting corrosion.

■ Surrounding environment

An understanding of the environment of an open recirculating system is very important, as the cooling tower functions as an "air scrubber". Pollutants from the air can be:

- Inorganic and organic fouling.
- Microorganisms.
- Gases (H_2S , SO_2 , NH_3).

7.3.3.3 Main types of corrosion and causes

Types of corrosion are very numerous and operators seldom have to deal with one single corrosion factor, since several parameters can coexist. Basically, the following types can be distinguished:

■ Even or generalized corrosion

The surface of the metal is evenly corroded, as a result the metal becomes thinner.
Example: low pH (H^+ ions), CO_2 , erosion.

■ Local corrosion, characterized largely by:

- Plate-type corrosion, when the anodic surfaces are large in comparison with cathodic surfaces.
 - Pitting, when the anodic surfaces are small in comparison with cathodic surfaces.
- When applied to very small surfaces, this type of corrosion is particularly severe and dangerous.

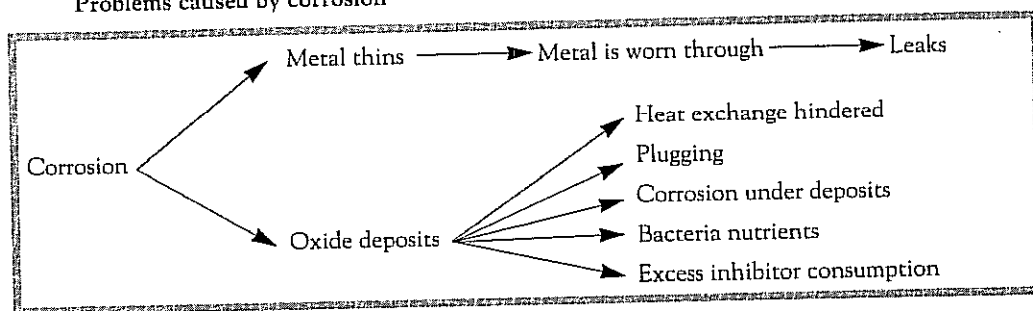
The following are some examples of the causes of local corrosion:

- Oxygen (corrosion tubercle).
- Deposits (differential aeration).
- Stagnant water (crevice or cavernous corrosion).
- Bimetallic (galvanic) couples.
- Sulfate-reducing bacteria.
- Cavitation.

The problems caused by corrosion are summarized in Table 57. They result in degradation of the equipment and in deposits that hinder heat exchanges.

Table 57

Problems caused by corrosion



As a result, the unit loses efficiency and the lifetime of the facilities is shortened.

7.4 Protection against fouling and biological growth

It is important to point out that prevention is better than cure with the threefold aim of effectiveness, ecological benefit and cost savings.

Earlier, fouling and deposits were seen to be highly detrimental to heat exchange quality and corrosion resistance. The particularly noxious action of colloidal matter coagulating on hot surfaces and creating an insulating film was also mentioned. This material is also known to serve as support and nutrient for biological growth. The remedies, i.e. the means of eliminating this colloidal matter, all center around the coagulation phenomenon.

7.4.1 Action taken on make up water

If the make up water is the source of fouling, corrective action will depend on the degree of pollution:

- Clarification with coagulation + filtration.
- Filtration with in-line coagulation.
- Possibly oxidation (chlorination, etc.).

7.4.2 Action on the system

Several additional measures are possible:

7.4.2.1 Side-stream filtration possibly with in-line coagulation

Filtration of a fraction of the circulating flow is highly recommended because it allows part of the suspended solids (SS) to be retained and eliminated from the system. The SS ratio in the system can thus be held to below 5 to 25 $\text{mg}\cdot\text{l}^{-1}$, depending on the system.

Generally speaking, the flow rate for side-stream filtration is set at 5 to 10% of the total flow of the recirculated water. It corresponds to one-tenth of the volume of the system. Of course, if the system is prone to specific pollution (sand storms, processes, etc.), the percentage must be much higher.

If the water has a tendency to clog, then cationic organic coagulants should be used upstream from the filter. The aim is to coagulate the colloidal matter in the water, retain it on the filter and thereby eliminate it from the system.

7.4.2.2 Using organic dispersing agents

These products are used to maintain the particles in suspension so as to prevent the formation of deposits in areas of low circulation rates and on the heat exchange surfaces.

They can also regulate the formation of protective layers by corrosion inhibitors. They are, in fact, often included in inhibitor formulation.

Among the products that are used, the following can be listed:

- Sulfonated compounds (lignosulfonates, arylsulfonates, etc.).
- Acrylic polymers and their derivatives.

These products are very often anionic and this must be taken into account if they are to be used in the presence of opposing ions.

7.4.2.3 Using surfactants

These products modify the surface tension of the water. Here, the aim is to lower the surface tension. This enables biocides to have access to and penetrate fouling, thereby enhancing their effectiveness.

Surfactants can be cationic, anionic, amphoteric or nonionic. The length of the carbon chain affects the different wetting, foaming, emulsifying or detergent properties.

Their use is particularly sought in the following cases:

- Preparation of the system.
- Disinfection associated with biocides.
- Cleaning-pollution removal (oils, greases, hydrocarbons, etc.).

7.4.2.4 Using chlorination and brominated compounds

The most commonly used reagent is sodium hypochlorite (chlorine bleach). Chlorine acts in two ways:

- By virtue of its oxidizing power, it destroys the organic matter which is the nutrient for algae and bacteria. It also has a coagulating effect. Cl_2 consumption can be considerable. Accordingly, the amount necessary for a cleaning treatment is often calculated based on the content of organic matter in the water. However, consumption by the matter retained on the surfaces of the system is several times (up to 10 to 15 times) that of the organic matter in the water.
- By virtue of its biocidal power, it can destroy living organisms. However, this function is related to the presence of hypochlorous acid, HOCl , and therefore depends on the pH of the water (see Fig. 77). With an alkaline pH, chlorine loses most of its biocidal effectiveness.

Chlorination is generally performed batchwise at highly variable intervals ranging from three times a day to four times a year. Efforts are made not to exceed $1 \text{ mg} \cdot \text{l}^{-1}$ of residual free Cl_2 in the system so as not to accelerate corrosion phenomena.

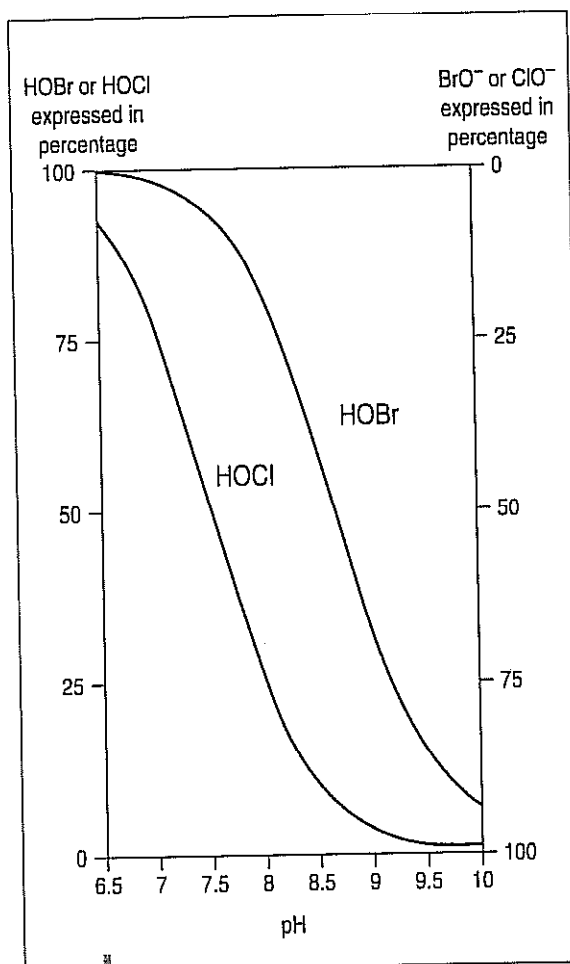


Fig. 77 Bromine and chlorine biocide activity versus pH

Brominated derivatives have an advantage over chlorine. They are more active in basic pH and in ammonia environments. In particular, the percentage of available hypobromic acid is greater than the percentage of hypochlorous acid, especially in alkaline pH (see Fig. 77). There are products that liberate both chlorine and bromine and that are very active in alkaline pH and at low dosage. The complementary features of halogens and the small amounts required to control the biofilm allow a significant improvement in relation to chlorine alone, especially for the protection of cuprous metals.

7.4.2.5 Using biocides

Implementing a preventive treatment as discussed above can often keep the use of biocides (algicides and bactericides) to a minimum (two to six times a year). They can then be reserved for shock treatments when the weather is more propitious to biological growth (spring and fall) or when accidental pollution has occurred.

However, in petrochemical plants, use of biocides and surfactants is an important part of system protection because of possible process leakage.

A. Biocide action

These products act on living cells and their growth in different ways, in particular:

- They impair the permeability of the cell and therefore hinder its exchanges.
- They deteriorate the cell wall and may cause the cell to burst.
- They impair the colloidal nature of the protoplasm (e.g. by coagulation) and destroy the cell.
- They inhibit enzyme activity causing growth to stop.

Biocides usually combine several effects. Basically, they can be classified according to two main modes of action:

■ Effect on the membrane of the cell wall

The biocides in this category are often surfactants and include:

- Quaternary ammonia (cationic products) with a surfactant effect.
- Substitute guanidine salts.
- Certain amine derivatives.
- Phenols and chlorophenols (very toxic in discharge water and so their use is prohibited in systems with blowdowns).
- Certain aldehydic compounds.

■ Effect on the cell's metabolism (enzymatic inhibitors)

In this category, the following can be mentioned:

- Organosulfur compounds (dithiocarbamate, etc.).
- Certain amine derivatives.

B. Choosing a biocide

When a biocide is being chosen for implementation, the following factors must be taken into account:

- Type of pollution (algae, bacteria, etc.).
- pH of the water, a factor that is often important in preserving the biocide and achieving maximum effectiveness.
- Compatibility with treatment additives (ionic nature, chemical affinities, etc.).
- Residence time.
- Tolerance phenomena.

C. Implementation

Biocide implementation must also take into account:

- Optimization of cost-effectiveness.
- Minimization of toxicity in discharges.

This means acting on cooling system operation with in particular:

- Limited blowdown during biocide treatment.
- Frequent pollution removal from the sand to safeguard filter beds.

Associating biocides with side-stream filtration helps optimize the processes.

To control the growth of microorganisms, the first steps are to:

- Find out the direct or indirect causes of their presence (contamination, nutrients, system design or operation).
- Define the preventive means that could be used.
- Monitor microorganism growth rigorously and objectively through reliable analysis.

This entails establishing a program that integrates both the direct effects that are being sought and the repercussions on the recipient environment with time.

7.4.2.6 Special case of hydrocarbon pollution

When there is significant pollution by hydrocarbons, the main steps to be taken are as follows:

- Isolate side-stream filtration.
- Get rid of the hydrocarbons by overflow in the basin under the cooling tower and by increased deconcentration blowdown.
- Spot and stop the leakage.
- Close blowdown.
- Carry out a dispersing agent and surfactant treatment.
- Renew the water in the system.
- Proceed to apply a biocide.
- Remove pollution from filter beds before and after putting operations back on stream.

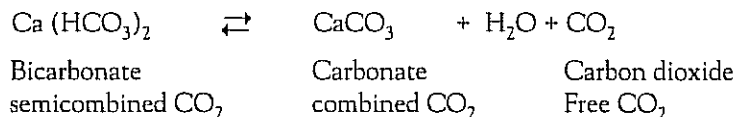
7.5 Protection against scale and corrosion

7.5.1 Note on calcium carbonate equilibrium and the Ryznar index

Natural water is not pure and contains a number of dissolved chemical elements. The most common is calcium bicarbonate. It was seen earlier that one of the first salts that is liable to precipitate out in water is calcium carbonate. Corrosion problems are often hidden or thrown off by the formation of a relatively thick layer of calcium carbonate.

In fact, the practical balance of calcium bicarbonate with carbon dioxide (CO_2) is governed by fairly complex relationships. A shift in the balance can cause chemical reactions that either dissolve calcium carbonate (i.e. aggressivity) or precipitate it (i.e. scale build up). These reactions may be compounded by electrochemical corrosion processes that are specific to metals.

