

# WASTE WATER IN METAL MINING INDUSTRIES

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## ABSTRACT

The different types of mineral industries wastes are characterized. Total tonnage in the world of finely ground wastes from i.a. flotation and leaching operations amounts to around 1500 million tons per annum. The major environmental problems arise from slowly settling fine particles, dissolved metal ions and chemicals retained in the effluent. The paper discusses the toxic effects of dissolved metal ions in waste water as well as the effect of pH and sediments on water fauna. The comminution in mineral processing operations yields the surface of the waste mineral products a high reactivity. Therefore mineral wastes have a high adsorptive power for dissolved contaminations, i.a. metal ions and organic substances. This has a very positive effect on the water environment. The layout and operation of settling ponds as well as the use of flocculation agents are discussed. Legal and environmental aspects of metal mining wastes are considered.

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## I. GENERAL

The mining and dressing of metalliferous ores has hitherto had relatively little adverse effect on the global water situation, the reason being that these ores seldom differ very much in character from natural rocks and soils and that quantitatively speaking by far the greatest part of the mineral process involves purely mechanical operations. Chemical treatment of minerals is however coming into the picture to an ever increasing extent in connection with flotation and leaching processes, which means that more attention will have to be paid to effluent cleaning problems. Another factor to be reckoned with is that the quantities of material being processed are growing in a geometric progression that corresponds to a doubling roughly every ten years. As we shall see, however, the handling of residues and waste water from mineral processing operations displays a number of features that are actually quite favourable from the point of view of nature preservation.

## II. THE ORE INDUSTRY AND ITS WASTES

The following roughly estimated figures will serve to give some idea of the quantities of ore and residual products resulting from world mining and dressing operations in 1970:

Type of ore	Crude ore million tons	Residues million tons
Iron	1200	>1000
Base metals	800	1000
Gold and uranium	250	300

Iron ores normally only undergo crushing and partial grinding plus cobbing and dressing of a purely mechanical nature without any admixture of chemicals. Base metal ores are ground to finer than 0.1 mm and concentrated by flotation after adsorption of organic reagents in dosages of the order of 100 g/ton. Gold and uranium ores, finally, are ground and leached with cyanide (dosage approximately 100 g/ton) and sulphuric acid (dosage approximately 50 kg/ton) respectively. It is thus evident that the iron ores have hitherto been fairly innocuous as far as environmental pollution is concerned, whereas the floated and leached ores have needed much more care in this respect. The quantities of residues involved also include the amount—difficult to estimate—of overburden rock that has to be removed before the ore can be mined.

Of the total amount of residues, about 1500 million tons is produced in finely ground form. The particle size distribution that results from grinding principally follows a pure probability curve and can be plotted more or less in the form of straight lines on graphs with suitably defined scales (*see Figure 1*). For

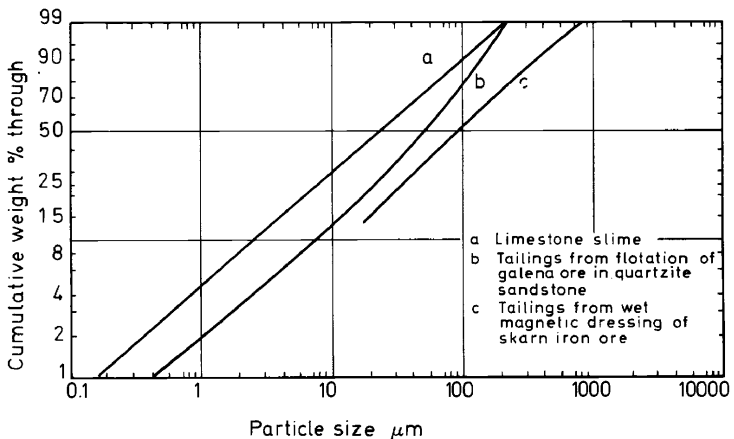


Figure 1. Particle size distribution

example a tailings product ground to 90 per cent by weight finer than 0.1 mm can be expected to contain at least about 2 per cent by weight of material finer than a thousandth of a millimeter ( $1\ \mu\text{m}$ ), while even coarser crushing operations produce some fine slime. This fine slime has a low settling velocity, a considerable adsorptive capacity and, in the long term, a certain tendency to decomposition. Most of the environmental effects of the mineral processing industry arise from this source.

