

CHAPTER 13

WASTE WATER FROM CHEMICAL AND ELECTROCHEMICAL METAL-TREATMENT PROCESSES

CHARACTERISTICS OF THE WASTE WATER

The processes used in this industry involve the use of several components such as alkalis, acids, heavy metals, cyanides, EDTA, oil, grease and fat. Table 13.1 is a survey of the various pollution sources in this industry.

TABLE 13.1

Sources of pollution in the metal-plating industry

Source	Pollutants	Suggested treatment
Pickling baths	Nitric acid, hydrochloric acid, sulphuric acid, hydrofluoric acid, phosphoric acid, acetic acid, alkalis	Neutralization
Degreasing baths	Sodium hydroxide, sodium carbonate, sodium silicate, cyanides, organic solvents	Neutralization, oxidation
Galvanic baths	Copper, nickel, zinc, cadmium, manganese, aluminium, iron, cobalt, chromate	Ion exchange, precipitation, reduction
Cyanide baths	Copper, zinc, cadmium, cyanide	Oxidation, precipitation, ion exchange
Polishing baths	Acid, chromate	Neutralization, oxidation, precipitation, ion exchange
Hardening processes	Cyanide, nitrate	Oxidation, reduction
Phosphating baths	Phosphoric acid, metal ions	Neutralization, precipitation, ion exchange
Eloxal baths	Metal ions, chromic acid	Reduction, precipitation, ion exchange
Other bath treatments	Nitrite, metal ions	Oxidation, reduction, precipitation, ion exchange

Metals are pickled in order to clean the surface from rust and scale. This applies both to ferrous and non-ferrous metals, mainly zinc and copper and their alloys. This treatment usually involves reaction with strong acid (see Table 13.1). Mainly sulphuric acid but also hydrochloric, nitric and hydrofluoric acids are used. Phosphoric acid is occasionally used with ferrous metals because of its corrosion inhibiting properties. Certain metals can be pickled in alkaline solutions. Either sodium or potassium hydroxide is used in a concentration of 10-20%. The pickling solution might also contain various salts such as sodium chloride, iron(II)sulphate, manganese(II)sulphate, magnesium sulphate, etc.

Usually relatively high concentrations of acids are used in pickling baths, namely 5-25%, and for some non-ferrous metals, chiefly copper and its alloys, the concentration might be as much as 50-60%.

Obviously, such highly acidic or alkaline waste water cannot be discharged without prior neutralization. The surface is often degreased with a 10-15% solution of sodium hydroxide or sodium carbonate, which requires neutralization before discharge. In some instances organic solvents such as petrol or trichlorethylene are also used.

The composition of the electroplating baths depends on the kind of plating process involved. The baths may therefore include a number of compounds such as potassium carbonate, sulphuric acid, sodium hydroxide, sodium chloride, copper(II)cyanide, potassium cyanide, sodium cyanide, zinc sulphate, copper(II)sulphate, mercury(II)chloride, nickel(II)sulphate, manganese(II)sulphate, chromate, lead(II)acetate and several organic substances such as dextrine, oil, glue, etc.

The cyanide baths and waste water from hardening processes can contain besides metal ions, cyanide, which requires special treatment. Several other types of treatment baths contain chromate or even chromic acid.

Phosphating baths contain metal ions together with phosphorous compounds, which components can be removed simultaneously by chemical precipitation. Baths containing nitrite must often be treated before discharge by oxidation of the nitrite to nitrate.

Table 13.2 gives a detailed survey of the materials used in typical processes.

TABLE 13.2

Typical process materials

Process	Materials
<u>Cleaning processes:</u>	
Aluminium	Solvents, alkali, phosphoric acid, nitric acid, chromic acid, sulphuric acid, sodium phosphate, various types of oil
Steel	Solvents, sodium phosphate, chromic acid, hydrochloric acid, sulphurous acid, silver cyanide, potassium cyanide, potassium carbonate, sodium cyanide, sodium hydroxide, cadmium oxide, sodium carbonate, copper(I)-cyanide, rochelle salt, sodium polysulphite, potassium stannate, hydrogen peroxide, nickel sulphite, nickel chloride, boric acid
Stainless steel	Potassium permanganate, sodium carbonate, sodium hydroxide, nitric acid, hydrochloric acid, solvents
Titanium	Alkali, solvents, sodium dichromate, sodium hydroxide
Magnesium	Alkali, solvents, oil
<u>Plating processes:</u>	
Aluminium	Sodium dichromate, chromic acid, sulphuric acid, nickel acetate, aluminium sulphate
<u>Passivating processes:</u>	
Aluminium	Chromic acid, nitric acid
Steel and stainless steel	Nitric acid, sodium dichromate, hydrochloric acid
Titanium	Nitric acid
<u>Coating processes:</u>	
Aluminium	Aluzinc, chromic acid, nitric acid, sulphuric acid
Steel	Sodium dichromate, sulphuric acid
Stainless steel	Titanium, magnesium, chromic acid, sodium dichromate, sulphuric acid

As seen from this short description, the waste water from the plating industry has a high concentration of contaminants.

The treatment required is not only dependent on the processes used, but also on the amount of waste water discharged.

Tables 13.3 and 13.4 give the characteristic composition of waste water discharged from the pickling process of ferrous and non-ferrous metals, respectively.

TABLE 13.3

Composition of waste water discharged from pickling of ferrous metals pH: 4-8

Free sulphuric acid (g/l)	up to 0.5
FeSO ₄ (g/l)	up to 0.5
Iron (metallic Fe) (mg/l)	100-2000
Suspended solid (mg/l)	up to 4000
Permanganate value (mg/l)	20-1500

TABLE 13.4

Composition of waste water discharged from pickling of non-ferrous metals pH: 1-3

Sulphate (g/l)	1-50
Copper (g/l)	0.02-1
Iron (g/l)	0.02-0.2
Zinc (g/l)	0.1-1
Free H ₂ SO ₄ (g/l)	0.2-2

Table 13.5 gives the composition of waste water from a hardening shop and Table 13.6 that from electroplating plants.