Calcium bicarbonate is unstable in an aqueous solution and can break down as shown in the reversible reaction below:



To keep a given calcium bicarbonate concentration in solution, the water must contain a corresponding amount of dissolved free CO₂. This is the "balancing CO₂".

The free CO₂ that is present beyond the amount required to keep the balance is called "aggressive CO₂" in the sense that it can dissolve calcium carbonate until it restores the balance:

$$\text{free CO}_2 = \text{balancing CO}_2 + \text{aggressive CO}_2.$$

If the free CO₂ is lower than the balancing CO₂, the water is said to be **scale-forming**.

If the free CO₂ is higher than the balancing CO₂, the water is said to be **aggressive** (to limestone, and this can be determined by the "marble test").

When the free CO₂ content is equal to the balancing CO₂ content, a "balance pH" or **saturation pH**, (pH_s), valid for a given temperature can be determined (see Langelier's chart, Fig. 78).

The theoretical **Langelier index**, $\text{LI} = \text{pH} - \text{pH}_s$, gives the behavior of water toward calcium carbonate. But the problem in cooling systems is rather the behavior of water toward steel.

It is important to distinguish between two concepts: aggressivity (toward marble) and corrosivity (toward steel). The two do not cover exactly the same area and nonaggressive water can be corrosive. Ryznar's observations of a number of industrial systems enabled him to establish an empirical formula based on the Langelier saturation pH:

$$\text{RI} = 2 \text{ pH}_s - \text{pH}$$

The **Ryznar index** gives the scale-forming or corrosive tendency of one given type of water toward steel at a given temperature:

- If $\text{RI} < 6$, the water has a scale-forming tendency.
- If $\text{RI} > 6.5$, the water has a corrosive tendency.
- If $6 < \text{RI} < 6.5$, the water is roughly at an equilibrium between scale and corrosion.

The pH_s is the saturation pH calculated by means of the chart (Fig. 78) based on the values of:

- Ca.
- M alk.
- Total salinity.
- Temperature.

The pH is that of the water measured at a temperature of about 20°C.

Nota bene:

The index can be applied only if the water contains at least a minimum O₂ content (about 5 g·m⁻³). Without dissolved oxygen, the protective layer does not form.

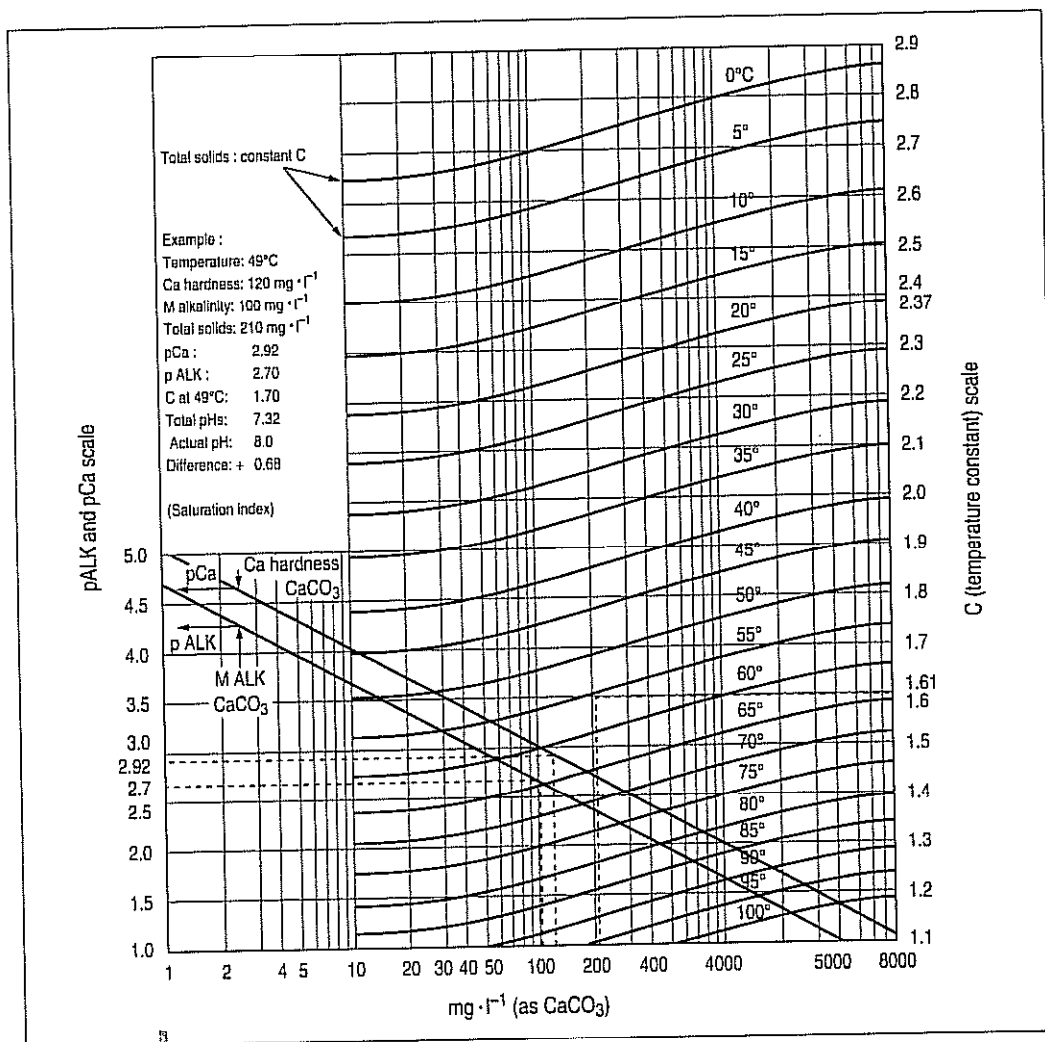


Fig. 78 Langelier's diagram

For a closer definition of the problem, the Ryznar index is often calculated in three different places in the system:

- The hottest water (skin temperature of the exchangers).
- The water at the exchanger outlet, or returning to the cooling tower.
- The coldest water (exchanger inlet or in the cold water basin).

This stability index has proven to be valid for both natural water and industrial cooling water.

For high-salinity water ($>5 \text{ g} \cdot \text{l}^{-1}$), the calculation of the stability index must be modified. The effect of the salts must be taken into account and the Stiff and Davis index must be used (for brackish water and seawater).

The Ryznar index gives a general tendency of course, but it does not show the influence of certain important parameters such as Cl^- and NO_3^- ions, NH_3 , miscellaneous pollution, etc. When the index is used, it should therefore be supplemented by information specific to the water, the system or its environment.

7.5.2 "Natural equilibrium" process

This consists in adjusting the pH, TH and M alk of the circulating water according to the Ryznar index, so that it is at a scale-corrosion equilibrium.

The simplicity of this process makes it very attractive, but it does have the following important limits:

- The water is in a state of unstable equilibrium. The pH can change dramatically if the water simply flows through the cooling tower (CO_2 equilibrium between the air and the water).
- There is an equilibrium for each temperature, whereas in a cooling system, the water temperature varies continuously. According to the adjustment made, either corrosion is seen at cool spots or too much scale is formed at hot spots.

The process is still used for power plant condensers that operate as virtual open systems (very low concentrations) with low Δt and Taprogge-type cleaning systems.

7.5.3 Scale-inhibitor or stabilization process

This is an improvement on the preceding process. It is used for water that has a scale-forming tendency. It consists in injecting chemicals into the system which delay the precipitation of calcium carbonate, especially at the hot spots.

The chemicals can broaden the "equilibrium range" by making it possible to operate with Ryznar indices as low as 4, and in some cases even lower.

There are three main basic categories of scale inhibitors:

■ **Polyphosphates**, with the following main characteristics:

- P – O – P bonds.
- Moderate stability with temperature (poly- transformed into ortho- accentuated if the water temperature exceeds 60°C).
- Compatibility with chlorination.

■ **Organic phosphorus (phosphonates)** with the following main characteristics:

- P – C – P or P – C – N – C – P bonds, etc.
- Good stability with temperature (test $> 200^\circ\text{C}$).
- Moderate stability with chlorine.

■ **Organic polymers (acrylics)** with the following main characteristics:

- Anionic: e.g. polyacrylates.
- Low molecular weight (approximately 10^3).
- Good stability with temperature.
- Good stability with chlorine.

Nota bene:

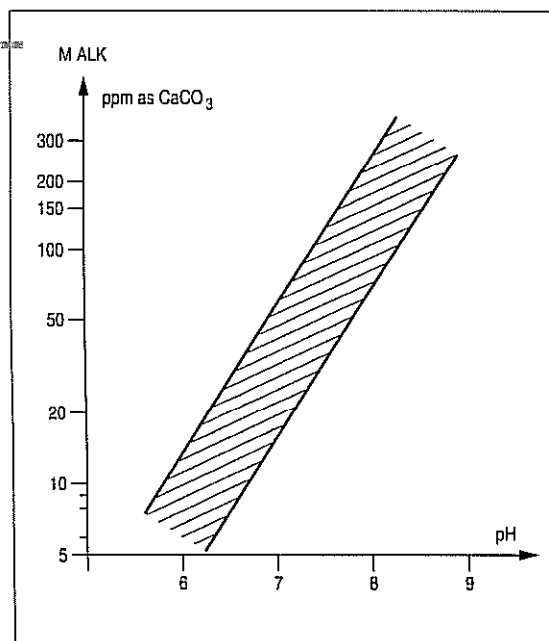
Each category may include more specific inhibiting products according to the different salts CaCO_3 , CaSO_4 , tricalcium phosphate, etc. (this is especially true for phosphonates).

Composite formulations are commonly found that can provide synergy in applications (this is true for phosphonate-acrylate associations).

7.5.3.1 Advantages and limitations of processes to delay precipitation

Stabilization processes are highly sought after to the extent that they make "free pH" operation possible. However, there is a direct relationship between the pH and the M alk. Fig. 79 was established based on experimental points read in recirculating systems with cooling towers.

Fig. 79
pH of circulating water
in cooling towers (90% of the
experimental points are located
in the cross-hatched area)



The users of free pH usually situate the M alk of the circulating water between 15 and 30°, i.e. a pH of 8.3 to 9.3.

There are increased corrosion risks when the M alk reaches 10° and more scale formation with a M alk of 40° (concept of fixed M alk).

Stabilization processes with scale inhibitors therefore lead to control of the formation of the protective calcium carbonate layer. Antiscale-dispersing agents can in fact prevent unwanted deposits effectively. But the calcium carbonate protective film can be very sensitive to variations in system parameters (acidity, SSA, lack of reagents, etc.).

Corrosion risks are limited by the water's scale-forming tendency and pH, but the importance of SSA (salts of strong acids) is paramount. Chlorides and sulfates accelerate depassivation of the protective films, thereby causing complications and increasing the conductivity and corrosion rate (V_{corr}).

Generally speaking, in a controlled scale-forming environment, the following applies (corrosion rates in mpy, thousandths of an inch per year):

- If $\text{SSA} < 500 \text{ mg} \cdot \text{l}^{-1}$ as CaCO_3 , it can be expected that $V_{\text{corr}} < 4 \text{ mpy}$.
- If $500 < \text{SSA} < 750 \text{ mg} \cdot \text{l}^{-1}$ as CaCO_3 , it can be expected that V_{corr} is 4 to 6 mpy.
- If $\text{SSA} > 750 \text{ mg} \cdot \text{l}^{-1}$ as CaCO_3 , then $V_{\text{corr}} > 6 \text{ mpy}$.

Lastly, particular attention must be paid to counteracting biological growth with an alkaline pH, since biocide effectiveness is reduced when the $\text{pH} > 8$.

Improvements achieved by additional inhibitors

In an attempt to reduce corrosion rates, additional elements have been included in antiscale formulations.

Zinc

Zinc is a cathodic corrosion inhibitor. At usual antiscale concentrations and routine free pH values of > 8.5 , the zinc content in the system will remain lower than $1 \text{ mg} \cdot \text{l}^{-1}$, whatever the amount added (too much excess zinc can give rise to extra sludge).

The presence of a dispersing agent has a positive impact on the zinc content.

The total improvement expected under these conditions is from 20 to 50% of the corrosion rate, particularly in water with a fairly low SSA.

In addition, zinc can also enhance the action of some biocides.

Copper corrosion inhibitors (azole derivatives)

These inhibitors are particularly recommended when phosphonates are present, since phosphonates can accelerate the corrosion of cuprous metals.