In the great majority of cases, the ores treated in mineral processes are

slurried in water. To the quantities of water required for actual processing must be added the underground and surface water that have to be pumped up and discharged. All this water must be released into the recipient with adequate safeguards and controlled contents of impurities.

As a result of the draining operations just mentioned and above all of the quarrying operations involved in taking out the ore, the rock minerals are exposed to attack by atmospheric oxygen, and weathering processes are initiated, which result among other things in the dissolution of some minerals. Mining and milling operations produce large piles of rock and tailings, and it takes a long time before these attain a degree of surface chemical stability comparable to that of natural gravels and soils. The mineralogical composition of the material and the acidity of the water determine whether this chemical instability is of a purely beneficial nature from the point of view of water conservancy or whether elements of pollution enter into the picture. I shall be returning to this point later, as well as to the possibilities of containing the volumes of slime produced by industrial operations.

Some mineral processes involve extensive use of organic and inorganic chemicals, partly for the purpose of altering the surface characteristics of the minerals—mainly in flotation processes—and partly to obtain solutions and precipitates in leaching processes. In most cases the added chemicals are precipitated, neutralized and adsorbed on the produced mineral surfaces, but in some cases dissolved substances of a pollutant nature remain in the effluent, and this may call for the application of measures in order to prevent harm. This is particularly the case in leaching plants, where precipitation and neutralisation of effluent impurities may represent a sizeable item in the cost budget.

The waste water problems of the mineral industry can be listed under the following heads:

- (1) Destruction of amenities due to the storing of waste piles and the provision of adequate settling ponds.
- (2) Pollution of recipients with slime and precipitates that sterilise the bottom.
- (3) Toxic effects of added inorganic or organic substances that disrupt the normal biological cycle in the recipient.
- (4) Overfertilization of the recipient by excessive discharge of nutrients.
- (5) Water rendered unfit for recreational, communal or industrial use due to the presence of slime, discoloration, objectionable tastes and odours, or objectionable substances in solution.

As will be explained later, it is not realistic for the mineral industry to attempt to restore the original natural condition of the water; instead, the object must be to apply water purification measures with a view to obtaining optimum results in the given circumstances. A measure which may be beneficial with respect to one of the problems I have just listed may aggravate one of the others, and it is thus necessary to find the optimum balance.

### III. TOXIC EFFECTS OF WASTE WATER

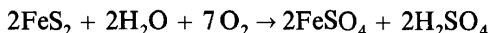
When considering the toxic effects of the various impurities that may be discharged into watercourses by the mineral industry, one should properly make a distinction between the effects on warm-blooded animals, cold-blooded

animals and water vegetation. Research in this field here in Sweden has made the greatest progress with regard to cold-blooded animals, largely thanks to the many years of work done by the Fresh Water Laboratory on Drottningholm, partly under the leadership of the Chief Inspector there, Dr. Sten Wallin. Warm-blooded animals, both wild and domestic, are quite well able to avoid consuming unhealthy water, and in fact it is generally found that they refuse to drink water that is contaminated. The situation with regard to plant life, finally, is fairly widely known, although it has not been dealt with so extensively in our research.

If then we consider the effects of the impurities in question on fish, we find that the most powerful toxic effects are attributable to copper and zinc ions and to cyanide in solution. The lethal concentration is about 0.1–0.3 g/m<sup>3</sup> for copper ions, about the same for cyanides, and about 2–3 g/m<sup>3</sup> for zinc ions. In addition, there are deleterious effects if the pH of the water is lowered below 5 or raised above 9 by substances discharged into it. Of the impurities concerned, the cyanide concentration is susceptible to full technical control while the others are largely connected with weathering and ion dissociation processes during the mining and stockpiling of the ores and rocks.

Atmospheric oxygen and water, either separately or in combination, attack and weather rocks, dissolving out salts. The various minerals and the rocks composed of them show differing degrees of resistance to this kind of decomposition due to a number of factors, viz. the solubilities of the different minerals in water, their susceptibility to oxidation, and the electric potentials that may arise in an aqueous environment between electrically conductive minerals in the rock. This last phenomenon is directly comparable to galvanic corrosion in metal alloys.

