

CHAPTER 14

WASTE WATER FROM THE IRON AND STEEL INDUSTRY AND MINING

CHARACTERISTICS OF THE WASTE WATER FROM THE IRON AND STEEL INDUSTRY

Waste water from iron and steel works, where smelting of pig iron in blast furnaces and of steel in open hearth furnaces, Bessmer converters, etc. takes place, contains a considerable amount of oil, dust, acid, iron and other metals. The main sources of waste are from the purification of blast furnace gas, crushing of slags, cooling of bearing and shafts of rollers and final cooling of pig iron.

Blast furnace gas is treated by water spraying to remove dust. This waste water contains cyanides, sulphur compounds, phenol, dust, metal ions, ash, slag and ore particles. 4-8 m³ of water are used per 1000 m³ of gas. After treatment of this water, it is returned to the process after replacement of the losses corresponding to evaporation (up to 10%).

Table 14.1 shows the composition of waste water from wet cleaning of blast furnace gas (Black, 1954).

TABLE 14.1

Composition of waste water from wet cleaning of blast furnace gas

pH: 7-9	
Total suspended solid (mg/l)	330-670
Volatile suspended solid (mg/l)	up to 200
Total dissolved solid (mg/l)	800-4000
Volatile solid in the dry residue (mg/l)	100-320
Permanganate value (mg/l)	40-150
Cyanide (CN ⁻) (mg/l)	0.6-1.3
Thiocyanates (CNS ⁻) (mg/l)	0-17
Phenol traces sludge (%)	0.5-1.2
Iron (mg/l)	140-1180

The temperature of the waste water varies between 30 and 40°C. Most of the suspended solid settles within 3 hours. The quantity of waste water used during slag crushing varies from plant to plant. About 8 m³ waste water/ton of slag can be used as a general figure. In most cases the treated waste water can be re-used after purification, requiring to be made up by 2 m³/ton. The average composition of this type of waste water (Zhukov, 1948) is given in Table 14.2. The temperature of the waste water is 30-50°C. The suspended solid easily settles. After half an hour more than 90% of the

suspended matter settles and after 2 hours almost clear water is obtained.

TABLE 14.2

Composition of waste water from slag crushing

Alkalinity (meq/l)	3-4
Total suspended solid (mg/l)	500-600
Volatile suspended solid (mg/l)	30.50
Loss of ignition (mg/l)	100-150
Total dissolved solid (mg/l)	450-550
Permanganate value (mg/l)	100-500
Sulphate SO_4^{2-} (mg/l)	100-150
Cyanide CN^- (mg/l)	nil
Thiocyanate CNS^- (mg/l)	3-4
Phenol traces sludge (%)	1-2.5
Sulphite SO_3^{2-} (mg/l)	10.30

Rolling mills produce waste water during the cooling of bearings and shafts. The water consumption is about $10 \text{ m}^3/\text{ton}$, but by recirculation it is possible to reduce this amount of water by a factor of 2 to 7.

The composition of the waste water varies considerably. An average composition (Zhukov, 1948) is listed in Table 14.3.

TABLE 14.3

Composition of waste water from rolling mills

Alkalinity (meq/l)	3-4
Total suspended solid (mg/l)	1000-1500
Volatile suspended solid (mg/l)	10-100
Total dissolved solid (mg/l)	400-500
Volatile solid in the dry residue (mg/l)	10-150
Sulphate SO_4^{2-} (mg/l)	100-150
Lubricating oil (mg/l)	2-50

The water consumption for the final cooling of pig iron and melting pots is about $1-1\frac{1}{2} \text{ m}^3/\text{ton}$ of pig iron. The basic impurities in the waste water are scales, lime and other additives. An average consumption of this type of waste water is presented in Table 14.4.

TABLE 14.4

Composition of waste water from cooling of pig iron
(after Sierp, 1959)

pH: 7.0-8.0	
Total suspended solid (mg/l)	500-3500
Total dissolved solid (mg/l)	500-2000
Volatile solid in the dry residue (mg/l)	350
Permanganate value (mg/l)	60-100
Chloride Cl^- (mg/l)	30-300
Calcium oxide (mg/l)	200-300
Sulphate SO_4^{2-} (mg/l)	20-650
Magnesium oxide (mg/l)	15-30

The suspended matter settles fairly easily, but recirculation of the clarified water is often not possible as the water cause the rapid deposition of scale in the pipes of the system.