Azole derivatives are adsorbed preferentially on copper and brass, thereby protecting them. As a result, the steel corrosion rate falls because there is less risk of forming Cu-Fe pairs.

Chromates

Chromates are anodic inhibitors. They are used associated with phosphonates at a concentration of a few milligrams per liter. They can reduce the corrosion rate of steel considerably in systems that operate under controlled scale-formation conditions.

The major drawback is the toxicity of Cr^{6+} , and it must be transformed into Cr^{3+} in blowdown water before it is discharged. However, the amounts of chromium that need to be treated are very small.

7.5.4 Corrosion inhibitor processes (with controlled pH)

7.5.4.1 Principle

Unlike the first two protection processes discussed above, these consist in:

- First, situating the water on the corrosive side of its calcium carbonate equilibrium with a pH of about 6.5 to 7. As a result, no CaCO_3 scale can be formed.
- Second, introducing an inhibitor at the same time into the system which offsets corrosion. The inhibitor acts by forming a bonded, homogeneous, nonporous, protective film that does not hinder heat exchange.

Most of these inhibitors have a binary compound base that enables them to block the corrosion anodes and cathodes at the same time. They act directly on electrochemical corrosion phenomena.

The presence of at least a minimum of calcium hardness (10 to $20 \text{ mg}\cdot\text{l}^{-1}$) is generally advisable to promote the formation of the protective film.

Additionally, one of the most common binary elements is zinc. In order to remain available in the vicinity of the walls, it requires a pH close to neutral or just slightly acid in the system water, depending on the formulation.

Reagent doses of several dozen $\text{mg}\cdot\text{l}^{-1}$ are sufficient because both the cathodic and anodic processes are under control. (Meanwhile, solely anodic inhibitors require much larger amounts, about one $\text{g}\cdot\text{l}^{-1}$, to prevent pitting. This is why they are mainly used in closed systems where there is no water loss.)

7.5.4.2 Main categories of corrosion inhibitors

There are three basic types:

- Zinc-chromates.
- Zinc-polyphosphates.
- Zinc-organophosphates.

Mixed formulation: multipurpose processes

To broaden the optimal pH range, avert risks of deposits and lessen corrosion rates, corrosion inhibitors often include the following in their formulation:

- One of the main categories of products listed above or even a combination of the three.
- Systematically, a dispersing agent.
- A cuprous metal corrosion inhibitor (azole derivative).

This is the case for the "phosphates + dispersing agents + organic inhibitors" process (fourth category).

Table 58 compares the properties of the four main types of inhibitors under discussion.

Table 58

Comparison of properties of the four main types of corrosion inhibitors for open recirculating systems with cooling towers

	Zinc chromate + dispersant	Zinc polyphosphate + dispersant	Zinc phosphonate + dispersant	Phosphates + dispersants + organic inhibitors
pH range	6.4-6.8	6.4-7.5	6.5-8	6.8-7.5
Residence time (hours)	>100	about 50	about 70	>100
Effectiveness	Excellent	Very good	Good	Excellent
Corrosion rate	<2 mpy	<2.4 mpy	<4 mpy	<2 mpy
Discharges	Need treatment	Tolerated	Tolerated	Tolerated

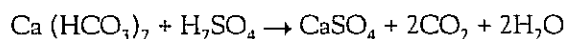
7.5.4.3 Obtaining the optimum pH

The alkalinity (and as a result the M alk) of make up water should be reduced so that the pH of the water in the system remains within the right range.

Three methods can be used to achieve this:

A. Adding acid

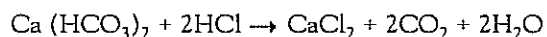
Sulfuric acid is the most commonly used in Europe as it is less expensive and easier to implement:



Ten grams of H_2SO_4 at 66° Bé are required per cubic meter of water to reduce its M alk by $10 \text{ mg} \cdot \text{l}^{-1}$ as CaCO_3 :

- The acid is usually injected in the system itself.
- The main drawback is the resulting additional sulfates with their effect on precipitating calcium sulfate and increasing water corrosivity.

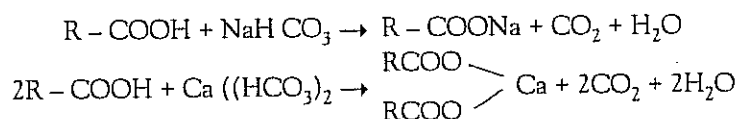
When hydrochloric acid is used:



Twenty grams of HCl at 22° Bé are required per cubic meter of water to reduce its M alk by 10 mg·l⁻¹ as CaCO₃.

Adding chlorides is not very advisable as they accelerate the corrosion of steel, stainless steel in particular.

B. Softening (carbonate removal) on carboxylic resin for all or part of the make up as shown in the principal reactions below:



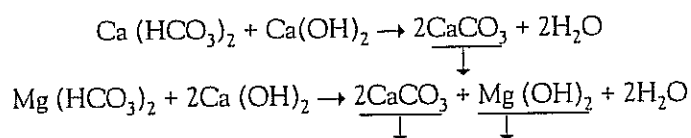
This is a selective exchange involving the bicarbonate part of the water. Afterwards, the liberated CO₂ just needs to be flushed out. When the resin is saturated it is regenerated with acid.

This method can reduce both the M alk and the hardness, and thereby decrease the water's salinity without introducing any new salts.

C. Lime softening

This is the preferred method if the quality of the make up water is such that it must be clarified before it is introduced into the system.

The main reactions are expressed as follows:



With this method, carbonate removal plus partial softening (with a reduction in M alk and TH), can be associated with clarification plus coagulation (with elimination of suspended, organic and colloidal matter) in the same settler.

7.5.5 Determining the optimum concentration rate

In order to economize on water as well as conditioning products, it is useful to determine the highest possible concentration rate.

Savings on make up water, A, result from the following equation (see Fig. 80):

$$D = \frac{E}{C-1}$$

For example if evaporation $E = 80 \text{ m}^3 \cdot \text{h}^{-1}$, there will be the following results:

- For $C = 3$ then $D = 40 \text{ m}^3 \cdot \text{h}^{-1}$ and $A = E + D = 120 \text{ m}^3 \cdot \text{h}^{-1}$.
- For $C = 6$ then $D = 16 \text{ m}^3 \cdot \text{h}^{-1}$ and $A = E + D = 96 \text{ m}^3 \cdot \text{h}^{-1}$.

The savings on the amount of inhibitors come from the fact that to keep 60 g of inhibitor in the system, all that is needed in the example above is to introduce:

- For $C = 3$ 20 g·m⁻³ of make up, i.e. 2.4 kg·h⁻¹.
- For $C = 6$ 10 g·m⁻³ of make up, i.e. about 1 kg·h⁻¹.

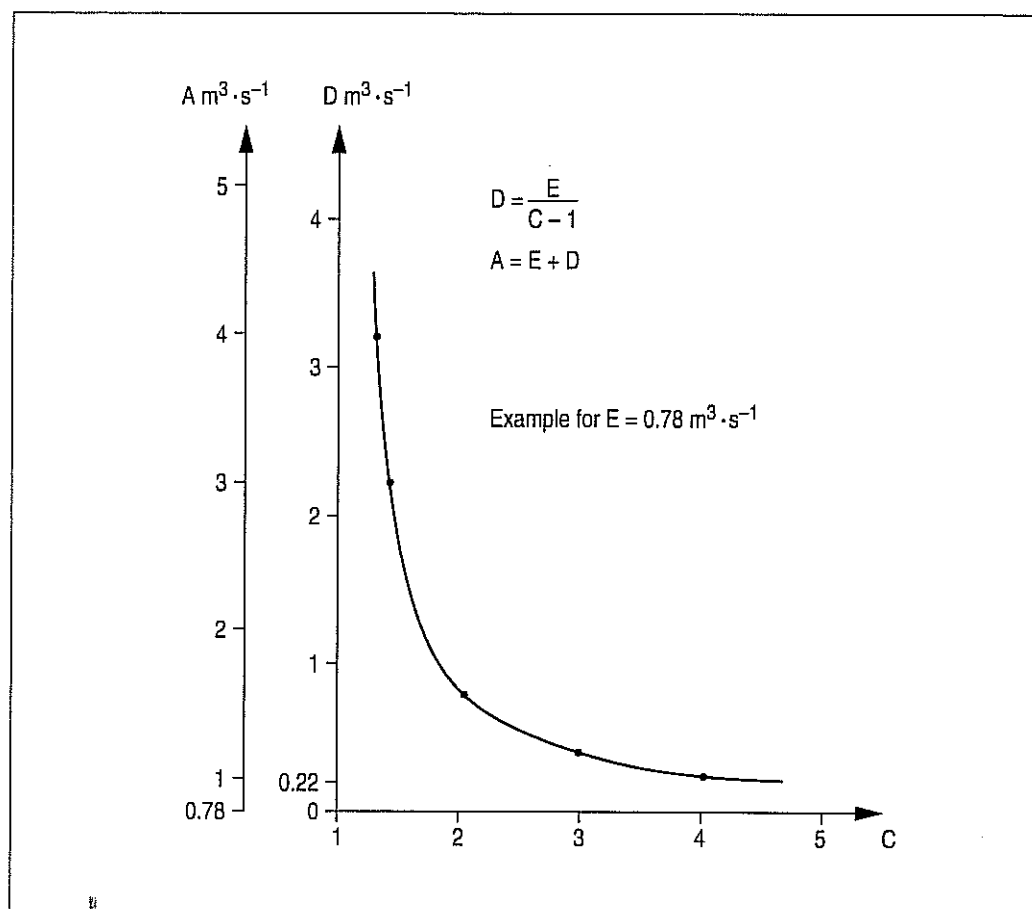


Fig. 80 Flow rates of blowdown, D , and make up, A , versus the concentration rate, C

The acceptable concentration rate will depend on:

- The operating conditions of the system (getting rid of unwanted leaks, etc.).
- The risk of salt precipitation.
- The recommended residence time for using the chosen inhibitor.

In cases where inhibitors are used with controlled pH, the pH is generally such that no calcium carbonate-based scale is anticipated.

However, if sulfuric acid is added to keep the pH stable, the Ca and SO_4 ion content may make it necessary to curb the concentration rate. The aim is not to exceed the solubility product of calcium sulfate. Prior softening to remove both the alkalinity and the calcium can prove very profitable as it allows an increase in concentration rate.

Silica is seldom a limiting factor, except in some regions like the Far East where make up water can contain several dozen milligrams per liter.

The target concentration rates are about 3 to 6, but there have sometimes been rates of up to 10. Discharge problems were accordingly lessened since blowdown was at a minimum. These rates were achieved with certain types of conditioning, especially zinc chromate-based processes.

7.5.6 Discharges

Very often blowdown can not be totally eliminated, so the problem of discharge arises.

It is prohibited to discharge chromate-rich water, generally above $0.1 \text{ g}\cdot\text{m}^{-3}$ of CrVI. However, there are tried and true, relatively inexpensive, industrial processes to break down and eliminate chromates. Zinc can be eliminated at the same time. As a result, the zinc-chromate process yields deconcentration blowdown that is free of corrosion inhibitor components.

The phosphate concentrations that are usually required in systems ($\text{PO}_4 < 25 \text{ mg}\cdot\text{l}^{-1}$ and $\text{Zn} < 5 \text{ mg}\cdot\text{l}^{-1}$) are generally authorized in discharges. Sector by sector, a maximum value of $2 \text{ mg}\cdot\text{l}^{-1}$ of PO_4 may be demanded and this is difficult to comply with. It may entail more thorough purification of the water and organic-type conditioning.

7.5.7 Choosing processes: how to design a cooling system

The chemical composition of the water is certainly not the only factor to be considered in designing a cooling system, but it does come into play in several ways. This is why right from the design stage, it is advantageous to consult a specialist in water treatment and conditioning:

- New but proven processes may have been developed and it would be a shame not to take advantage of them for a new plant.
- It is sometimes possible to choose between the water from two or more origins.
- The treatment of make up water can be harmoniously integrated with general plant waste water treatment.
- The quality of the water available on the site may enable the choice of a type of apparatus that is easier to protect than another. It is almost impossible to protect surfaces by adding chemicals to the water, when the water in contact with them is not renewed often enough.
- The type of protection chosen affects the choice of building materials: cooling towers, pumps, connecting piping, etc.