Susceptibility to oxidation is of particular importance with regard to the effects of weathering on sulphide minerals and sulphide ores. Oxidation of the most common sulphides—pyrite and pyrrhotite, both sulphides of iron—results in the formation of ferrous sulphate and, in the case of pyrite, of sulphuric acid as well:



Further oxidation produces ferric sulphate, which is hydrolysed to ferric hydroxide and sulphuric acid. The essential point is, however, that both H<sub>2</sub>O and O<sub>2</sub> must be present for these reactions to occur; in completely dry mines, and in mines flooded with water or concentrate stockpiles stored under water, the reaction is inhibited.

The various sulphide minerals differ a great deal as to stability. Pyrrhotite is the least stable, oxidizing readily and exothermically in the presence of water. The reaction rate, however, varies considerably from one deposit to another. Pyrite is usually fairly stable. Galena often oxidizes easily, while sphalerite is very stable.

In some mines containing massive pyritic ore, oxidation and weathering phenomena occur at a rate that increases with the age of the mine, producing acid mine water with a high content of sulphate, iron and copper ions. The pH may be as low as 2 or 3, and the copper content of mine waters in Sweden has been known to exceed 100 g/m<sup>3</sup>, while in desert regions abroad the concentration may be ten times higher. In these acid mines sulphide oxidation has gained

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the upper hand, and carbonate rocks and alkaline solution products have been unable to stop the process. In other similar mines containing massive pyritic ore the mine water is relatively neutral. The reason for these wide differences has not been fully established. Reference has been made to powerful corrosion in certain sulphide mineral structures of massive pyritic ore, as well as to the activity of sulphur bacteria. However, carbonate rocks play an important part in maintaining the pH of the mine water by neutralizing sulphuric acid, precipitating calcium sulphate and iron hydroxide, and preventing the dissolution of copper.

The toxicity of waste water depends, however, on combined effects, increasing sharply where several factors are at work together. The toxicity of contaminated water can be expressed as the number of times it must be diluted with pure water to enable fish fry to live in it without suffering ill effects for a period of, say, five days. The following very rough figures can be quoted on this basis:

Acid mine water	1 : 100–1 : 200
Neutral mine water	1 : 0    –1 : 4
Waste water from sulphide flotation	1 : 2    –1 : 7
Waste water from oxide or cationic flotation	1 : 1
Neutralized leaching liquors	1 : 2    –1 : 10
Waste water from purely mechanical mineral dressing plants	1 : 0

It should perhaps be pointed out that even abandoned mines with extensive excavations above the water table can poison water-courses. In the most beautiful part of Ireland the River Avoca flows past the old Avoca mines in a mountainous district of the county of Wicklow. These mines have now been reopened, but while they were abandoned the acid, copper-polluted water flowing from them lowered the pH of the river and emptied it of fish downstream of the sulphide ore zone.

## IV. INFLUENCE OF FRESHLY GROUND MINERALS ON WATER ENVIRONMENT

It would be quite wrong, however, to assume that all the weathering products of ores and the inorganic and organic reagents used in mineral processes add up to a serious water pollution problem from a normal mineral processing plant. The fact that this is not the case—indeed that measured toxicity and pollution are usually tolerable—is attributable to the activity of the freshly ground mineral surfaces.

The basic phenomena at work here are as follows:

The mineral particle surfaces exposed for the first time by grinding have a very high chemisorptive capacity, as they have not yet been passivated by permanent adsorption layers.

These unstabilized mineral surfaces are surrounded by microenvironment that usually has a higher ion concentration including a higher pH, than the ambient water.

After comminution the surfaces of silicate minerals are covered with reactive layers of silica gel that eagerly combine with foreign ions and substances.

Some minerals in finely divided form undergo almost complete chemical reaction immediately after grinding by diffusions with, for example, heavy metals in aqueous solution.