TABLE 13.5

Composition of waste water from a hardening shop

Colour	dark yellow
pH	9-11
CN ⁻ (mg/l)	156
Cl ⁻ (mg/l)	750
Ether extract (mg/l)	3800

TABLE 13.6

Composition of waste water from electroplating plants

	Range	Average value	g/m ² surface area of object plated
Suspended matter (mg/l)	150-180	270	35
Volatile content of suspended materials (%)	20-60	30	-
Total solid (g/l)	1-6	3	362
Volatile content of total solid (%)	6-12	9	-
KMnO ₄ value (mg/l)	8-100	20	4
Fe (mg/l)	2-20	12	1.5
Sulphate (mg/l)	30-120	75	25
Nitrate NO ₃ -N (mg/l)	10-120	45	30
Cyanide CN ⁻ (mg/l)	1-6	3	0.3
Copper (mg/l)	0-20	12	1.5
Chromium (mg/l)	5-25	15	<6
Nickel (mg/l)	5-40	18	<12.5
Sludge (ml/l)	1-15	2.4	270

Industrial waste water is often discharged into the sewage system and the waste water from the electroplating industry is quite harmful to the sewer pipes and the municipal treatment plant. Sulphate and especially free acids corrode concrete and all non-acid proof elements. Cyanides are very harmful to the biological process. The presence of cyanide ions makes it difficult to determine the biochemical oxygen demand as cyanide is toxic. Cyanide at a concentration of 0.1 mg/l, for instance, reduces the BOD₅ value by 5%, while 1 mg/l reduces it by 40%.

Heavy metal ions as well as cyanide are harmful to activated sludge treatment plants. On the basis of the literature the maximum concentration for waste water discharged into a biological treatment plant can be established (Table 13.7).

As concentrations higher than the values indicated in Table 13.7 are harmful to the biological processes used in the treatment of waste and since this effect can last for several days, it is clear that the spent bath must be discharged as continuously as possible. Instant discharge of a complete galvanic bath into the biological treatment plant might give it a shock, whereas the same bath would have been harmless for the biological treatment plant if it had been continuously discharged over a day.

TABLE 13.7

Maximum concentrations for biological treatment plant. Some values are indicated as ranges reflecting the different values of the various sources

Metal ion	Concentration (mg/l)
Cr ³⁺	2-10
Cu ²⁺	1
Zn ²⁺	1-10
Ni ²⁺	1-6
Cd ²⁺	2-5
Fe ²⁺ or Fe ³⁺	100
CN ⁻	30-180

TABLE 13.8

Poisonous effect on anaerobic sludge treatment

	Poisoning effect	
	Moderate	Strong
Na (mg/l)	3500	8000
K (mg/l)	2500	12000
Cr (mg/kg dry matter)	200	1500
Cu (mg/kg " ")	500	2000
Zn (mg/kg " ")	4000	10000
Fe (mg/kg " ")	5000	15000
Ni (mg/kg " ")	4000	9000

Metal ions have also a poisoning effect (Jørgensen, 1970) on anaerobic sludge treatment, as shown Table 13.8.

The toxicity of the heavy metals to the organisms involved in the anaerobic digestion of sludge has been examined by Mosey (1976). He suggests limiting the total weight of metal that can be tolerated in municipal sewage in accordance with the following expression:

$$\frac{\text{Zn}/32.7 + \text{Ni}/29.4 + \text{Pb}/3.6 + \text{Cd}/56.2 + \text{Cu}/47.4}{\text{solid concentration} \geq 400 \text{ meq/kg}}$$

The amount of waste water discharged from the electroplating industry is summarized in Table 13.9.

TABLE 13.9

Amount of waste water from the electroplating industry

Process	Quantity of waste water l per m ² surface area of the object	Average
Pickling of ferrous materials	0.4-1.2	0.7
Pickling of non-ferrous materials	0.8-1.5	1.1
Washing and rinsing of pickled objects	25-50	35
Neutralization (pickling)	0.3-0.4	0.35
Chemical degreasing	0.5	-
Electrolytic degreasing	0.3	-
Degreasing with petrol	0.05	-
Degreasing with trichloroethylene	0.05-0.1	0.07
Neutralization (electroplating)	0.25	-
Postacidification of ferrous metals	0.2	
Postacidification of non-ferrous metals	0.3	
Washing after electroplating	10-40	25

Table 13.10 shows the maximum allowable concentration for fish Liebmann (1960).

TABLE 13.10

Noxious limits for fish

Metal ion	Concentration (mg/l)
Hg ²⁺	0.1-0.9
Zn ²⁺	2
Cd ²⁺	3-20
Ni ²⁺	15-55
CN ⁻	0.03-0.25
CrO ₄ ²⁻	15-80
Cr ³⁺	15-80
Cu ²⁺	0.08-0.8

Table 13.11 shows the typical effluent requirement for discharge into a storm sewer or stream.

TABLE 13.11

Maximum allowable concentrations in an effluent being discharged to a storm sewer or stream

pH	6.5-9.0
Cations:	ppm
Ammonia (as NH ₃)	< 2.5
Arsenic	< 1.0
Barium	< 1.0
Cadmium	< 0.05
Chromium:	
Hexavalent	< 0.5
Trivalent	< 1.0
Copper	< 0.5
Iron	< 2.0
Lead	< 0.1
Manganese	< 1.0
Nickel	< 2.0
Selenium	< 0.01
Silver	< 0.05
Tin	< 2.0
Zinc	< 1.0
Anions:	
Chloride	<150
Cyanide	< 0.05
Fluoride	< 1.5
Nitrate	< 45.0
Sulphate	<250
Suspended solids	< 20.0
Oil	< 10

Economy in water

In the metal finishing industry there has been a tendency for finishing processes to be carried out by highly specialized firms. These are generally small, efficient units. In large factories metal finishing is subsidiary to other processes. In the regrouping of factories within one organisation it is often possible to achieve considerable economy in water consumption by concentrating all the water-consuming and effluent-producing operations within one factory. Thus, from an amalgamation of three factories making fasteners, the plating operations were concentrated in only one factory. The total water consumption of 727 m³ per day at the three factories was reduced to 354 m³ per day. At another factory making motor cars the water system within one factory was rationalized. This resulted in a fall of 613 m³ per day in the volume of contaminated effluent (Jenkins, 1970).

Furthermore, it is possible to obtain a considerable saving of water by reorganizing the use of water for the different processes:

1. By use of counter-current rinsing
2. Reuse of baths
3. By setting up strict schedules for rinsing
4. By use of high pressure air rinsing
5. No running water streams

Precipitation of metal hydroxide

One of the processes most used for the removal of metal ions from water is precipitation, as metal hydroxide.

Table 13.12 lists the solubility products for a number of metal hydroxides.