7.5.7.1 Controlling parameters

- Water analysis and system design:
 - Ryznar index or RI stability.
 - pH.
 - M alk.
 - Ca.
 - SSA, Cl and SO_4 .
 - Temperatures.
 - Residence times.
 - Apparatus requiring cooling: throughputs and materials.
 - Types of problem (CO_3 , Ca, SO_4 , etc.), hot spots.
 - Fouling (be careful with overconsumption).
 - Environment.

- Chlorination.
- Quality of make up water.
- Effectiveness sought
- Operating constraints.
- Whether or not concentration is possible.
- Handling of acid reagents (H_2SO_4 or HCl).
- Discharge constraints.
- Operating balance sheet.

7.5.7.2 Guidelines

The guidelines are based on a comparison of the properties of the different processes.

Antiscale-dispersant processes	
Advantages	Drawbacks
• More flexible operation (higher M alk in system) • No discharge problem	• Requires water with scale-forming tendency • Limited Cl_2 biocidal action • More limited concentration rate
Controlled pH corrosion inhibitors	
Advantages	Drawbacks
• Very good anticorrosion protection • Better control of biological problems • Higher concentration rate	• Rigorous pH monitoring • Investment often heavier (acidification or softening)

7.5.7.3 Operating balance sheets

Several alternatives may have to be contemplated and operating balance sheets can be established to compare the various protection processes.

The study should, if possible, take all the operating cost components into account, e.g.:

- Consumption of products.
- Cost of water, often the most expensive item (two to five times the cost of products, even more if drinking water is used).
- Manpower for monitoring and maintenance of equipment.
- Depreciation.
- Reduction in maintenance costs and improvements in production capacity, very hard to estimate and variable, usually several times the cost of products.

This type of study helps give a better idea of the impact of an increase in concentration rate which, by reducing operating costs, enables a rapid return on purification facility investments (softening, filtration, etc.). If such studies are handled carefully, they can be very useful as decision-making tools.

7.5.8 Comments on stainless steel corrosion

The corrosion resistance properties of stainless steel are achieved by a very thin bonded passive film. The Cr_2O_3 -based film is several dozen angströms thick and can protect the metal from corrosion by contacting fluids only if it is continuous and intact.

The passivation coating may sometimes not have formed (particularly if there are iron hydroxide or oxide deposits).

The continuity of the passivation coating may also be impaired, especially by Cl^- ions that may cause perforating pits to form. The presence of deposits is conducive to saline overconcentrations under them.

Stainless steel degradation phenomena often appear after carelessly run hydraulic testing (wrong choice of water, incomplete draining, stagnation, etc.).

Protection against stainless steel corrosion is based on a number of complementary factors:

- Choose a stainless steel known to be more resistant to chloride corrosion, i.e. containing molybdenum. For example: specification number 316 L.
- Run hydraulic testing carefully, avoiding stagnation and if possible rinsing with water containing less than $50 \text{ mg}\cdot\text{l}^{-1}$ of Cl^- . Never dry with steam but with dry air instead.
- Avoid deposit risks (control of fouling is therefore an important parameter).
- Prefer water containing a Cl^- content lower than $100 \text{ mg}\cdot\text{l}^{-1}$.

7.5.9 Comments on degradation of concrete

The phases in concrete degradation are first mechanical in origin, then chemical.

Mechanical causes

- Permeability too great.
- Pocks and cracks (formed when it was poured).
- Erosion due to water circulation velocities $> 4 \text{ m}\cdot\text{s}^{-1}$ in piping, or because of overly high thermal gradients.

Chemical causes

- Strong CO_2 aggressivity $> 15 \text{ mg}\cdot\text{l}^{-1}$ or in soft water.
- Strong acidity.
- Action of ammonia.
- Action of sulfates.
- Action of magnesia.

A reminder of German standard DIN 403 is printed below. It defines boundary values for assessing saline water aggressivity toward concrete.

	Slightly aggressive water	Highly aggressive water	Very highly aggressive water
pH	6.5-5.5	5.5-4.5	Less than 4.5
Aggressive CO_2 according to Heyer ($\text{mg}\cdot\text{l}^{-1}$)	15-30	30-60	More than 60
NH_4^+ ($\text{mg}\cdot\text{l}^{-1}$)	15-30	30-60	More than 60
Mg^{2+} ($\text{mg}\cdot\text{l}^{-1}$)	100-300	300-1 500	More than 1500
SO_4^{2-} ($\text{mg}\cdot\text{l}^{-1}$)	200-600	600-2 500	More than 2500

For highly aggressive water, it is recommended to use a coating. Meanwhile for fairly strongly aggressive water, the use of slag-based cement with a high hydraulic index can be contemplated (unless other chemical parameters of the water interfere).

- Strong alkalinity: Certain alumina-based components involve solubilization risks. As a result, operators should refrain from using water with $\text{pH} > 12$ for ordinary cement and $\text{pH} > 8.5$ for alumina cement when there is no coating.

- Bacterial corrosion in an anaerobic environment (e.g. under a deposit), with formation of H_2S and then H_2SO_4 . These reactions are accelerated at $\text{pH} < 6$ and with temperature increase (they are found in the transfer of municipal waste water).

In cooling systems, operation is seldom really hampered by degradation of concrete. However, when high concentration rates are sought with very saline water, it is wise to proceed carefully.

7.6 Saving water

Saving water is increasingly a definite concern for the system operator. Motivation can be:

- The lack of fresh make up water.
- The cost of make up water depending on where it comes from (municipal water system, etc.).
- Increasingly tough regulations on discharges.
- Suitability of recycling spent water (process water, waste water, etc.).

To meet this need, a number of solutions can be envisaged:

- Decrease the amount of make up water necessary by increasing the concentration rate by more thorough purification of make up water, or side-stream purification (on a fraction of the circulating flow).
- Reuse spent water by treating it so it can be recycled as cooling system make up.

7.6.1 Purification of make up water

High concentration rates can be achieved by thoroughly purifying make up water, e.g. softening as already mentioned and even demineralization.

Accordingly, water that has undergone osmosis or demineralization can be used on sites with little available water. This can allow concentration rates of over eight with phosphate-dispersant-type conditioning.

7.6.2 Side-stream purification

This treatment is carried out with a by-pass inside the system itself with, for example, in the same settler (Fig. 81):

- Clarification-coagulation.
- Carbonate removal-softening and possibly silica removal.

This allows high concentration rates (> 6), so blowdown can practically be eliminated (zero blowdown) and zinc-chromate conditioning becomes feasible.

This type of purification is sometimes used in the United States. Side-stream chemical purification could be supplemented by other physical treatments such as evaporation, reverse osmosis or nanofiltration. The last two techniques use membranes and require careful pretreatment to reduce fouling risks.

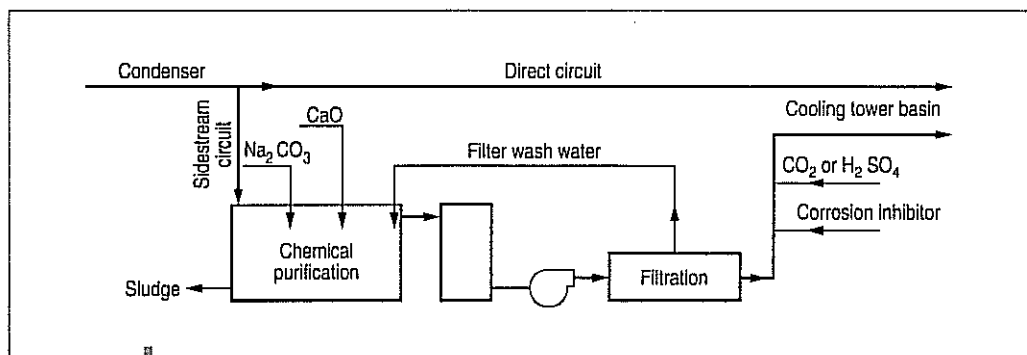


Fig. 81 Flow scheme of side-stream purification

7.6.3 Reusing industrial waste water

Recycling purified waste water can improve the economics of the plant's balance sheet or it may be needed because water resources are insufficient.

The most well-known example is refinery waste water.

These effluents are reused after purification when there is side-stream filtration on the system with an incorporated coagulant to retain colloidal matter and prevent exchanger fouling (see Chapter 3 Section 4: Recycling and Chapter 6: Treatment Systems).

7.7 Implementing protection

7.7.1 Preparing the system

Good quality protection depends largely on how well operating instructions are applied. Special care is required during start-up periods as they are crucial for the future of the system.

When a cooling system is started up on a new unit, the water is chiefly considered from the hydraulic (testing) and mechanical (cleaning piping) angles.

However, as soon as the steel comes into contact with the water, irreversible corrosion phenomena may be initiated.

Additionally, problems of deposits that are inadequately dealt with in the beginning are hard to control later on. They can cause plugging and corrosion under deposits.

This means that the chemical features of the water must be considered, i.e. conditioning as soon as the water is pumped into the system.

The aim of cleaning and surface preparation operations is to eliminate as many deposits as possible in the systems (sludge, oil, soil, scale, etc.). This yields clean surfaces so that scale-forming and corrosion phenomena can be readily controlled by appropriate conditioning.

It is recommended to start up any and all existing filtration facilities as soon as systems begin to fill up with water. In this way, deposits will be eliminated properly.

Three main phases should be considered when systems are being prepared:

- Filling, cleaning and hydraulic testing.
- Chemical cleaning of the system with dispersants and detergents.
- Start up and formation of the protective coating (pretreatment) with reinforced doses of inhibitors.

7.7.2 Maintaining protection

After achieving the equilibrium phase, the inhibitor concentration planned for normal operation must be maintained and periodical monitoring must be carried out.

The inhibitor is usually injected into the system in the cool water basin near the circulating pump intake and make up water inlet. The aim is to ensure proper homogenization (the same holds true for any acid injection).

The product-metering unit usually includes:

- A dilution tank with an electric mixer or a storage tank if the product is a liquid.
- An electric proportioning pump group.
- Servocontrol by the make up flow rate so that dosage is proportional (with a pulse emitting meter and a timing device).

In addition, regulation of blowdown flow rate by make up servocontrol or by conductivity meter helps control the concentration rate.

Product-metering units often have to be built of protected material: e.g. ebonite-coated steel, polyethylene, etc. This holds true even for corrosion inhibitors that are often corrosive in their preparation concentration.

As for chlorination and biocidal treatment, the way they are introduced into the system depends on how often they are used and how long their residence time is:

- They are often used in shock treatments lasting a few days per month and it is possible to dump them in manually one to three times a day during the period involved.
- If they are added in repeated batches (short residence time, permanent pollution, etc.), a proportioning pump with a timer must be used.

7.7.3 Precautions required when systems are shut down

When a system is shut down, corrosion phenomena can occur very quickly if no precautions are taken, in particular:

- If the system remains filled with water, keep circulating to prevent stagnation and help homogenize the medium (do not stop circulating for over 48 hours).
- If the system is emptied, make sure all liquid has been drained out (otherwise spectacular wet-atmosphere corrosion or corrosion under deposits may occur). Dry out the network (or apply an overdose of corrosion inhibitor prior to shutdown).
- When the system is brought back on stream, plan a pretreatment phase just like in a new system with a reinforced amount of inhibitor.

7.8 Monitoring and effectiveness

Monitoring must be done to ensure that conditioning has been properly administered and is effective. The monitoring operations below are complementary.

7.8.1 Monitoring water and reagent consumption

Earlier, the importance of water in plant economics was discussed. Controlling consumption is therefore crucial and the aim is to reduce it to the strict minimum by:

- Spotting leaks and uncontrolled losses.
- Placing a meter on the make up water.
- Governing blowdown by the make up flow rate or by the salinity of the circulating water.

Information on product consumption, for example recording amounts added to tanks, is a useful added verification. This is especially true since some organic inhibitors are known to be hard to analyze by simple means in the systems.

It should be noted that the addition of conditioning products can be governed by make up flows in the same way as blowdown.

7.8.2 Monitoring purification and metering stations

Keeping these stations (lime softening, filtration, acidification, proportioning pumps, etc.) in proper operating order is a must.

Interrupted inhibitor injection or an overdose of acid can be highly detrimental, causing damage to materials and lessening thermal exchange efficiency.

7.8.3 Analytical monitoring

It is not enough to add the amount of inhibitor theoretically required in a cooling system. There must be some guarantee that it is effectively present.