Much of the adsorptive capacity that freshly ground mineral masses are found in practice to possess as regards their ability to bind dissolved metallic ions is an effect of the variation of solubility with pH. Here we see a Bjerrum graph (*Figure 2*) showing the solubilities of a number of substances at different

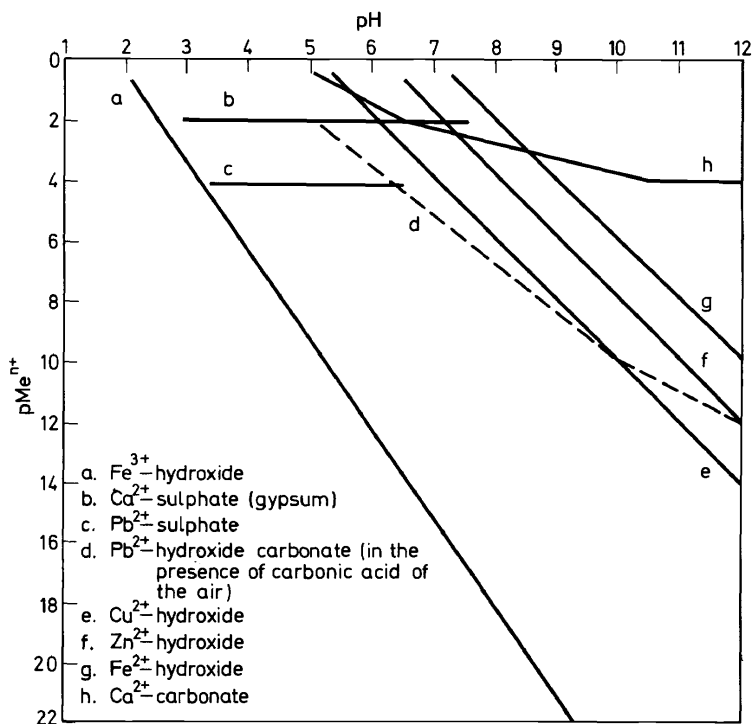


Figure 2. Limits for metal ion contents at different pH values

pH levels. We note how the solubilities of heavy metal hydroxides and calcium carbonate decline with rising pH, whereas the solubility of sulphate salts in their range remains constant. A further point to bear in mind here, however, is that the adsorbed substances are taken up as layers on the mineral surfaces instead of being precipitated as voluminous watery hydroxide flocs.

The ability of freshly exposed mineral surfaces to adsorb organic substances, sometimes selectively but more often unselectively, is likewise known from flotation techniques. This ability also embraces oils, such as lubricating oils, and even water pollutants from municipal sewage.

A few examples of the effects of ion adsorption would be in place here. In several large installations it has been found that mixing heavily copper-contaminated water from the mines with tailings slime from the processing plants has resulted in almost complete removal of the toxic copper ions from the effluent and made it possible to restock the recipient with fish. In a large leaching plant, a high concentration of magnesium was extracted to the leaching liquor, which was then neutralized. After passage through the sand trap, the greater part of the magnesium had disappeared. Mercury leached from certain ores is totally adsorbed by the gangue tailings in the settling ponds of the dressing plants.

It will be realized from what I have just said that the comminution involved in mineral processing imparts to the freshly generated rock and ore surfaces a degree of reactivity greatly exceeding that of the stabilized mineral surfaces which we are otherwise accustomed to finding in nature. This process, however, has another effect too. The greatest surface area is represented by the finest particles, which in general can be classed as unstable in an aqueous suspension, since the solution pressure is a function of the particle radius. These particles are created by the statistical effects of grinding and certain zones of weakness in the crystal lattice, but in water they are destined to dissolve rapidly in inverse order of fineness up to a limit of about 0.5 micron, even though their normal solubility in water may be low.

Freshly ground mineral tailings therefore release much greater quantities of nutrient mineral salts than do older, stabilized mineral substances of otherwise similar character. This often results in a richer abundance of life forms, fish in particular, downstream of the outfall, a phenomenon which has often caused surprise. In this respect mineral processing plants appear to have an effect similar to that of glaciers, which likewise release unstable glacial slime into recipients.

The tailings from a small dressing plant in Sweden are being discharged direct into the inlet of a small lake on a heavily polluted watercourse with extensively appearing dirty-water algae. This results in a shift in the ecology of the stream. Clean-water algae gains the ascendancy, and fish are flourishing downstream of the tailings discharge.

## V. SEPARATION OF MINERAL SAND FROM WATER

A carefully prepared technique of storing tailings in the vicinity of mineral processing plants has been generally practised in Sweden since the beginning of this century. We are of course in a better position to do so than in countries that are densely populated. In recent years there have been widely reported disasters in Britain, on the Continent and in Japan, where overloaded sand piles have given way and buried communities and industries.