Waste water from pickling of ferrous metal will contain sulphuric or hydrochloric acid. These acids react with the scales according to the following process:



Table 14.5 gives the composition of typical pickling waste water.

TABLE 14.5

Average composition of pickling waste water

pH	1.5-4.5
Iron Fe^{2+} (mg/l)	80-600
Sulphate SO_4^{2-} (mg/l)	200-2000
Calcium Ca^{2+} (mg/l)	50-200
Al^{3+} (mg/l)	0-50

Composition of waste water from the mining industry

Waste water from the mining industry shows a wide spectrum of compositions. Many of the components present in waste water from the iron and steel industry are also often present in the water from the mining industry. This justifies the treatment of the two types of waste water in the same chapter. An exception is the waste water from flotation and enrichment of lead and zinc ores, which in addition to components present in waste water from other mining industries also contains xanthate, zinc and lead.

Lead and zinc can be removed by the methods mentioned in Chapter 13, dealing with the electroplating industry, but, preferably precipitation with calcium hydroxide is preferred, a process which is widely used for the treatment of waste water from mining industries and from the iron and steel industries.

The flotation and enrichment process require water to the amount of 4-7 m³/ton of ore processed. A typical composition of this waste water is given in Table 14.6.

TABLE 14.6

Approximate composition of waste water from flotation and enrichment of lead, and zinc ores

Component	Concentration (mg/l)
Total suspended solid	20000-140000
Permanganate value	80-120
Cyanide	2-5
Thiocyanide	2-5
Lead	5-10
Zinc	0.1-10
Xanthate	0.1-5
Copper	0.4-8
Terpene ketones and alcohols	2-4
Cresols	1-30

As pointed out by Jennett et al. (1972) it is possible to minimize lead mining wastes using the closed-loop approach and by treatment in lagoons for retention and settling before discharge.

Draining of mining water is essential since otherwise normal operation of the mine will be difficult or even impossible. The amount of drainage water depends on local hydrogeological conditions and will sometimes vary throughout the year. In British coal mines an average of 4.5 tons of water is pumped to the surface for every ton of coal produced. In most mines the underground water is only slightly polluted and is clear enough to be discharged into rivers or used for various purposes without any further treatment.

A further treatment of coal-mine drainage is possible by use of ion exchange, by which method it is possible to achieve potable water quality in accordance with Walther Sabban et al. (1972).

In some cases it is even pure enough to be used as a potable supply.

Often mine water is neutral or slightly alkaline; in some cases it is acidic, due to a high content of either carbon dioxide or sulphuric acid. In the latter case the drainage water will contain considerable amounts of iron salts (Barnes et al., 1968).

A typical composition of such an acidic drainage water is shown in Table 14.7.

TABLE 14.7

Typical analytical values for acidic drainage from mines

Component	pH 2.0-3.0
Iron (mg/l)	50-200
Sulphate (mg/l)	500-2000
Calcium (mg/l)	100-400
Al ³⁺ (mg/l)	20-80

In some instances the mine water contains sulphides which must be removed by oxidation or aeration (see below).

Removal of oil and grease from waste water

Waste water from the iron and steel industry can contain up to 5% of grease and oil when recirculation of the waste water takes place. The following treatment methods are available:

1. Addition of sodium chloride for breaking up the emulsion.
2. Addition of calcium hydroxide for saponification of the grease and oil.
3. Addition of aluminium sulphate as flocculation agent.

Since the quantities are small and the concentration high, the waste water is generally treated batchwise.

Balden (1969) describes the waste water problem associated with the manufacturing of automobiles. It is possible to treat this waste water by a combination of air flotation, chemical precipitation and sedimentation. The reclaimed oil and scum removed by the flotation tank can be combusted in an incinerator.