TABLE 13.12

pK_s values at room temperature for metal hydroxides

$pK_s = -\log K_s$, where $K_s = [Me^{z+}] [OH^-]^z$

Hydroxides	$z = \text{charge of metal ion}$	pK_s
$AgOH(\frac{1}{2}Ag_2O)$	1	7.7
$Cu(OH)_2$	2	20
$Zn(OH)_2$	2	17
$Ni(OH)_2$	2	15
$Co(OH)_2$	2	15
$Fe(OH)_2$	2	15
$Mn(OH)_2$	2	13
$Cd(OH)_2$	2	14
$Mg(OH)_2$	2	11
$Ca(OH)_2$	2	5.4
$Al(OH)_3$	3	32
$Cr(OH)_3$	3	32

From the solubility product it is possible to find the pH value at which precipitation will start for a given concentration of the metal ion. Fig. 13.1 shows the solubilities of metal ions at various pH values. By means of this diagram it is possible to find the concentration in solution at any given pH. For example, at pH 6.0 the concentration of Cr^{3+} is 10^{-6} M. This concentration for Zn^{2+} is obtained at pH 8.0.

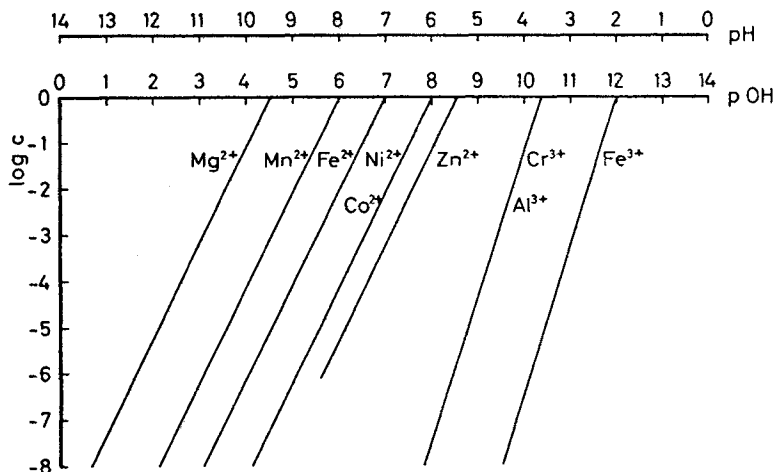


Fig. 13.1. $\log(\text{solubility})$ versus pH and pOH.

The slopes of the lines in Fig. 13.1 correspond to the valency of the metal ions. The slope of the Cr^{3+} and Al^{3+} lines, for example, is +3, while the other ions in the figure have lines with a slope of +2.

From the basis of the solubility product it is possible to find one point through which the line must pass. For example, for the solubility product of iron(II)hydroxide, which is 10^{-15} , we have

$$[\text{Fe}^{2+}] [\text{OH}^-]^2 = 10^{-15} \quad (13.1)$$

The line will therefore go through the point $-\log c=5$ and $\text{pOH}=5$ (c = concentration of Fe^{2+}), since $(10^{-5})^3 = 10^{-15}$.

In Table 13.13 is given the pH value at which the solubility is 10 mg or less of the metal ion per liter (respectively 1 mg or less per liter).

From these considerations it is presumed that other ions present do not influence the precipitation, but in many cases it is necessary to consider the ionic strength

$$I = \sum \frac{1}{2} CZ^2 \quad (13.2)$$

where C is the molar concentration of the considered ions and Z is the charge.

TABLE 13.13

The pH value indicates where the solubility is ≤ 10 mg/l and ≤ 1 mg/l

Metal ion	Solubility	
	≤ 10 mg/l	≤ 1 mg/l
Mg ²⁺	11.5	12.0
Mn ²⁺	10.1	10.6
Fe ²⁺	8.9	9.4
Ni ²⁺	7.8	8.3
Co ²⁺	7.8	8.3
Zn ²⁺	7.2	7.7
Cr ³⁺	5.1	5.4
Al ³⁺	5.0	5.3
Fe ³⁺	3.2	3.5

TABLE 13.14

Activity coefficient f at different ionic strengths

I	$\frac{\sqrt{I}}{1 + \sqrt{I}}$	f for Z = 1	f for Z = 2	f for Z = 3
0	0	1.00	1.00	1.00
0.001	0.03	0.97	0.87	0.73
0.002	0.04	0.95	0.82	0.64
0.005	0.07	0.93	0.74	0.51
0.01	0.09	0.90	0.66	0.40
0.02	0.12	0.87	0.57	0.28
0.05	0.18	0.81	0.43	0.15
0.1	0.24	0.76	0.33	0.10
0.2	0.31	0.70	-	-
0.5	0.41	0.62	-	-

I = ionic strength, Z = charge, f = activity coefficient

On the basis of the ionic strength, it is possible to find the activity coefficient, f, from

$$-\log f = \frac{0.5 \cdot Z^2 \cdot \sqrt{I}}{\sqrt{I} + 1} \quad (13.3)$$

Table 13.14 gives the activity coefficients for different charges of the considered ions, calculated by use of equation 13.3

The solubility product is changed by the presence of other ions, as the activity, $a = f \cdot c$, replaces c in the solubility product. An example will illustrate the calculation.

Example 13.1

Find the solubility of Fe^{2+} when the ionic strength is 0.1 and $\text{pH} = 8.0$.

$$[\text{OH}][\text{H}^+] = 10^{-14} \quad (13.4)$$

$$a_{\text{Fe}^{3+}} \cdot a_{\text{OH}^-}^2 = 10^{-15} \quad (13.5)$$

$$f_{\text{Fe}^{3+}} \cdot [\text{Fe}^{2+}] \cdot f_{\text{OH}^-}^2 \cdot [\text{OH}^-]^2 = 10^{-15} \quad (13.6)$$

from Table 13.14:

$$f_{\text{Fe}^{2+}} = 0.33 \quad (13.7)$$

$$f_{\text{OH}^-} = 0.76 \quad (13.8)$$

Thus

$$[\text{Fe}^{2+}] \cdot 0.33 \cdot 0.76^2 \cdot [10^{-6}]^2 = 10^{-15} \quad (13.9)$$

$$[\text{Fe}^{2+}] = 6 \cdot 10^{-3} \text{ mol/l} \quad (13.10)$$

The precipitation of ions also depends on the formation of complexes. If we use the symbol Me for the metal ion and L for the ligand (the complex-forming compound), the complex formation can be written as:



The mass equation gives:

$$\frac{[\text{Me}(\text{L})_n]}{[\text{Me}] [\text{L}]^n} = K_{\text{complex}} \quad (13.12)$$

where K = the stability constant.