Besides a malfunction in the injection station, other causes of insufficient inhibitor in the circulating water can be:

- Consumption when the protective coating was formed.
- Adsorption by suspended particles, particularly metallic oxides and hydroxides.
- Accidental loss of system water.
- Deregulated pH.
- Sensitivity to the presence of other compounds (e.g. reducers with chromates, opposing ionic nature, etc.).

Analyzing the water is therefore an immediate way of making sure that the treatments are applied according to instructions. It also allows the program to be adapted if the basic design characteristics get thrown off or if accidental pollution occurs.

Comparing the analyses carried out in the system and in the make up is useful for interpretation. Likewise, to gather information on changes or trends in the system water, it is recommended to perform several analyses over a period of time.

The parameters monitored will mainly be the following:

- pH
- TH (hardness)
- Ca
- M alk
- Cl
- SO₄
- SiO₂
- Inhibitors (PO₄, Zn, etc.)
- Iron
- Organic matter
- Suspended solids
- COD, TOC, HC content
- Clogging potential (fouling index)
- Microbiological monitoring
(observation with a microscope, counts
and possibly identification).

During routine operation, it is not absolutely necessary to know all these parameters. Daily measurements mainly involve pH, M alk, Ca and Cl content; and inhibitor, HC or TOC content if there are risks of pollution (petrochemical plants particularly).

Concentration rates based on chloride and calcium values in the system and in the make up are compared. They can give information on the rate itself (if there is no Ca and Cl introduced elsewhere in the system) and on the possible scale-forming tendency of the circulating water.

7.8.4 Monitoring and measuring corrosion

Whatever the method of measurement chosen, the place where it is made must be carefully selected to prevent misinterpretation.

Three types of measuring devices can be distinguished.

7.8.4.1 Measuring the corrosion current: corrosion meters

Corrosion meters are directly derived from laboratory devices and generally operate potentiostatically. In other words, they evaluate the intensity resulting from a potential imposed on a measurement electrode.

They were first used to monitor corrosion in oil and gas piping and are now being applied to water.

Isolated measurements can be made with a portable meter and continuous recordings can be made of the corrosion current as well.

They require rigorous, sometimes sensitive calibration between corrosion current and corrosion depth.

It would seem that the significance of the measurement is mainly relative. An increase in the corrosion current indicates faulty regulation has occurred. The meters can therefore be used to monitor operations. They can give the alarm if faulty regulation occurs in the product-metering facility.

7.8.4.2 Measuring by test samples

Metal coupons are immersed in the system water and pulled out periodically to be weighed. The weight of missing metal per unit of area directly expresses the depth of corrosion. Table 59 gives the correlation between the most commonly used units.

A number of precautions must be taken in designing, preparing, setting up and examining the corrosion test coupons.

Table 59

Corrosion rate of steel. Correlation between the different units

	$\mu\text{m} \cdot \text{y}^{-1}$	mpy	mdd
Micrometers/year ($\mu\text{m} \cdot \text{y}^{-1}$)	1	0.04	0.2
Thousandths of an inch/year (mpy)	25	1	5
mg/dm ² /d (mdd)	5	0.2	1
Protection quality			
-----	-----	-----	-----
Excellent	0	0	0
-----	-----	-----	-----
Good	50	2	10
-----	-----	-----	-----
Average	125	5	25
-----	-----	-----	-----
Fair	250	10	50

Each one is made up of a metal identical to that used in building the relevant part of the system. If they are in the shape of plates, they must be polished to get rid of any artificial heterogeneities caused by cutting or sawing the metal.

They are held in place in such a way as to avoid any contact between the test coupon and a component made of a different metal or of a different grade. Otherwise a battery would be created and would cause spurious corrosion.

The test coupons remain immersed in the circulating water.

Effective protection requires the corrosion inhibitor to be constantly present and in contact with the surface that is being protected. The inhibitor is conveyed by the water that must therefore circulate along the surfaces, coupons or piping in the system. Coupons placed in stagnant water, in basins for example, are not representative.

It is therefore recommended to place the coupons in the axis of the piping. If they are placed in a by-pass to make disassembly and checking easier, care must be taken that circulation can not be interrupted without the monitoring personnel noticing.

In addition, spurious turbulence from the water flow or the coupon mounting device must not be allowed to occur.

It should be pointed out that corrosion begins very quickly in the first days then declines to an equilibrium. The equilibrium is variable depending on the characteristics of the water, the conditioning applied and the state of the metal. In a system, what is important is the corrosion rate that is established after several months and the way it changes. Monitoring devices should therefore comprise several coupons that can be removed after different time periods have elapsed.

This is why a set of platelets (Fig. 82) or rings assembled to make up a cylinder (Fig. 83) are used. These devices are placed parallel to the liquid flow like the walls of the piping. The assemblage can be placed in cold or hot water (Fig. 84).

A ring or a platelet can be removed the first month and another the second month. Then measurements can be spaced out according to the stabilization of the system.

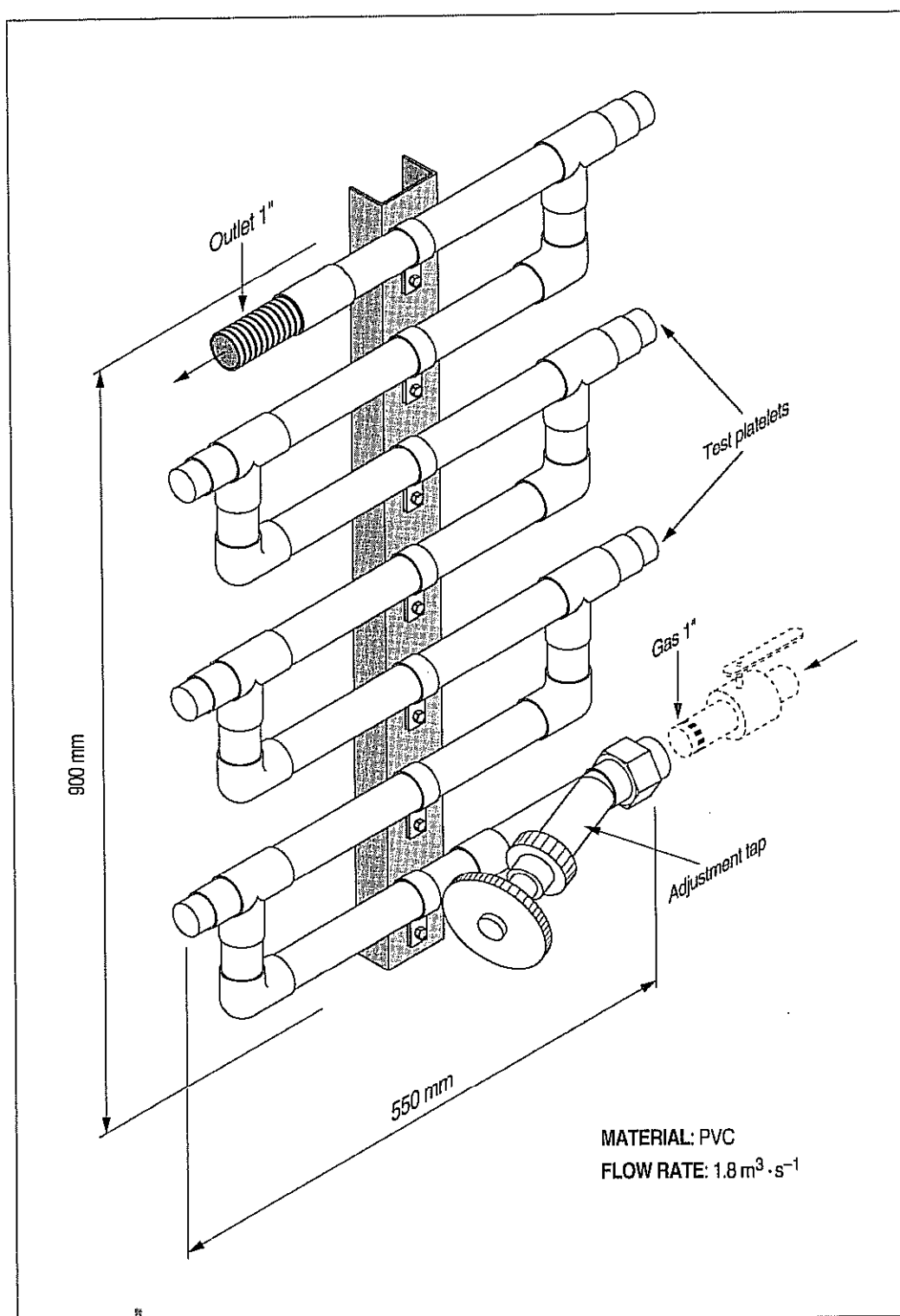


Fig. 82 Corrosion coupons

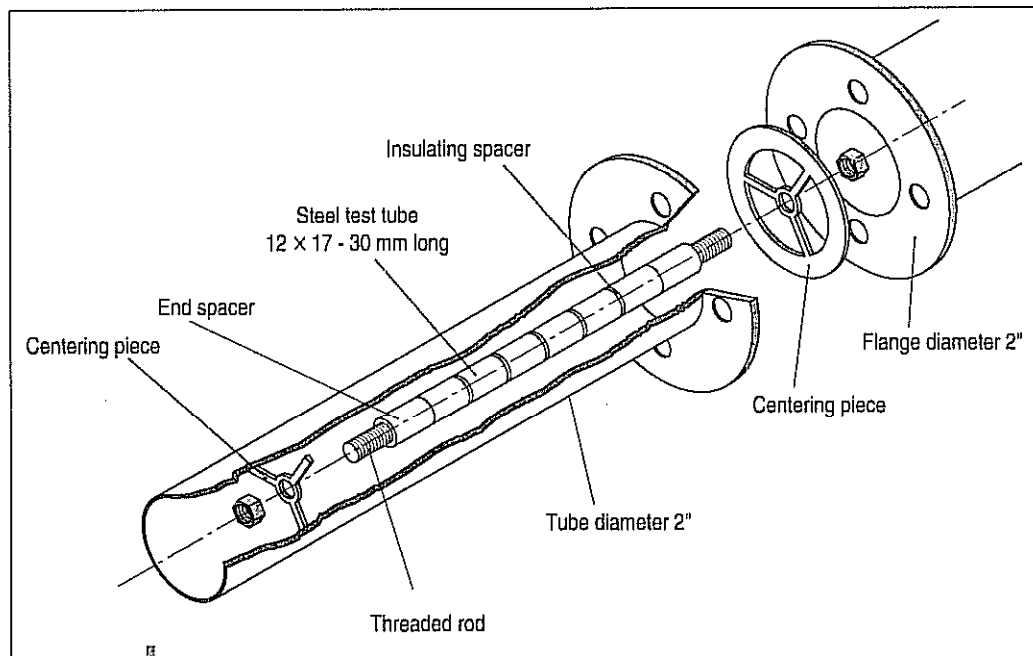


Fig. 83 Corrosion test probe

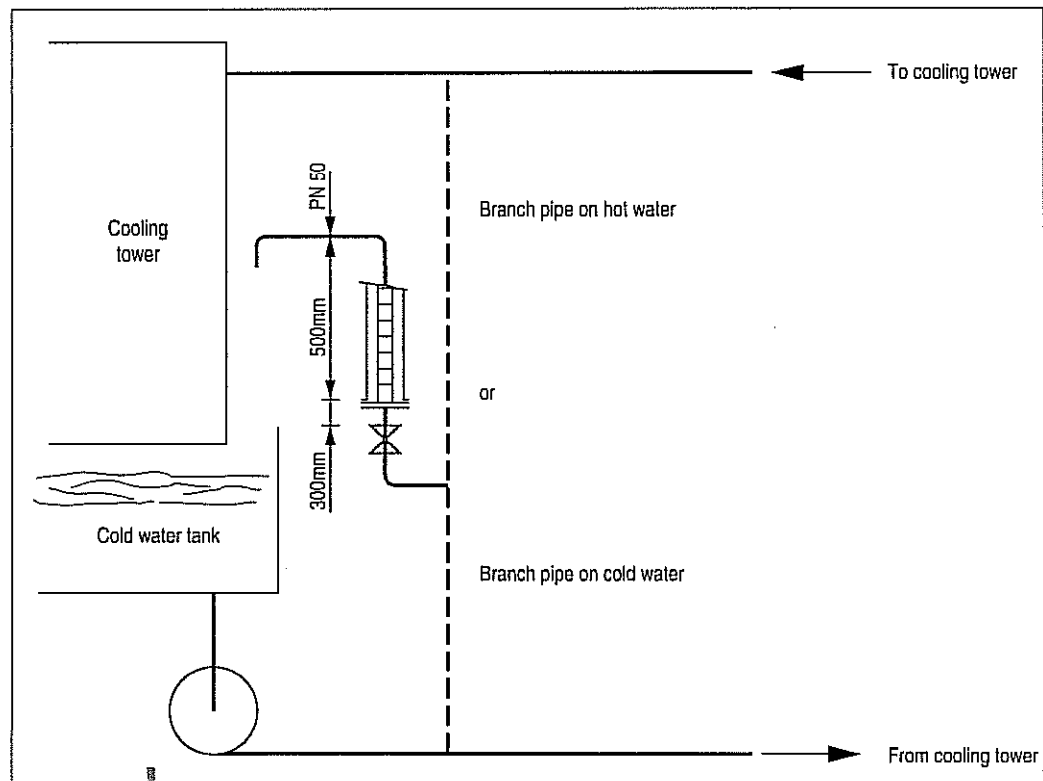


Fig. 84 Installation of test sample

Each measurement represents the effective rate from the beginning. Based on two measurements, the approximate value of corrosion during the period can be deduced by differential calculation.