Treatment of waste water containing acid and iron

Waste water from the iron and steel industry and from the mining industry can be treated by neutralization followed by a precipitation. The pH of the water is often below 2.0 and the iron concentration can be as high as 4-6 g/l.

Fig. 14.1 is a flow-sheet of a treatment combining neutralization and precipitation.

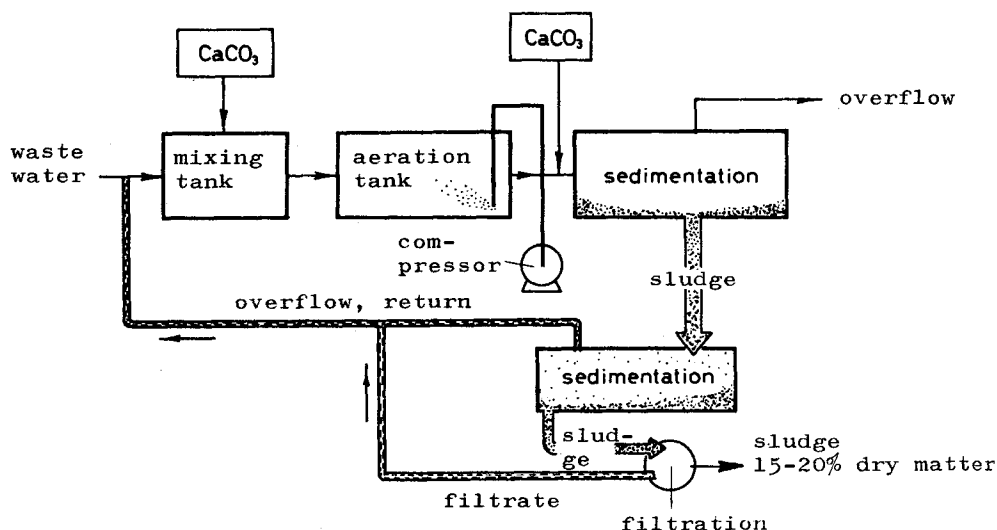
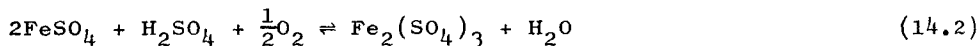


Fig. 14.1. Flow-sheet of a treatment plant combining neutralization and precipitation.

Calcium carbonate is used for neutralization. The pH is adjusted to 4-5 (Hoak, 1950). The iron(II) ions are then oxidized to iron(III) ions with air. The following reaction takes place:

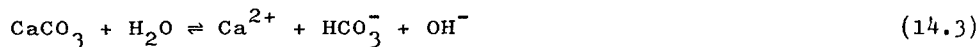


It is very important to oxidize iron(II) ions to iron(III) ions as iron(II)hydroxide settles considerably more slowly than iron(III)-hydroxide. This is illustrated in Fig. 14.2.

As shown in Fig. 14.3, the reaction rate for the oxidation is dependent on the temperature.

After the oxidation process further addition of calcium carbonate and calcium hydroxide precipitates the iron(III) ions as iron(III)-hydroxide. Calcium carbonate is cheaper than calcium hydroxide and the precipitated material will settle slightly better (Lowell, 1967).

The precipitation with calcium carbonate follows the reaction:



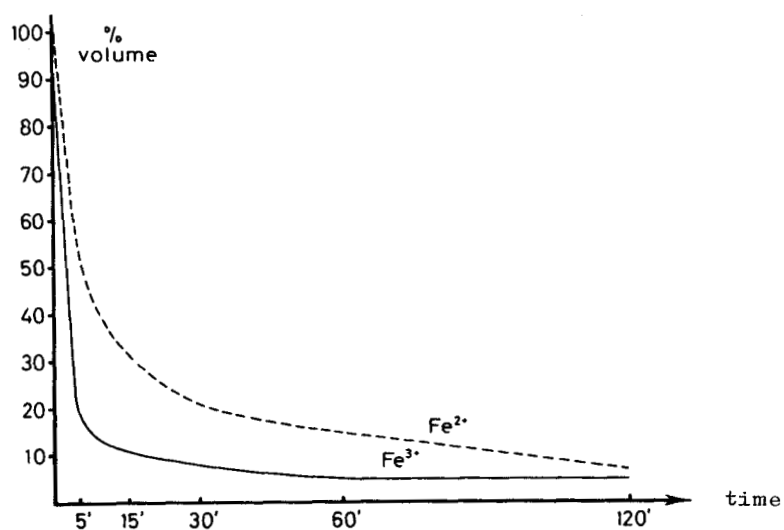


Fig. 14.2. Settling of iron(II)- and iron(III)hydroxide.