Table 13.15 gives values of the K_{complex} for the formation of some generally used complexes.

TABLE 13.15

Complexes formation

Metal ion	log K_{complex}			
	Cyanide	Ammonia	Hexamine	EDTA
Fe^{2+}	36.0	-	-	14.3
Cu^{2+}	27.3	12.6	22.4	18.8
Zn^{2+}	16.9	9.1	16.2	16.5
Cl^{2+}	16.8	4.9	16.8	16.5
Ni^{2+}	22.0	8.5	19.3	18.6

An example will show the influence of complex formation on the solubility.

Example 13.2

Find the solubility of Zn^{2+} at pH 9.0 when $[\text{NH}_3] = 1 \text{ mM}$.

As $\log K_{\text{complex}} = 9.1$, $\text{Zn}(\text{NH}_3)_2^{2+} = \frac{1}{2} \text{NH}_3\text{-start}$.

According to Fig. 13.1 at pH 9.0 $[\text{Zn}^{2+}] = 10^{-6} = 0.001 \text{ mM}$.

The solubility of $[\text{Zn}^{2+}]$ is therefore 0.5 mM.

Table 13.16 gives the amounts of different chemicals needed to precipitate 100 kg of various metal ions. Neither complex formation nor ionic strength are taken into consideration.

TABLE 13.16

Theoretical consumption of chemicals (in kg) for precipitation of 100 kg metal ion

Chemical used	Metal ion precipitated					
	Fe^{2+}	Fe^{3+}	Cu^{2+}	Ni^{2+}	Cr^{3+}	Zn^{2+}
CaO	100	150	88	96	162	86
$\text{Ca}(\text{OH})_2$	134	201	116	126	213	114
NaOH	144	216	126	136	231	122
Na_2CO_3	190	285	168	181	307	162
MgO	73	110	63	69	117	62
$\text{Mg}(\text{OH})_2$	105	158	92	100	169	90

Precipitation in practice

Since calcium hydroxide is the cheapest source of hydroxide ions, it is most often used for the precipitation of metals as the hydroxide. In most cases it is necessary to determine the amount of calcium hydroxide required in the laboratory.

Flocculation is carried out after the addition of the chemical and before the settling. If the amount of waste water which must be treated per 24h is 100 m^3 or less, it is preferable to use a discontinuous treatment. The system in this case consists of two tanks with a stirrer. The waste water is discharged into one of them while the other tank is used for the treatment process. If chromate is present the treatment processes will follow the scheme below:

1. The concentration of chromate and the amount of acid required to bring the pH down to 2.0 are determined.
2. On the basis of this determination the required amount of acid and reducing compound (SO_2 or Fe^{2+} , see p. 111-112) is added.
3. Stirring 10-30 minutes.
4. The concentration of chromate remaining is determined and the pH checked. If chromate is present further acid or reducing agent is added. In this case the stirring (10-30 minutes) must be repeated.
5. The amount of calcium hydroxide necessary to obtain the right pH for precipitation is measured. If Cr^{3+} is present a pH value of 8-9.5 is normally required.
6. Flocculation 10-30 minutes.
7. Settling 3-8 hours.
8. The clear phase is discharged into the sewer system. The sludge can be concentrated further by filtration or centrifugation.

Stages 1-5 can of course be left out if chromate is not present, and the metal ions can be directly precipitated.

If the amount of waste water exceeds 100 m^3 in 24h, the plant shown in Fig. 13.2 can be used.

This plant includes the reduction of chromate to Cr^{3+} .

A potentiometer and pH meter are used for controlling the addition of acid and reducing agent. These instruments can be coupled to an automatic dosing control. As seen from the figure the plant consists of a reaction tank, a flocculation tank and a sedimentation tank. Usually a settling time of 2h or more is used.

A concentration of $1\frac{1}{3}$ -3% dry matter for the sludge is usually obtained, which is slightly less than that obtained by the discontinuous treatment.

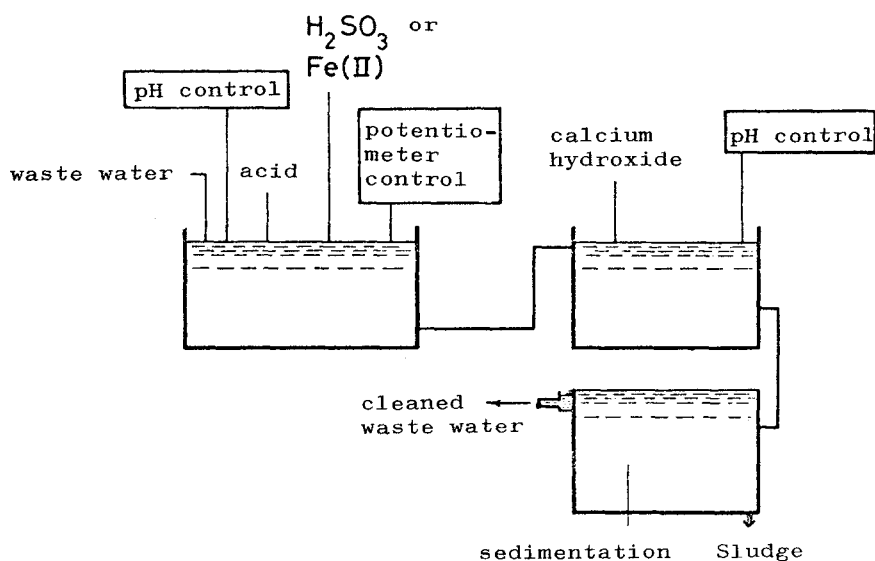


Fig. 13.2. Flow-sheet of plant for precipitation of metal ions.

Fig. 13.3 shows the so-called Lancy system for treating waste water containing chromate.

