CHAPTER 15

NON-FERROUS METALS INDUSTRIES

GENERAL ASPECTS OF WASTE WATER PURIFICATION IN NON-FERROUS METALS INDUSTRIES

It is difficult to survey all the waste water problems in the non-ferrous metals industry since a wide range of metals and processes are used. Some of the problems are similar to those already dealt with in the two preceding chapters; in this chapter, therefore, the more specific problems will be discussed.

Some of the heavy metal ions are strongly toxic, which emphasizes the importance of dealing with these waste water problems.

Table 13.11 lists the recommendations for different qualities of water with regard to their metal content.

The non-ferrous metals industry will in the future inevitably be required to pay more attention to following possibilities (Teworte, 1970):

1. Processes for decreasing the amount of water used. Recirculation, regeneration, recooling, etc., must be considered. The prospect of saving water is as important as the necessity of purifying waste water.
2. The use of heating methods even in a protective gas atmosphere or in a vacuum with pickling being restricted.
3. Processes for decreasing metal losses in washing water and in waste water. The cascade washing technique, spraying technique, and use of ion exchangers should be considered.
4. Recovery of metal or metal compounds.
5. Investigation into the utilization of plant level of metal -bearing solutions, sludges and other residues from water purification plants. The sale of the material or treatment at a central plant could well be more economical.
6. The location of new non-ferrous metal plants should be examined carefully, and the proper handling of waste water taken into consideration.

Waste water problems by aluminium electrolysis

It is necessary to prevent any harmful effects of the gaseous, fluorine compounds from aluminium plants.

Two processes are used: Purifying potroom and washing concentrated waste gases from enclosed furnaces.

In both processes waste water is obtained from which utilizable sludges and clear water with a low chloride content are produced at a purification plant.

It is possible to convert the fluorides into usable compounds such as Na_3AlF_6, NaF, AlF_3 and CaF_2.

The furnace emission of fluorine is approximately 10-15 kg F/ton of aluminium used. By the purification process the total fluorine emission (gaseous) is reduced to 0.5-1.0 kg/ton of aluminium.

The quantity of washing water is approximately 200 m^3/ton of aluminium for potroom gas cleaning and about 20 m^3 for furnace gas extraction and cleaning. This quantity of water will contain the fluorine removed by gas purification. In view of the price (about $.100/ton of F in the chemicals Na_3AlF_6 and AlF_3, required for electrolysis) it is of great interest to recover the fluorine material.

Precipitation from the washing water is effected by controlled addition of sodium hydroxide and aluminium hydroxide. Calcium hydroxide is also used at some plants. The sludge is concentrated by filtration and the filter cake can be worked up to obtain the fluorine compounds at a central station.

Copper recovery from waste water

By addition of iron powder it is possible to reduce copper(II) to metallic copper.

The following process takes place:

$$Fe + Cu^{2+} \rightleftharpoons Fe^{2+} + Cu \qquad (15.1)$$

The copper is precipitated as metallic copper. After settling it is concentrated by filtration. The iron(III) ions can be removed from the solution by precipitation as iron(III)hydroxide.

It is possible to economize in the use of iron by using lime precipitation instead. Cu_2O will then be produced as the copper is only reduced to Cu(I) ions. This seems to be a more economical process than the reduction to metallic copper. The drum filter cake, which contains 40% of moisture and almost 60% Cu_2O, can be worked directly to yield copper (Teworte, 1969).

Ion exchange as a concentration step for purifying waste water containing non-ferrous metals

The ion exchange system represents a useful process for separating non-ferrous metals from waste water. The effluent obtained by re-extraction of the saturated exchange resin produces a mixed concentrate of the metals, which makes it useful as a basis for recovery of metals.

It is often preferable to use selective ion exchangers for non-ferrous metals (see p. 210). It is possible to separate heavy metals from alkali metals and alkaline earth metals by passing waste water through a column with a selective resin. The possibility of selectively fixing zinc and cadmium in a chelating resin is of special interest. Acid washing of the loaded resin produces a concentrated solution of 10-20 g/l of zinc and cadmium.

For the selective recovery of precious metals, gold, platinium, palladium, irridium, uranium, ruthenium and osmium, from extremely dilute solutions such as 1 µg/l, an anion exchanger resin with chelating groups or a xanthate ion exchanger are recommended. Combustion of the resin allows complete recovery of the precious metals.

Purification of waste water from smelting furnace plants producing zinc and lead

The specific amount of water required is up to 100 m^3/ton of zinc and lead produced, including the production of sulphuric acid in a preceding roasting plant.

In the literature a process is mentioned which can be used to recover zinc and lead and simultaneously purify the waste water. Water is heated with dust and soluble compounds at the following points:

a) Scrubber for the exit gas from the preheater for the coke.
b) Ventury scrubber for precipitating the dust from the coke discharge.
c) Furnace gas washing with an injection tower.
d) Ventury scrubber for extraction of the dust from the room of the melting shop.