This monitoring method is very often used. Weighing is performed after the metal has been bared by cleaning and scouring.

It is of course recommended to note down the appearance of the coupons before and after scouring to see whether corrosion is generalized or local.

7.8.4.3 Examining system materials

Easy-to-disassemble test sleeves can be used and examined periodically. Samples of sections of pipe can also be removed from a network or an exchanger and examined in a laboratory, but the number and choice are often restricted.

There are devices that can help perform in-situ examinations:

- They can be used to visualize areas that are not accessible to the naked eye and photograph them (e.g. the endoscope).
- They can be used to measure the thickness of the wall of a pipe and situate pitting or local corrosion in two dimensions. Possible applications for probing tube bundle heat exchangers (e.g. the Probolog).
- They can be used to situate corrosion in three dimensions (e.g. the Linalog).

7.8.5 Heat exchange quality

7.8.5.1 Monitoring a reference exchanger in the system

This is a very important measurement because it expresses the efficiency of the production unit.

Heat exchange quality is represented by the heat transfer coefficient:

$$K = \frac{q}{S \times \Delta_{tm}} \text{ with } \Delta_{tm} = \frac{(t_1 - t_4) - (t_2 - t_3)}{\text{Log} \frac{t_1 - t_4}{t_2 - t_3}}$$

K = heat transfer coefficient ($\text{kcal}/\text{m}^2 \cdot \text{h} \cdot ^\circ\text{C}$)

q = heat loading ($\text{kcal} \cdot \text{h}^{-1}$)

S = exchange surface area (m^2)

t_1 = temperature of incoming cooling water ($^\circ\text{C}$)

t_2 = temperature of outgoing cooling water ($^\circ\text{C}$)

t_3 = process input temperature ($^\circ\text{C}$)

t_4 = process output temperature ($^\circ\text{C}$)

with: $q = Q \times (t_2 - t_1)$

Q being the cooling water flow rate.

The heat transfer coefficient can be measured and systematically monitored if six values are known: four temperatures and two flow rates. Here again, reliable measurements are a must.

7.8.5.2 Measuring scale deposits: the scale meter

This type of apparatus comprises a heating cell through which the fluid under analysis circulates.

Thermocouples placed on the wall and at the inlet give the temperature differences and allow variations to be detected. A data acquisition console uses this information to compute the resistance of the scale deposit.

The fluid can also circulate inside a heated tube instead of in the annular space.

7.8.6 Remote monitoring

Operators are concerned with two basic objectives:

- Optimizing operating costs.
- Safeguarding quality and continuous service.

Water treatment techniques have evolved to meet these requirements by the development of computerized monitoring procedures.

However, it must be remembered that all automatic systems have their limits. The reliability of automatic system components has greatly outstripped the reliability of sensors and of the equipment they are supposed to monitor or control.

As a result, human intervention and action remain unavoidable. There is a need for maximum information as soon as possible to decide whether an emergency situation has arisen and what action is required to restore normal operating conditions rapidly.

In this connection, computerization has brought solutions that are flexible, powerful, fast, economical and effective in detecting and correcting operating anomalies.

Figure 85 gives a simplified diagram of computerized monitoring of a cooling system based on an automatic system and a processing unit.

Principle:

A variety of measurements are acquired and processed; remote monitoring.

Function of the automatic system:

- Acquires measurements: pH, TOC, % NTU, Cl_2 , $^{\circ}\text{C}$, mpy, concentration rate, bacteria counts, etc.
- Computes:
 - A scale deposit coefficient based on the reference exchanger's temperatures or a scale meter.
 - The concentration rate $C = \frac{A}{D}$.
- The proportionality coefficient between make up and reagent dosage.
- The coherency coefficient between the amount of reagents added and amounts actually injected into the system (operating time of proportioning pumps).
- Actuates the various operating components (pumps, valves, etc.).

Function of the processing unit:

- Remote monitors parameters and manages alarms.
- Calls operators with telephone distribution.
- Displays facility's monitoring operations on the telephone computer system.
- Remote manages the automatic system.

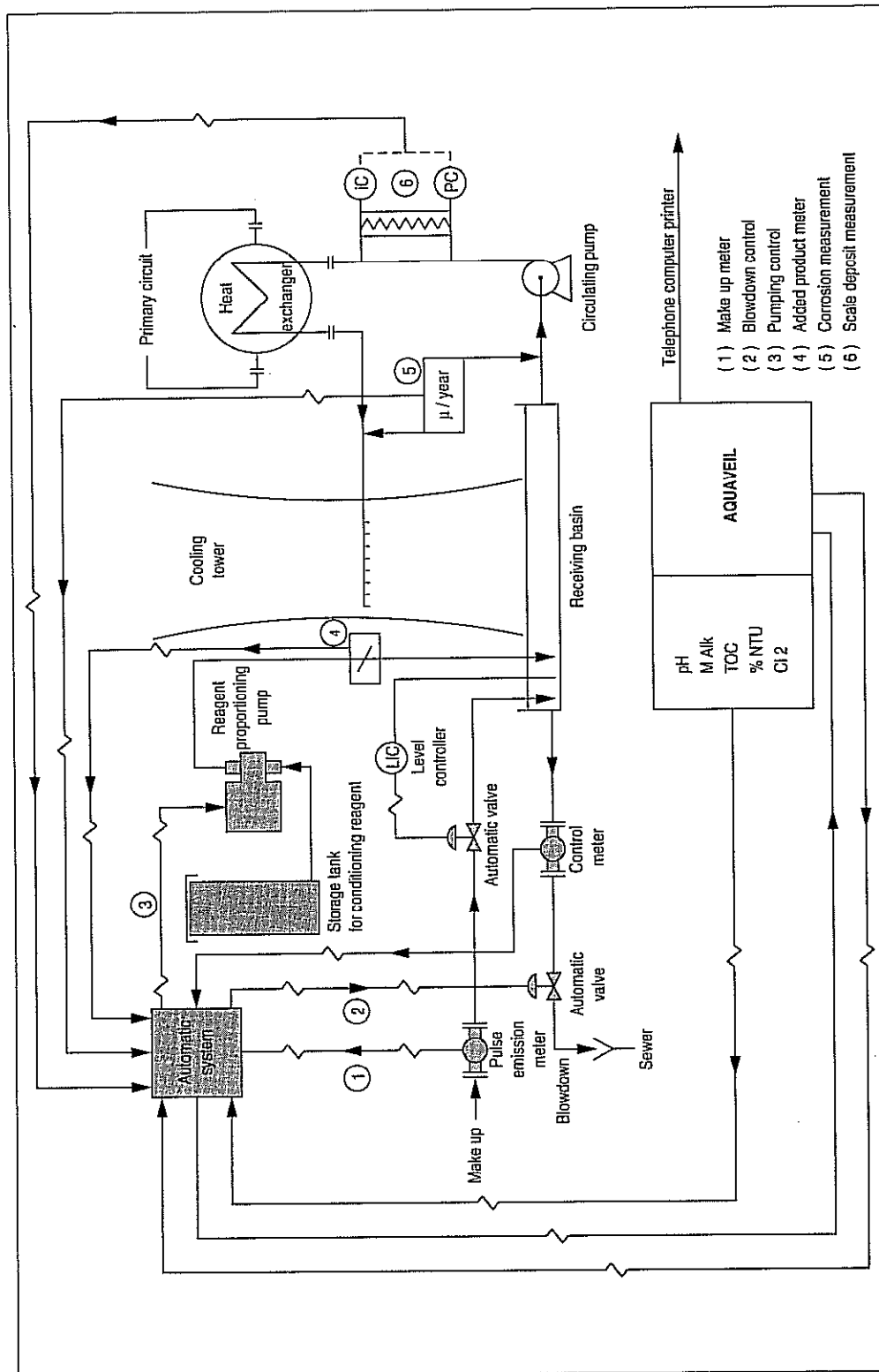


Fig. 85 Remote monitoring. Simplified diagram.

7.9 Once-through systems

There is no concentration phenomenon in this type of system to limit reagent consumption. However, residence times are generally short.

7.9.1 Protecting against fouling and biological growth

The system is protected by:

- Prior purification of the water if needed (clarification-coagulation, coagulation-filtration).
- Conditioning with dispersants, chlorination.

The use of biocides is difficult because of problems with discharges and reagent consumption. It can sometimes be envisaged when temporary recycling is possible.

7.9.2 protecting against scale and corrosion

7.9.2.1 If the water is close to stability or scale-forming when cold

The major risk is scale formation, especially on hot surfaces.

The stabilization process with antscale-dispersant inhibitors will therefore be used.

7.9.2.2 Special case of strongly mineral water from deep wells

It should be remembered that the protective calcium carbonate coating is formed only if the dissolved oxygen content in the water is greater than $5 \text{ mg} \cdot \text{l}^{-1}$.

Water from deep wells often has no dissolved oxygen and contains a significant amount of soluble CO_2 and ferrous iron. When it gets to the surface, the water gradually becomes loaded with oxygen. The oxygen is first consumed by oxidation of the iron from the soluble ferrous Fe^{2+} state to the ferric Fe^{3+} state which precipitates out.

Here it is recommended to remove the iron from the water by aeration-filtration possibly followed by neutralization of the excess CO_2 and then by antscale-dispersant conditioning.

7.9.2.3 If the water is corrosive but very slightly mineralized (Ca, M alk and SSA) or has high chloride salinity, for example, the use of a zinc-polyphosphate-type corrosion inhibitor is recommended.

Given the short residence time, very good protection can be achieved with smaller amounts of inhibitor than in an open recirculating system. Inhibitors can be cut down to values of around 5 to $10 \text{ mg} \cdot \text{l}^{-1}$ of P_2O_5 .

In piping that conveys brines, this type of zinc-polyphosphate protection is used, or the system is protected by reducing the oxygen with sulfite-based compounds.

Table 60 gives a summary of protection procedures.

Table 60
Once-through systems

Trouble	Protection
Fouling and biological growth	• Sieving and/or • Clarification-filtration • Iron removal (from some well water) • Dispersants • Chlorination • Biocides (batch treatment)
Scale formation	• Antiscale-dispersants
Corrosion	• Corrosion inhibitors (e.g. zinc – polyphosphates) • pH adjustment

7.10 Closed recirculating systems

7.10.1 Controlling fouling and scale formation

Here protection consists in filling the system with "noble" water, i.e. softened or demineralized water. In some instances, complementary action may be called for with dispersants and possibly side-stream filtration.

7.10.2 Controlling corrosion

It is absolutely necessary to provide anticorrosion protection. This is especially true since the softened or demineralized water chosen to fill up the system is particularly aggressive and corrosive.

Two types of processes are used:

- Corrosion inhibitor that forms a protective film.
- Oxygen reducer.

7.10.2.1 Corrosion inhibiting processes

These are the most common. They usually give rise to anodic reactions and produce an insoluble, bonded, compact film.

Since protection is anodic, it will be successful only if all the anodes are passivated and if there is sufficient inhibitor content in the solution to keep up a passivation "pressure" (about a gram per liter).

Additionally, since closed systems are often built of a variety of metals, inhibitors must imperatively be valid for all of them (they must include cuprous metal corrosion inhibitors).

These products are used in an alkaline pH and this means that acid corrosion can be avoided.