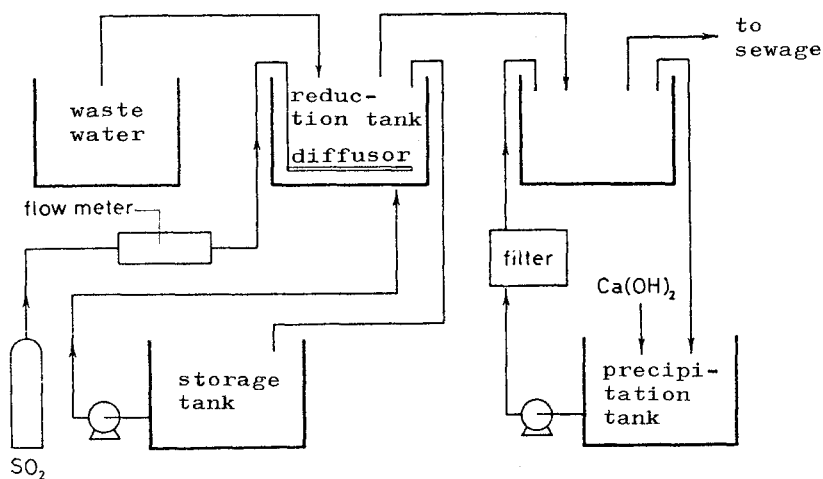


Fig. 13.3. The Lancy system.

This system contains a recirculation tank connected to the reduction tank as well as to the precipitation tank. Filtration of the sludge is continuous and 20-35% dry matter is obtained.

Thomas et al. (1976) have shown that the coagulation and settling of colloidal chromium(III)hydroxide is a function of both the quantity and type of impurity ions present.

The treatment might not operate effectively because of the complexing or stabilizing effects of high carbonate or pyrophosphate concentrations in the water.

It is possible to eliminate the problems caused by carbonate and phosphate by modifying the treatment scheme for the combined waste. Prime consideration should be given to the modification consisting simply of using lime instead of caustic soda to neutralize the waste after the chemical reduction of chromate to chromium(III) has taken place. The use of lime will cause precipitation and removal of most of the carbonate and pyrophosphate species from the solution while also providing doubly charged counter-ions to aid in coagulating the negatively charged chromium(III)hydroxide colloids that exist at pH values of about 8.

Other treatment modifications such as the use of polyelectrolytes to flocculate the stabilized chromium(III)hydroxide system may or may not be effective alternatives depending on the amount of complexation present in a particular waste system.

Data presented indicate that a hydrogen carbonate alkalinity of 250 mg/l as CaCO_3 and a pyrophosphate concentration of 30 mg/l as P together cause appreciable complexation and may make alternatives other than lime neutralization impractical.

The formation of calcium carbonate flocs during lime neutralization could also aid in the removal of chromium(III)hydroxide colloids by the enmeshment mechanism and at the same time making the resulting sludge easier to dewater because of the presence of the large volume of calcium carbonate. The increased treatment efficiency and better sludge handling characteristic may make the use of lime a more favourable solution even though the quantity of sludge may be somewhat increased.

The last treatment modification to be considered is the use of Fe^{2+} ions as the reducing agent in the chromate-reduction step. The end product of this reaction is Fe^{3+} ions. In the neutral pH range this is very effective in removing chromium(III)hydroxide colloids.

Phosphate removal should also be enhanced. This method will regenerate approximately four times more metal hydroxide flocs than would be produced when sulphite is used as reducing agent. The additional quantity of sludge produced makes this scheme less desirable, but it is one that might have advantages in individual cases.

Treatment of waste water containing cyanide

Cyanide is widely used in the plating industry for the formation of metal complexes. The complexation constant for cyanide complexes is included in Table 13.15. The toxicity of cyanide is due to the formation of hydrogen cyanide. The pK_a for this acid is 9.14 at 25°C. The percentage HCN can be found from the following equation:

$$\frac{CN^-}{HCN} = \frac{K_a}{[H^+]} = \frac{7.2 \cdot 10^{-10}}{[H^+]} \quad (13.13)$$

or

$$\log\left(\frac{[HCN]}{[CN^-]}\right) = pK_a - pH \quad (13.14)$$

The percentage of HCN is plotted against the pH in Fig. 13.4.

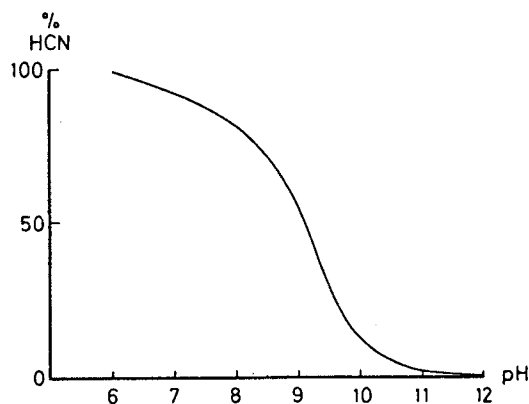


Fig. 13.4. % HCN plotted to pH.

HCN is a volatile compound, having a melting point of -14°C , and a boiling point of 26°C . It is soluble in water in all proportions. HCN combines with haemoglobin to prevent uptake of oxygen by the haemoglobin. However, waste water containing cyanide in small concentrations can be treated biologically (compare Table 13.1). The concentrations of cyanide toxic to various forms of life are given in Table 13.17.

TABLE 13.17

Toxicity of cyanides

	Toxic concentration (mg/l)
Daphnia	1.8 : LD_{50} 48h
Fish	0.1-1.0 : LD_{50} 24h
Biological treatment	abt. 30 : 50% reduction, but strongly dependent on the culture
Anaerobic sludge treatment	50 : 10% reduction

Cyanide is oxidized by aerobic biological treatment provided the concentration is below the toxic limit. Even with smaller cyanide concentrations it is of advantage to acclimatize the treatment plant to the cyanide concentration in question. Anaerobic treatment of waste water containing cyanide is based on the following reaction:



As seen ammonium formate is formed.

Most often cyanide is oxidized by the use of chlorine in accordance with the reaction:



This last reaction is dependent on the pH since OH^- is involved in the reaction.

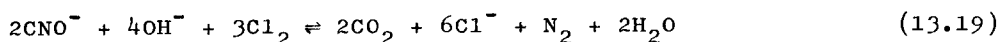
At pH values lower than 8.5 the reaction velocity is too small.

In accordance with a stoichiometric calculation 2.5 mg chlorine and 2.9 mg sodium hydroxide must be used per mg of cyanide. As seen from the equations, cyanate ions are formed which are considerably less toxic than cyanide. Cyanate is 1000 times less toxic to fish, for example, than cyanide.