The high dust content in the furnace gas (about 35 g/standard m^3) decreases in the purified gas to less than 40 mg/m^3.

The following operations serve the purpose of waste water purification in the precipitation vats preceding the final thickener:

a) Alkalization with calcium hydroxide up to pH 10.0,
b) Chlorine oxidation in the case of a cyanide content over 0.1 mg/l,
c) Neutralization to pH 6.5-7.5 by addition of acid washing water from the wet electrical purification of the gas purification,
d) Addition of $FeSO_4$, $7H_2O$ for precipitating traces of arsenous compounds,
e) Addition of small amounts of flocculating agents.

Brass production

A plant for the purification of waste water from the production of brass is shown in Fig. 15.1.

In the first tank pH is adjusted. The second tank is made of wood and contains several lengths of iron pipes, which will reduce the copper in accordance with the following process

$$Fe + Cu^{2+} \rightleftharpoons Fe^{2+} + Cu \qquad (15.2)$$

Furthermore, sulphur dioxide is added to the waste water reducing chromate to chromium(III) ions. The pH must be maintained at 3.0 or below.

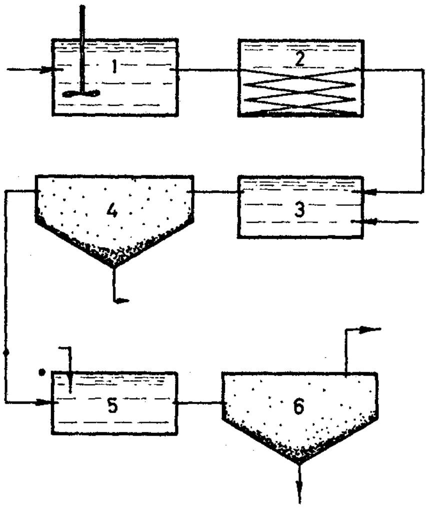

Fig. 15.1. In tank (1) pH adjustment, (2) Reduction of copper with iron, (3) Reduction with sulphur dioxide, (4) Settling of metallic copper, (5) Precipitation of metal as metal hydroxide, (6) Sedimentation of metal hydroxide.

The metallic copper is removed from the waste water by sedimentation followed by the addition of calcium hydroxide which raises the pH to 8.0 or above. The metal hydroxides are precipitated at this pH and are removed by further sedimentation. The sludges from the two sedimentations of copper and metal hydroxides can be filtrated on a rotary vacuum filter to obtain 30% dry matter or more.

A typical analysis of the metal hydroxide filter cake is shown in Table 15.1.

TABLE 15.1

Filter cake analysis

	% dry matter 40-45%
Iron	11.8
Copper	4.2
Chrome	6.4
Zinc	2.1
Calcium	1.3
Sulphate	2.5

It has been an incentive for treatment of waste water from this industry that it is possible to recover expensive metals.

Removal of vanadium

Kunz et al. (1976) have studied the removal of vanadium.

They found that vanadium is taken up by activated sludge to an extent of 6.8 mg V/g suspended solid without adverse effect.

Beyond this sorption capacity soluble vanadium appears in solution and begins to influence the micro-biological population and to inhibit waste stabilization activity at about 20 mg/l.

Vanadium can, according to Kunz et al., be removed to the residual level of 1-2 mg/l by using 4 kg of iron(II)sulphate/kg vanadium. It is also feasible to use activated carbon to remove vanadium. However, it should only be removed for polishing operations as the equilibrium loading is as low as 0.00016 kg V/kg carbon.

Purification of arsenetrioxide

A typical composition of waste water from the purification of arsenetrioxide is shown in Table 15.2.

TABLE 15.2

Composition of waste water

Component	Concentration
As	13
Cu	0.2
Fe	4
Zn	0.5
Sulphate	12
pH	1.0

This waste water can be treated by precipitation with calcium hydroxide, which reacts with the sulphuric acid present according to the following reaction:

$$H_2SO_4 + Ca(OH)_2 \rightarrow CaSO_4,H_2O \qquad (15.3)$$

At higher pH values a mixture of metal hydroxides will be precipitated, and above 8.0 a substantial part of the metal ions will be precipitated. At pH 9.0 arsenite will precipitate as calcium arsenite:

$$2H_2O + 2AsO_3^{3-} + Ca(OH)_2 \rightarrow Ca(AsO_2)_2\downarrow + 6OH \qquad (15.4)$$

To get the heavy soluble form of calcium arsenite a pH of 11.5 is required, when the following reaction takes place:

$$Ca(AsO_2)_2 + Ca(OH)_2 \rightarrow 2CaHAsO_3\downarrow \qquad (15.5)$$

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