Often the pH is obtained by incorporating a buffer salt such as borax in the inhibiting reagent (which regulates the pH of the system to between 8 and 9).

Three different types of inhibitors are basically used:

- High-content chromates.
- High-content nitrites.
- Molybdates (sometimes combined with phosphates).

These inhibitors are often associated with dispersants.

7.10.2.2 Oxygen reducer processes

These processes are used when hot systems are involved and when resistivity requirements entail constraints on saline products introduced into the environment.

The processes consist in carrying out boiler water-type conditioning by introducing:

- An oxygen reducer.
- An alkaline substance (trisodium phosphate, amine, etc.) to achieve a pH > 9.5 in the system.

The main types of reducers are as follows:

- Sulfites
- Tannates
- Hydrazines
- Organic reducers.

Table 61 summarizes the protection procedures for closed recirculating systems.

Table 61
Closed systems

Trouble	Protection
Fouling	Side-stream filtration Dispersants
Biological growth	Biocides (shock treatments)
Scale formation	Softening make up water Demineralization
Corrosion	High-content corrosion inhibitor conditioning: • Chromates • Nitrites • Molybdates • Organic + buffer salt possibly (borax) or oxygen reducer conditioning: • Sulfite • Tannate • Hydrazine • Organic + pH booster • Amine • Phosphate

7.10.3 Comments on so-called "closed" systems

"Strictly closed" systems have been discussed, but systems are increasingly called "closed" when in fact they have rather significant water losses. This implies make up and potential pollution.

Depending on the length of residence time, the following can be considered:

- Conditioning of the nitrite-dispersant or molybdate-dispersant type (possibly with protection against biological growth) if residence time is over one week. Here, dosage can approach the minimum range.
- Conditioning similar to what is proposed for open recirculating systems if residence time is under one week. The quality (scale-forming or corrosive) of the available water must be taken into account.

Here, installation of side-stream filtration and use of a dispersant are recommended.

7.11 Seawater systems

This subject is dealt with more thoroughly in "Materials and Treatments for Seawater Systems", 420 pages, soon to be published by Editions Technip.

7.11.1 Seawater and brackish water

Typical composition of a "standard" seawater (according to ASTM): see Table 62.

Table 62

Typical analysis of seawater

CHEMICAL ANALYSIS							
(meq·l ⁻¹)				(meq·l ⁻¹)			
Total hardness (TH)				130	Free alkalinity		
Carbonate hardness				3	P alk		
Permanent hardness				127	M alk		
Calcium hardness (CaH)				22	Salts of strong acids (SSA)		
Magnesium hardness				108	Total salinity		
Silica expressed as SiO ₂				4	mg·l ⁻¹		
ANIONS		(mg·l ⁻¹)	(meq·l ⁻¹)	CATIONS		(mg·l ⁻¹)	(meq·l ⁻¹)
Chlorides	Cl ⁻	19 880	560	Calcium	Ca ²⁺	440	22
Sulfates	SO ₄ ²⁻	2 740	57	Magnesium	Mg ²⁺	1 315	108
Nitrates	NO ₃ ⁻	—	—	Sodium	Na ⁺	11 040	480
Bicarbonates	HCO ₃ ⁻	183	3.0	Potassium	K ⁺	390	10
Bromide	Br ⁻	68	0.9	Strontium		1.3	0.3
		22 871	620.9			13 186.3	620.3

The salinity of seawater is high and can vary depending on geographical location:

Baltic Sea	17 g·l ⁻¹
Atlantic and Pacific.....	32 to 35 g·l ⁻¹
Mediterranean	38 to 40 g·l ⁻¹
Red Sea	43 to 45 g·l ⁻¹
Dead Sea	270 g·l ⁻¹

The resistivity of different seawaters versus temperature is shown in Fig. 86.

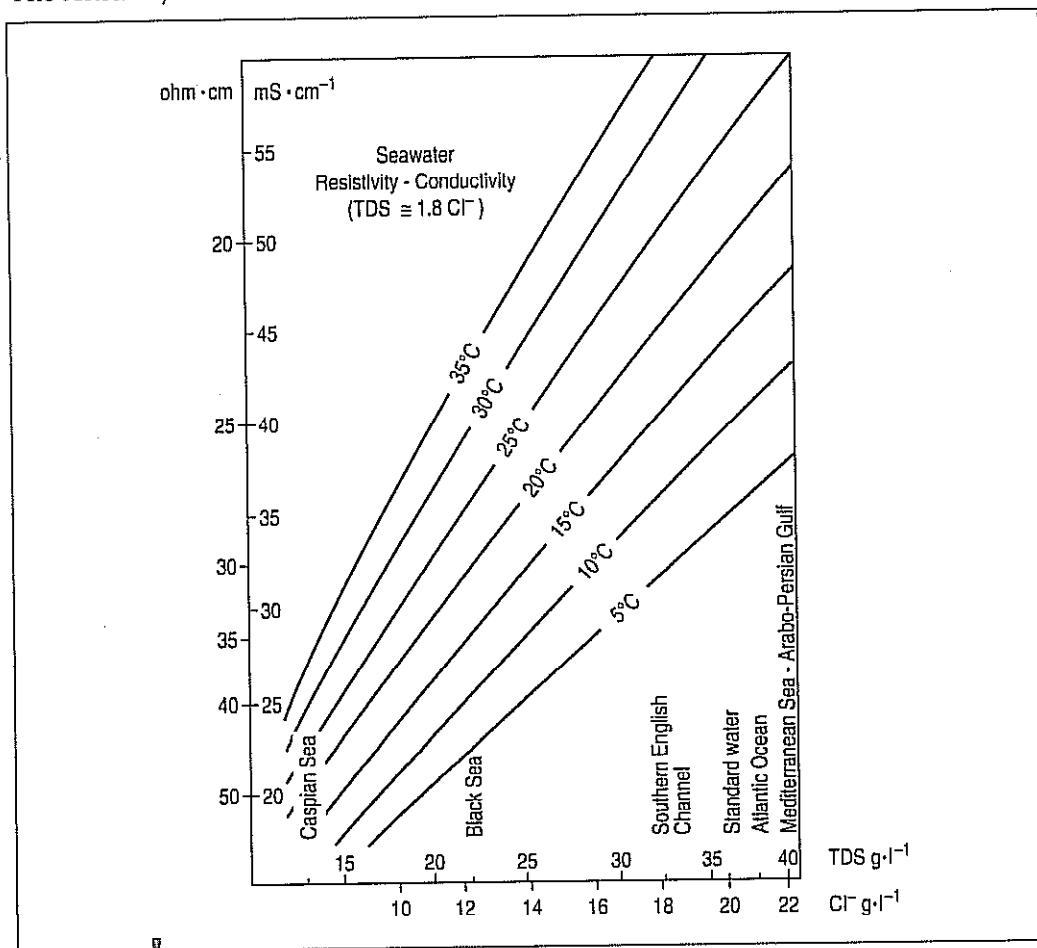


Fig. 86 Resistivity of different seawaters versus temperature

Some physical characteristics of seawater are particularly important: turbidity, suspended solids, number of particles, and fouling index. They can vary widely according to geographical location.

- Far out at sea, suspended solids are mainly plankton (generally several milligrams per liter, but the content depends on geographical and climatic conditions).
- Near the shore, the following can be found:
 - Very high sand content.
 - Pollution from municipal or industrial discharges (SS content of 10 to 200 mg·l⁻¹).

- Between the two, several hundred meters from the shore, there are sporadic seasonal algae fields that can cause very severe sieving problems.

7.11.2 Organic fouling

Fouling is a common cause of increased head losses and deterioration of the through-tube bundle heat exchange coefficient.

It can have several origins:

- Organic mucus of bacteria and algae.
- Attached soft organisms such as anemones and Ascidiacea.
- Embedded colonies of hard organisms such as crustaceans, mussels, oysters and barnacles that are hard to get rid of and give rise to pitting corrosion under deposits by differential aeration.

7.11.3 Scale formation

As a general rule with seawater:

Type of precipitation	Precipitation temperature
CaCO_3	60-70°C
$\text{Mg}(\text{OH})_2$	90°C
CaSO_4	105-110°C

7.11.4 Corrosivity of sea water

Main factors (see Fig. 87):

- Oxygen content.
- Chloride content.
- Biological fouling.
- Pollutants (sulfides, etc.).
- Temperature.
- Water velocity.

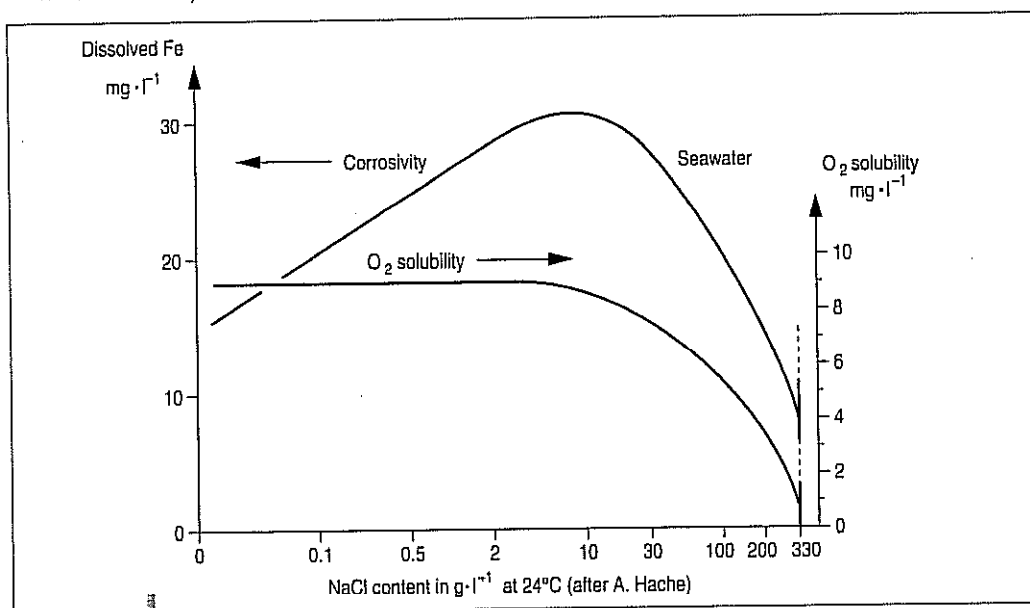


Fig. 87 Relationship between seawater corrosivity and salinity

The Ryznar index can hardly be used because it is based on the Langelier graph. The latter is valid only for salinity lower than $5 \text{ g}\cdot\text{l}^{-1}$. The Stiff and Davis index must therefore be used.

When oxygen is completely lacking, corrosion is much less intense (e.g. degassed, clean, cold seawater).

Brackish water (estuaries) is always polluted and often more dangerous than seawater.

7.11.5 Choosing materials

Certain building materials provide protection against corrosion:

- Coated steel (plastic, Säkaphen): e.g. waterbox.
- Enameled cast iron: e.g. pump barrel.
- Special steels (with chromium, nickel and molybdenum).
- Cuprous alloys (admiralty brass, cuproaluminum, etc.): e.g. exchanger tubes, valves.
- Nickel alloys: e.g. exchanger tubes.
- Special metals (titanium): e.g. exchanger tubes.
- Concrete, asbestos cement: e.g. pipes.
- Plastics: e.g. piping.

7.11.6 Once-through cooling systems

7.11.6.1 Protecting against organic fouling

- Mechanical sieving and screening around 4 mm at water inlets.
- Chlorination to control organic fouling:
 - Means: distribution of chlorine liberated by electrolysis in situ in the seawater (electrochlorination).
 - Dosage: around 3 g of Cl_2 per cubic meter of seawater for 10 to 15 min, so as to achieve $0.2 \text{ g}\cdot\text{m}^{-3}$ to $1 \text{ g}\cdot\text{m}^{-3}$ at the network outlet.
 - Frequency: in batches three to six times a day if the temperature $<30^\circ\text{C}$, continuously if the temperature $>30^\circ\text{C}$.

7.11.6.2 Protection against scale formation

- Cleaning by circulating balls which also reduces the bonding capacity of any scale in condenser exchange tubes in power plants.
- Possible use of antiscaling-dispersants (polyphosphates, phosphonates, acrylates).