Cyanate can react with water at a pH of 7.0 or less:



In accordance with this reaction cyanate is decomposed in the receiving water, with the formation of ammonia and carbon dioxide. Cyanate can also be oxidized by the addition of further chlorine, as the following process occurs:



This process can be carried out at the same pH as the oxidation of cyanide, i.e. at a pH of 8.5.

If the complete oxidation of cyanide to carbon dioxide and free nitrogen is to be carried out, 4.0 mg chlorine and 2.9 mg sodium hydroxide per mg of cyanide are required.

If ammonia or protein is present in the waste water the nitrogen compounds also will be oxidized by chlorine.

Table 13.18 gives the Redox potentials for the different oxidation processes involved; in Fig. 13.5 these potentials are shown in a diagram.

TABLE 13.18

Redox potentials (pH = 8.5; concentration 1 μM)

Compound	Redox potential	Relative potential
CN^- , NH_3	- 360	0
CNO^- , NH_2Cl	+ 250	610
Cl^- , OCl^- , N_2	+ 600	960

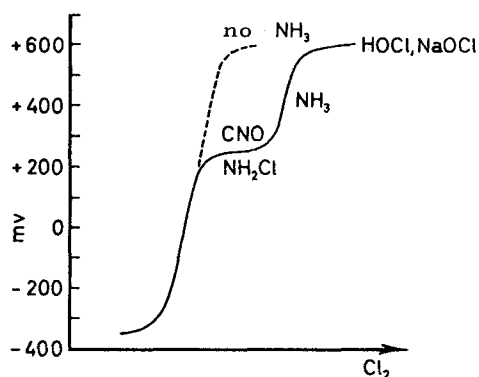
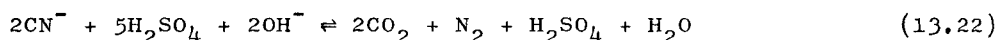


Fig. 13.5. Oxidation potential versus added chlorine.

The process can continue at elevated temperatures and chlorate is formed. This must be avoided as chlorate is considerably more toxic than chloride. Below pH 12 cyanogen chloride can be released and since this gas is toxic this must be avoided as well. If peroxomonosulphuric acid is used as oxidizing agent cyanogen chloride is not formed. The oxidation is based on the following reactions:



This last reaction occurs rapidly in acidic conditions at a low pH, while in alkaline solution the following reaction can take place:



This reaction requires a stoichiometrically larger amount of peroxomonosulphuric acid. Peroxidisulphate, for example diammoniumperoxidisulphate, $(\text{NH}_4)_2\text{S}_2\text{O}_8$, can also be used.

Although these chemicals are more expensive than chlorine less alkali is required since the pH can be lower. This is also an advantage of course in the neutralization which follows the total treatment.

The chemical oxidation of cyanide can be accomplished as described for the reduction and precipitation of heavy metals for which there are three possibilities: Batchwise oxidation; continuous oxidation; and the Lancy system.

Fig. 13.6 represents a flow-sheet for the batchwise treatment of cyanide. The addition of chlorine is controlled by a potentiometer and the pH by a pH meter. An excess of chlorine of 0.5-1.5 mg/mg cyanide is recommended.

Since the stoichiometric ratio between chlorine and cyanide is 6.5 mg chlorine/mg cyanide, 7-8 mg chlorine/mg cyanide must be used.

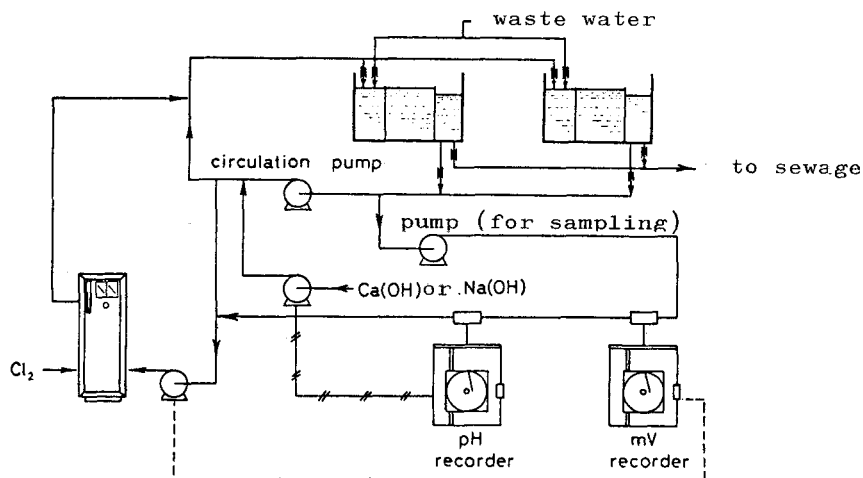
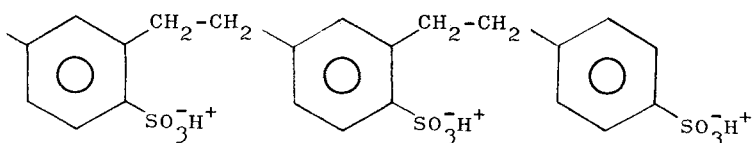


Fig. 13.6. Batchwise treatment of cyanides.

Ion exchange

A cation exchanger can be used for the removal of metal ions from waste water, such as Fe^{2+} , Fe^{3+} , Cr^{3+} , Al^{3+} , Zn^{2+} , Cu^{2+} , etc. (Spanier, 1969).

The most common type of cation exchanger consists of a polystyrene matrix which is a strong acidic ion exchanger containing sulphonic acid groups:



The practical capacity of the cation exchanger is 1-1.5 eq/l of ion exchange material (Rüb, 1969). To ensure high efficiency, a relatively low flow rate is recommended, often below 5 bed volumes/hour.

A recent development has brought a starch xanthate and a cellulose xanthate ion exchanger onto the market (WRL, 1977). They have a lower capacity than the conventional cation exchangers, but since they are specific for heavy metal ions they have a higher capacity measured as the volume of water treated between two regenerations per volume of ion exchanger.

Waste water containing heavy metals can be treated by a precipitation process using starch xanthate, which is a precipitant containing functional groups capable of forming insoluble metal salts. Cd^{2+} , Cr^{3+} , Cu^{2+} , Pb^{2+} , Hg^{2+} , Ni^{2+} , Ag^{+} are essential completely removed from the waste water by this method (Wing et al., 1974).

Chromate can be removed by anion exchangers. Exchangers with polystyrene or cellulose as matrix and amino groups can be used.