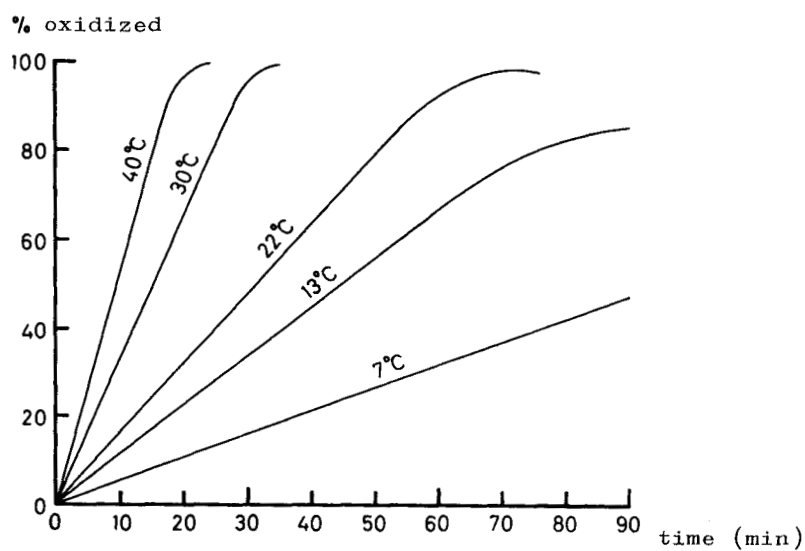


Fig. 14.3. Oxidation of iron(II) versus time for different temperatures.

Settling follows the precipitation. Finally, concentration of the sludge can be carried out with a vacuum filter. A dry matter concentration of 15-20% can be obtained. Fortunately, Al^{3+} , Cu^{2+} and Zn^{2+} will also be precipitated simultaneously with Fe^{3+} . If a too high amount of Al^{3+} is present, it might create difficulties by the upconcentration of the sludge. On settling only 1% dry matter or less will be achieved in the sludge if aluminium is present in a concentration corresponding to 10% of the total metal ion concentration.

It is also possible to treat this type of waste water by ion exchange and it is preferable if the Al^{3+} concentration is too high, as it will cause problems during the concentration of the sludge.

A strong, acidic cation exchanger is used and with the concentration in practice it is possible by eluting with a 15% chloride solution to achieve a 50 times upconcentration by this process (Lowell, 1967).

If, for example, 1 g of ions is present in 1 l of waste water, a concentration of about 50 g/l in the eluant liquid will be achieved. The eluant is neutralized by addition of calcium carbonate and precipitation of Fe^{3+} will take place simultaneously. Further sedimentation will give a 2-3 times higher concentration of the sludge. By subsequent filtration a concentration of 25% of iron or even more can be obtained.

Fig. 14.4 shows the principle of this process.

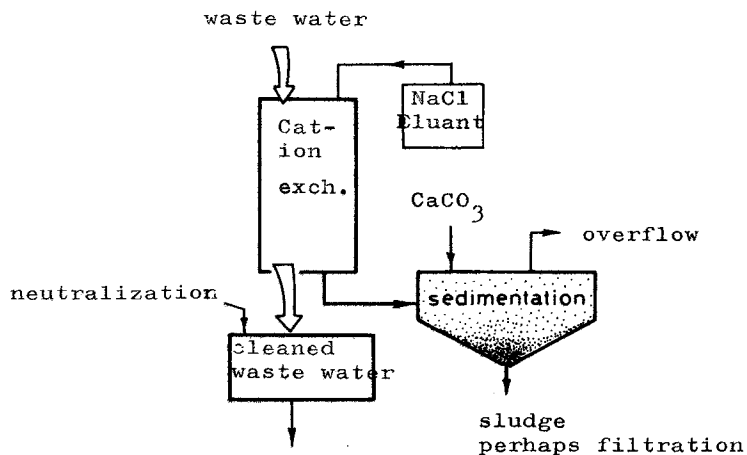


Fig. 14.4. Ion exchange of waste water containing acid and iron ions.