7.11.6.3 Protecting against corrosion

- Cathodic protection by imposed potential (or by soluble anode).
- Cathodic protection by injecting ferrous sulfate at a rate of 1 g of Fe^{2+} per cubic meter of water for one hour a day at the inlet of copper alloy tube bundles (admiralty copper). The protective coating that is formed must be even and continuous, but as thin as possible so as not to hinder heat exchange. In normal operation, treatments could be brought down to an hour per week or every two weeks and possibly even less.

7.11.7 Open recirculating systems with cooling towers

Though they seldom operate with this type of water, they sometimes have to. In addition to the precautions defined for once-through systems, the following should also be pointed out:

- Limited concentration rates because of the salinity (generally <2).
- Side-stream filtration with in-line coagulation on filters is advantageous.
- Corrosion protection possible with pH close to 7 and injections of zinc-polyphosphate compounds associated with dispersants.
- Biocide program with combined action of chlorination, biocides and biocides.

7.12 Conclusion

Several important points should be stressed:

- Conditioning of cooling water, i.e. the protection of systems, is not a secondary problem. The lifetime of the equipment and the efficiency of the production unit may depend directly on it.
- The choice of water treatment (purification and conditioning) must be studied effectively during the project stage since it is associated with the system's design and environment.
- Water conditioning must be an automatic reflex as soon as water is pumped into the system. The first weeks are always crucial in the life of a network.
- Maintaining protection requires monitoring of course, but also close cooperation between users and water treatment specialists.

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Index

A

- acidified spent caustic steam stripping, 139, 140
- activated sludge plant
 - application area, 112
 - bacterial mass growth, 97
 - blowered air, 106
 - excess sludge production, 107
 - loads, 104
 - monitoring, 111
 - O₂ consumption, 106
 - powdered activated carbon addition, 116
 - principle, 96
 - sizing, 103
 - surface aerators, 105
 - upsets, 109, 110, 111
- alkaline ion content, definition of, 7
- alkalinity control in open cooling systems
 - acid addition, 217
 - carboxylic resin softening, 218
 - lime softening, 218
- alkalinity, measurement of, 5
- alkalinity precipitation
 - by lime and caustic, 38
 - processes, 9
- ammonium
 - measurements and standards, 20
 - reactivity, 21
- API separator
 - design, 70, 74
 - disposal of bottom sludge and floating matter, 73
 - feed, 72
- aromatic HC removal, 108, 109, 121
- ASP (see activated sludge plant)

B

- bicarbonates, dissociation of, 7
- biocides, 210, 211
- biofilters, 102, 103
- biofiltration on granular media
 - application area, 114
 - downflow filters, 101
 - process, 101, 114
 - upflow filters, 102, 103
- brackish water, definition of, 8

C

- carbonic attack, 3
- carbonic equilibrium, definition of, 6
 - aggressivity, definition of, 6, 212
 - aggressivity parameters, 7
 - balancing CO₂, 6, 212
- case studies (refineries and petrochemical plants)
 - Elf, Grandpuits, 171
 - Esso SAF, Gravenchon, 178
 - Mobil Oil, Gravenchon, 167
 - Shell complex, Berre, 182
 - Shell Oil, Petit-Couronnel, 75
- catalytic alkylation WW, 48
- chemical oxygen demand
 - breakdown, 36
 - measurement and significance, 16
- circular oil separator, 75
- closed recirculating systems
 - corrosion inhibitors, 235
 - oxygen reducers, 236
 - protection against leaks, 237
- coalescence deoiling, 92, 93, 120
- coalescer filters, 93

COD equivalences
 hydrocarbons, 19, 20, 108
 inorganic reducers, 17, 107
 oxygenated compounds, 18, 107, 108
 COD fractional breakdown, 107, 116
 COD (*see chemical oxygen demand*)
 collectors of oil layers
 by capillarity, 80
 dynamic, 80
 weir-type, 79
 colloidal material
 assessment by turbidity, 11
 assessment by zeta potential, 11
 definition of, 12
 color of water, measurement of, 12
 concrete degradation in open cooling systems, 222
 conductivity of water versus salinity, 10
 continuous centrifuges, 189
 cooling system protection
 corrosion inhibitor process
 main inhibitors, 216, 217
 principle, 216
 Langelier Index, 213
 natural equilibrium process, 214
 Ryznar index, 212
 scale inhibitor process, 214
 Stiff and Davis Index, 213
 cooling tower
 blowdown, 50
 number of cycles, 117
 cooling water savings
 reusing industrial WW, 118, 224
 reusing municipal WW, 118
 sidestream purification, 119, 223, 224
 corrosion measurement and monitoring
 corrosion meters, 227
 corrosion rates, 228
 test samples, 227, 230
 corrosivity of water, 7
 cracking condensates
 composition, 45, 48
 diagram, 47

D

DAF (*see dissolved air flotation*)
 deballasting WW, 51
 demulsifiers, 83
 denitrification, 98
 desalter effluent
 composition, 44
 salt discharge, 45

desulfurization process, 124, 125
 extractive sweetening, 124, 125, 127
 Merox-type sweetening, 124, 125, 126
 discharge regulations
 quality, 54, 55, 56
 volume, 52
 dissolved air flotation
 diagrams, 87
 operation, 88, 89
 principle, 86
 dissolved organic matter
 measurement by permanganate value (PV), 12
 measurement by total organic carbon (TOC), 13, 193
 distillation condensates
 composition, 48
 diagram, 46
 dual media filters, 91
 dynamic thickening by DAF, 189

F

FeS precipitation
 with dissolved O_2 , 85
 without dissolved O_2 , 84
 filter-presses, 190
 filtration on granular media
 downflow, 89, 91
 upflow coalescence, 90, 92, 120
 flocculation
 with flocculants, 82, 83
 with inorganic coagulants, 82
 with organic coagulants, 82, 83, 84
 foaming, 111
 French degree, definition of, 4

G

gram-equivalent, definition of, 4
 gravity-fed belt filters, 191

H

hardness
 permanent, definition of, 6
 temporary, definition of, 6
 titration of, 5
 definition of, 5
 heating condensates, 48
 heating condensate recycling
 coalescence, 120
 granular activated carbon filters, 121
 precoat filters, 121

hydrocarbon analysis
 by direct extraction, 23
 by indirect extraction, 23
 by infrared spectrophotometry, 24, 25, 26, 27, 192
 by ultraviolet, 28, 192, 193
 hydrocarbon dispersion in WW, 57
 hydrocarbon leaks in cooling systems, 211
 hydrocarbon oxidizability, 21
 hydrocarbon solubility, 21

I

IAF (*see induced air flotation*)
 induced air flotation, 94
 inorganic coagulants
 precipitation as hydroxides, 37, 82
 precipitation as sulfides, 38, 84, 85
 ion balances
 establishment of, 7
 examples of, 9
 interpretation, 34, 35

L

lamella oil separator
 CPI separator, 77
 principle, 76
 lube oil plant solvents, 49

M

M alk (*see methyl orange alkalinity*)
 mercaptans
 characteristics, 30
 dissociation, 31
 titration, 33
 methyl orange alkalinity, definition of, 5
 mineralization of water, 3

N

Na_2SO_4 solution, 136, 137
 naphthenic acids
 organic acidity, 34
 titration, 25
 nitrification, 98
 normality, definition of, 4
 nylon plant effluents (caprolactam polymerization), 165

O

once-through cooling system protection, 234
 open recirculating cooling system
 analytical monitoring, 226

bacteria counts, 14
 circuit preparation, 224
 concentration factor, 13
 concentration rate, 117, 198, 218, 219
 deconcentration blowdown, 50, 198, 219, 220
 drift loss, 197
 evaporation, 197
 fouling and biological growth, 199, 200, 201, 202
 fouling volume, 13
 make up flow rate, 198
 reference heat exchanger, 23
 remote monitoring, 232, 233
 shutdown precautions, 225
 oxidizing agents versus, O_2 42

P

P alk, M alk, relationship between, 5
 P alk (*see phenolphthalein alkalinity*)
 petrochemical effluent biodegradation
 exothermic reactions, 156
 mass loading, 158
 salinity influence, 155, 157
 sludge settleability, 157, 158
 petrochemical effluent chemical treatment
 GAC adsorption, 159
 strong oxidizing agents, 158
 tertiary flocculation, 159
 wet air oxidation, 159
 petrochemical effluent features, 155
 COD/BOD₅ ratios, 156
 toxic pollutants, 156, 157
 volatile solvents, 156
 pH meters, 193
 phenol biological degradation, 152
 phenols
 analysis, 29
 biodegradation, 29, 114
 phenol solvent extraction
 centrifuge extractors, 152
 key parameters, 147, 148
 mixer-settlers, 148, 149, 150
 principle, 145, 146
 pulsed columns, 149, 150, 151
 solvents, 147
 phenolic compounds, 130, 131
 phenolphthalein alkalinity, definition of, 5
 physicochemical purification
 aims, 81
 processes, 81
 polypropylene plant effluents (aqueous dispersion), 163
 polystyrene plant effluents (H_3PO_4 dispersion), 164

ppm CaCO_3 , definition of, 4
 propylene oxide plant (epichlorhydrin process)
 discharges and pollutants, 162
 treatments, 162

R

rainwater, 50
 reference polyaromatic hydrocarbons, 28
 resistivity of water versus salinity, 10
 reusing WW in cooling towers
 municipal WW, 118
 process WW, 118, 119
 reusing WW in MP boilers, 120
 rising velocity of oil droplets, 69

S

salts of strong acids, definition of, 7
 sanitation WW, 51
 seawater analysis, 237, 238
 seawater systems
 corrosivity, 239, 240
 materials, 240
 once-through, 240
 open recirculating, 241
 organic fouling, 239
 scale formation, 239
 sewer segregation, 56, 59
 silica, ionization of, 7
 sludge bulking, 110
 sludge disposal, 189, 191
 sludge production, 188, 191
 sludge types, 188
 sludge volume index, 112
 soft water, definition of, 8
 sour condensate desulfurization
 air oxidation, 64, 65
 preacidification and air stripping, 62, 64
 preacidification and steam stripping, 62, 63
 spent caustic
 chemical composition, 128, 130, 133
 neutralization, 135, 138
 oxidation, 141
 physical composition, 128, 129
 prewashing, 134
 recycling, 123
 washings, 134
 spent caustic oxidizers
 with air, 143, 145
 with O_2 , 144
 sprung acids, 132
 SSA (see salts of strong acids)

steam cracking WW
 composition, 52
 diagram, 53
 styrene plant
 discharges, 160
 treatments, 161
 sulfides
 analysis, 32, 33
 dissociation, 30, 41
 interference with M alk, 33
 sulfide precipitation as FeS , 84, 85
 sulfur compounds
 air oxidation, 64, 65
 biological oxidation, 40
 oxidation levels, 39
 oxidation reactions, 40, 41
 surge tanks and basins, 59
 suspended solids
 description of, 11
 measurement of, 11
 standards, 14, 15

T

tanker cleaning WW, 51
 tertiary treatments
 COD and TOC reduction, 116
 granular activated carbon, 116, 121
 powdered activated carbon, 116
 SS elimination, 115, 116
 thiosulfates
 analysis, 32
 oxidation, 32
 total alk, definition of, 5
 total oxygen demand, 193
 total salinity, assessment of, 10
 trickling filters
 application area, 113
 process, 99, 113
 random and ordered fill, 99
 upsets, 100, 109, 110, 111

U

UV absorption (turbidimetry), 193
 UV fluorescence, 192

V

volatile solids, 96

F. BERNÉ J. CORDONNIER

INDUSTRIAL WATER TREATMENT

This book aims to introduce waste water and cooling water treatments to student and graduate engineers in the oil and chemical industries. It is based on industrial implementation of these treatments and describes operators' experiences in running their own facilities in a number of plants.

The following points are developed:

- An introduction to the vocabulary and chemistry of waste water purification with a discussion of the organic and inorganic pollutants that are inherent to the oil industry.
- The main sources of polluting effluents characterized according to processes, along with a number of excerpts from discharge standards.
- The sequencing of treatments as per the three conventional stages of gravity deoiling, physicochemical and biological purifications, with an extension to some cases in petrochemical plants.
- The potential for recycling some purified effluents that is made possible through tertiary purification.
- Case studies of five leading French refineries.
- A chapter dealing with the different types of spent caustic and how treatment can be improved.
- The definition and implementation of cooling system conditioning processes in order to protect them from fouling, scaling and corrosion.

The challenge for both effluent purification and cooling water conditioning is the search for minimum makeup water consumption and consequently optimum effluent recovery in order to ensure better environmental protection.



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