Cation exchangers can be regenerated by sulphuric acid and anion exchangers by sodium hydroxide.

Example 13.3

An ion exchange system for the treatment of chromate-containing waste water at $5 \text{ m}^3/\text{h}$ must be treated. The analysis of the water (after treatment on the cation exchanger) is:

	meq/l
OH^-	0.2
CrO_4^-	1
HCO_3^-	4
PO_4^{3-}	0.4
SO_4^{2-}	0.4
NO_3^-	0.1
Cl^-	1

The regeneration should be carried out every 24 hours. The practical capacity of the ion exchanger is 1.2 eq/l.

6.9 meq/l must be ion exchanged since OH^- is not exchanged as the ion exchanger is in the OH^- form. $6.9/1.2 = 5.8 \text{ l}$ ion exchange material per m^3 must be applied.

After 24 hours of operation $24 \cdot 5 \cdot 5.8 \text{ l} = 0.70 \text{ m}^3$.

This gives a flow rate of 7 bed volumes/hour, which might be too high. Laboratory experiments will probably show that 1 m^3 must be applied.

It is often preferable to separate waste water from the chromate baths and the rinsing water, since this opens up the possibility of re-using the water. Chromate can be recovered and the waste water problem can be solved in an effective way (Mohr, 1969).

Fig. 13.7 is a flow sheet of an ion exchange system in accordance with these principles.

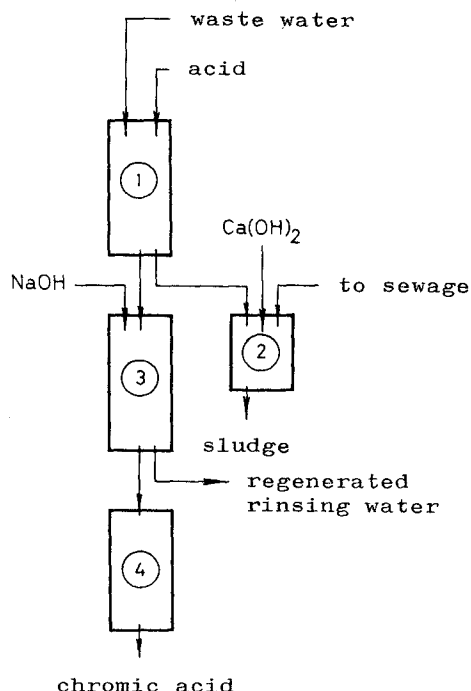


Fig. 13.7. Ion exchange of waste water containing chromate. 1) cation exchanger; 2) precipitation tank; 3) anion exchanger for removal of chromate; 4) exchange of Na^+ with H^+ .

Re-use of the elution liquid from the anion exchanger might be considered and also re-use of the treated waste water.

The pH of the elution liquid from the cation exchanger must be adjusted and the metal ions precipitated for removal by the addition of calcium hydroxide (see Fig. 13.7).

In some instances it is too costly to separate the different types of waste water and rinsing water. In such cases a more simple ion exchange system is used (Schaufler, 1969) although it is of course possible to recover the chromate from the elution liquid.

Since, as well as inorganic impurities, the waste water also contains organic material such as oil, fat, dust, etc., the ion exchange system often becomes clogged if the waste water is not pretreated before being passed into the ion exchange system. Macro-porous ion exchangers have only partly solved this problem since suspended matter, emulsions and high molecular weight organic compounds will also affect this type of ion exchanger.

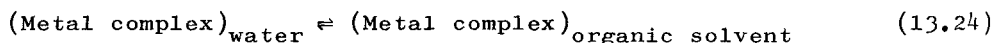
Consequently it is an advantage to pretreat the waste water on sand filters or activated carbon. The sand filter will remove the suspended particles and the activated carbon most of the organic impurities.

Since most of the ions are eluted in the first 60-75% of the eluting volume, it is often of advantage to use the last portion for the subsequent regeneration,

Extraction of metal ions

Most heavy metal ions can be recovered from aqueous solutions by extraction. Complexes of the metal ions are formed, for example by reaction with Cl^- , and these metal complexes are then extracted by means of organic solvents.

By using different concentrations of the ligand it is possible to separate different metals by extraction, again opening up the possibility of recovering the metals. The calculation of the equilibrium is based on the following reactions:



From reaction (13.23) and by use of the mass equation it is possible to set up the following expression:

$$\frac{[\text{Me L}]}{[\text{L}] [\text{Me}]} = K \quad (13.25)$$

Reaction (13.24) can be quantitatively expressed by means of the distribution coefficient, D , where

$$D = \frac{[\text{Me L}]_{\text{organic solvent}}}{[\text{Me L}]_{\text{water}}} \quad (13.26)$$

Combining equations (13.25) and (13.26) gives

$$K \cdot D = \frac{[\text{Me}]_{\text{org.}}}{[\text{L}] [\text{Me}]} \quad (13.27)$$

where $[\text{Me}]_{\text{org.}}$ is the total metal ion concentration in the organic phase. By applying this reaction in practice it is possible to vary: the concentration of the ligand, and the volume of the organic phase.

On increasing the concentration of the ligand and increasing the volume of the organic phase, $[Me]_{org}$ will increase and $[Me]$ decrease (see equations (13.26 and (13.27)).

Fig. 13.8 shows the extraction efficiency of various concentrations of chloride for several metal ions. These calculations are based upon the application of the same volume of organic solvent as the waste water treated. As seen from the diagram, it is possible, for example, to separate Fe^{2+} ions from cobalt by extracting with 60 g Cl^-/l . The extraction can also be carried out by a liquid ion exchanger of the trialkylamine type R_3NHCl .