The Ruthner process

The so-called Ruthner process has been developed for treating pickling waste water. This process makes it possible to recirculate the hydrochloric acid used as well as the water.

The chemical reaction for the pickling process is:



The hydrochloric acid recovery takes place by the following process:

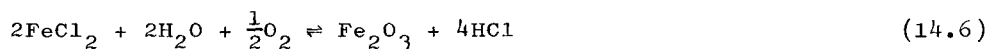


Fig. 14.5 is a flow-sheet of the Ruthner process (Wurmbauer, 1970).

The water from the pickling baths is pumped into a spray drier, where iron(III)oxide is collected. Further dust is removed from the gases by a cyclone and the hydrochloric gas is absorbed in an absorption tower, where a 20% hydrochloric acid solution is produced.

The whole system is maintained under vacuum by a vacuum pump, which is placed after the absorption tower.

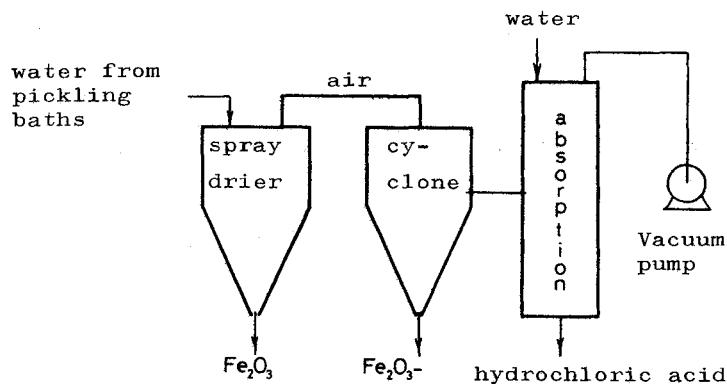


Fig. 14.5. The Ruthner process.

The Ruthner process has three great advantages compared with the waste water treatment of pickling waste containing sulphuric acid:

1. The by-product, Fe_2O_3 , is produced and is able to pay a (small) part of the cost of the process.
2. The hydrochloric acid consumption is low as a substantial part of the acid is recovered.
3. The Ruthner process does not produce any waste water and thus the waste water problem is completely solved.

Magnetic separator

High gradient magnetic separators are used in steel plants for the removal of suspended solid.

The suspended solid in steel mill effluents is principally iron and iron-bearing particles.

These effluents can therefore be treated by direct, high magnetic field gradient filtration without filter aids. Experiments (Marchton et al., 1975) have shown that it is possible by this method to reduce the suspended solid from 1000 ppm to below 10 ppm.

High magnetic field gradient filtration consists in its simplest form of a special magnetic matrix placed in a strong uniform magnetic field through which the contaminated water is passed.

The matrix is of a ferro-magnetic fibre structure, which creates severe localized perturbation in the magnetic field and thus produces an extremely high magnetic field gradient and forces over a large surface area in a relatively open volume.

Hydraulic impedance is low even at high filtration rates.

Sludge concentration is efficiently produced by back-washing the filters with the applied magnetic field reduced to zero.

Suspended solids in hot strip-mill effluents are reduced from 100 mg/l to 5-20 mg/l at filtration rates of 100-1000 m^3/h .

Also steel mill scrubber water and effluents from coke plants can be treated by high gradient magnetic separators.

Total treatment cost of 1000 m^3/h strip-mill effluent is approximately 2.5 U.S.cents/ m^3 for purification to 20 mg/l. The corresponding effluent treatment cost is probably round U.S. cents 4.5/ m^3 when purified to 5 mg/l.

These costs include capital costs for machines and building and, the cost of wages and maintenance. The high flow rate allows compact installation, hence the floor space requirement is modest compared to conventional treatment plants.

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