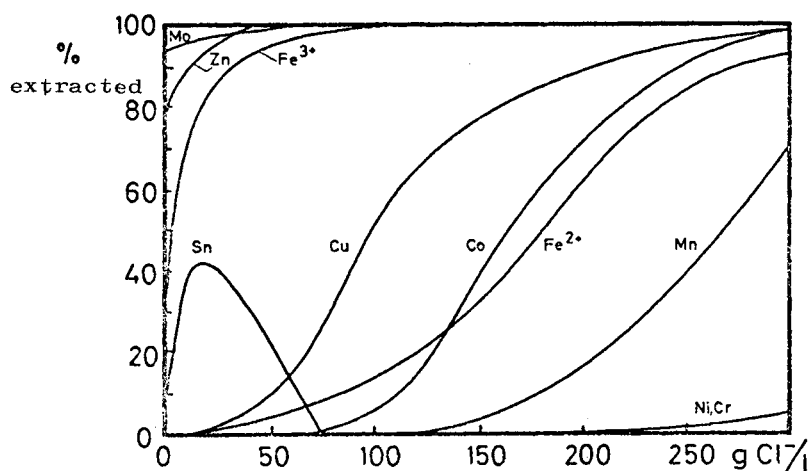
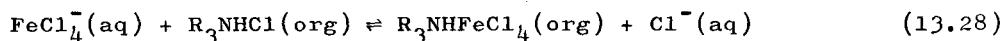


Fig. 13.8. Efficiency of extraction versus Cl^- concentration.

The process for $FeCl_4^-$ in aqueous solution will take place according to the following reaction:



Recovery of copper from a solution containing Cu^{2+} , SO_4^{2-} , Na^+ and H^+ (pH = approx. 2.0) is possible by extraction with acetone. The efficiency should in accordance to patent DDR 67541 be 99.9%. On recovering the acetone by distillation a loss of 0.3 kg acetone/100 kg copper is recorded.

An amine extraction process has also been developed for the recovery of cyanide and metal cyanide from waste streams of plating processes (Chemical Week, 1976).

The process uses high molecular weight quarternary amines dissolved in a carrier solvent to extract zinc and cyanide. An interesting aspect of this new extraction process is that its success hinges on the use of a carrier solvent for the chemical extraction. Carrier solvents can reduce the solubility of the extraction in the aqueous raffinate, improve phase density differences and reduce viscosity and freezing point.

Example 13.4

Waste water containing 1.2 g Zn^{2+} and 1.8 g Cu^{2+} /l must be treated. With which efficiency is it possible to separate these ions by extraction? Fig. 13.8 can be used.

By using 45 g Cl^- /l 100% extraction of Zn^{2+} and 8% extraction of Cu^{2+} will be possible. By increasing the Cl^- concentration to 300 g Cl^- /l, almost 100% extraction of the remaining copper will occur. If a better separation of the two metal ions is required, multi-step extraction must be used.

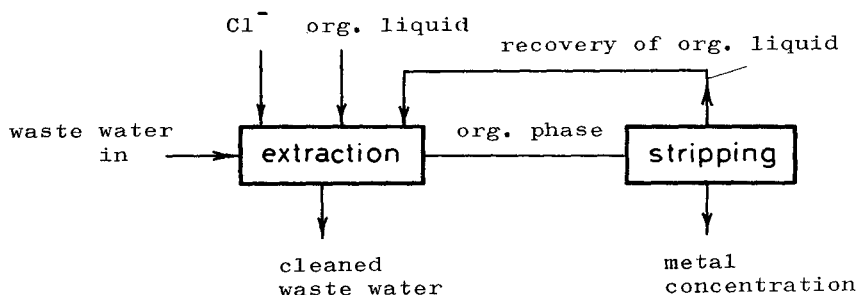


Fig. 13.9. Flow-sheet of the extraction process.

Fig. 13.9 is a flow-sheet of the extraction process. In the first step the waste water and the chloride and organic solvent are mixed. The organic solvent is recovered by a stripping process. A concentrated solution of metal ions which can be re-used is obtained from the stripping column. In some instances it might, in spite of the high efficiency of the extraction, be required to posttreat the extracted waste water by ion exchange to obtain a sufficiently low concentration of the metal ions.

It is of advantage to use the extraction method in cases where the metal concentration is too high to allow an economical ion exchange process.

Other processes

Depending on the composition of the waste water, it is sometimes advantageous to precipitate metal ions as compounds other than hydroxides, for example, copper can be recovered by precipitation of thioacetamide (Yakovlev, 1968).

As mentioned in Table 13.7 copper is highly toxic for the biological treatment and its effective removal is often required.

Cadmium is highly toxic and causes the so-called itai-itai disease, of which several hundred cases have been recorded in Japan (Hasebe et al., 1970).

Since cadmium hydroxide has a higher solubility product than iron and zinc hydroxide (see Table 13.12), the removal of cadmium by precipitation with calcium hydroxide is not sufficient. This problem can be solved by the addition of calciumalkylxanthate corresponding to 2-3 equivalents of cadmium. The cadmium xanthate precipitated can be removed by flotation (Wilke, 1969).

Reverse osmosis is particularly well suited for treatment of nickel plating rinsing water.

Cellulose acetate membranes are recommended (Hauck et al., 1972). The treatment can contribute significantly to both water pollution control and recovery of nickel.

Push et al. (1975) have demonstrated that it is possible to fractionate metal salts by reverse osmosis.

By tailoring membranes for specific applications and by optimizing the process parameters such as pressure applied, solute concentrations, added polyelectrolyte, it is possible to fractionate metals from waste water and recover valuable materials.

By using polyamide membranes for reverse osmosis experiments at 100 atm with an equimolar solution of AgNO_3 and $\text{Al}(\text{NO}_3)_3$, the membrane was able to reject 99.8% of aluminium salt, while the silver salt was enriched in the permeate.

General remarks

Waste water from the electrochemical industry varies considerably from plant to plant, since not all manufacturers use the same operations. It is not possible, therefore, to give general guidelines about which process is most effective and less costly; each case must be treated individually.

The first step towards a solution of the manufacturer's waste water problem must be to examine the water consumption, sources of waste water and the concentration of pollutants in the different types of waste water.

On the basis of this information it is often possible to re-use considerable amounts of water without any waste water treatment installation (see Table 13.2).

Many of the operations used in the electrochemical industry involve extreme pH values. This requires adjustment of pH before discharge of the water.

Throughout the industrialized world legislation for the discharge of waste water from the electrochemical industries has been tightened. The waste water process must in these cases not be considered separately, but should be included in the overall economic analysis of the manufacturing process. In some cases it might be more economic to use sulphate, chloride or borate baths instead of cyanide baths as the treatment of cyanide-containing waste water is rather costly (Sieburg, 1969).

Furthermore, it must be foreseen that the cost of water will increase during the next decade. It will be increasingly difficult to provide enough high quality water for the industry, as the consumption is increasing. This means that recovery of the water must be taken into consideration. Often the cost of the treatment process can be reduced considerably by keeping different types of waste water separate and thereby enabling the recovery of a part of the waste water (Weiner, 1976).

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