To establish a tailings pond one chooses an area that is suitable from the point of view of development and cost and can be dyked. In some cases it is possible to utilize lake or sea beds below the vegetation line by piping the tailings down to a depth of more than 20 m, relying on the greater density of the waste water relative to clean water to seek out the deep depressions and fill them with sediment. This occurs outside Europe in large scale more or less well

organized. In Sweden we always have to reckon with some uncertainty as to the cost of such measures, as any nuisance or damage must eventually be paid for by the party responsible, and effects cannot be fully controlled.

The most usual practice in Sweden is to select a suitable stretch of marshland or lakeland that can be purchased and dammed for controlled storing and slime settling. The drawback here is that these depressions in the terrain collect the runoff from a large catchment area, with the result that unduly large volumes of water, especially in spring when the snow melts, enter the system and have to be passed through the slime traps. Containment with dykes and canals is therefore common. The choice of sites for tailing ponds has great economic significance. The slime-bearing sand can nowadays be conveniently pumped to the site through pipelines, distances of up to 3 km or more being quite usual. The pumping technique involved is well developed and works with relatively high efficiency and reasonably low wear. This is a necessity, as in some cases millions of cubic metres are pumped out annually.

The normal layout includes a pond to collect the coarse sediment in the tailings followed by a clarification pond, often a former lake, providing a sufficiently large area for the final sedimentation. The dams are usually erected in the first place with gravel material and subsequently built up with sedimented tailings. The level of water rises steadily as a result of sedimentation, and the area covered by water migrates to different parts of the pond. Spillways in the form of weirs are therefore provided at a number of points in the form of vertical shafts which can be extended upward and which issue into watertight drainage conduits buried in firm soil. A flocculant may be added to the tailings at the point they are discharged into the pond in order to prevent the otherwise fragile flocs of slime from being broken up by pumping or a long fall. Flocculant can of course also advantageously be added to the slime water at the inlet to the clarification pond.

It is particularly interesting to note that the arrangements for purifying the waste water are dimensioned with respect to conditions in the spring season. As I have already pointed out, the natural runoff is augmented by melted snow at that time of the year. At the same time the water is close to freezing point, and its viscosity is something like 60 per cent higher than in summertime. Sedimentation is much slower under these conditions, and a sufficient dammed volume must therefore be provided for partial containment of the spring flood until more favourable conditions are restored.

The fine slime has a low settling velocity in water as long as it is dispersed, giving rise to muddiness, cloudiness or opalescence according to prevailing conditions. To clarify the enormous volumes of industrial water in question to a limit particle size of, say, 1 micron, would require a well-balanced clarification area of the order of 100 000 m<sup>2</sup>, and even then the formulae for settling velocity show that a few per cent of the material would escape with the effluent.

Settling can however be accelerated by flocculation, either as a result of the industrial process through which the material has passed or, occasionally, by the addition of special flocculants, usually lime, ferric sulphate or an organic agent (glue or polyacrylamide).

The slime content of the waste water is measured in g/m<sup>3</sup>, and its turbidity photometrically in ZP units. The relationship between these factors varies according to the type of tailings, but 1000 ZP units normally correspond to a



slime content of about 25 g/cum and represent a secchi disc transparency of about 1 m.

A very important question is, how far should slime separation be carried and I wish to emphasise strongly that this must be decided in each individual case. Generally, a slime content of 100–1000 g/cum can be considered normal for non-flocculated slime water from a non-sulphide dressing plant. Such water may of course flow through the recipient without sedimentation, but it may also be partially trapped in the deepest part of the lakes or run into a flocculating environment and precipitate. Flocculating lime additives to flotation processes are often used when milling sulphide ores. This addition gives on the same time flocculation and higher purification from slime.

## **VI. INFLUENCE OF WASTE WATER PROBLEMS ON PROCESS TECHNOLOGY IN THE MINERAL INDUSTRY**

In the case of metalliferous ores there is normally no choice with regard to the location of the actual mining operations, this being determined by the location of the actual mineral deposits. Concentration plants and other processing industries can on the other hand be sited to give an optimum balance of technical, economic and amenity considerations.

Water purification and the disposal of tailings are expensive operations and usually are influential factors with regard to the location and design of mineral industry plants. These plants normally fall within the category of industries requiring establishment permits, i.e. application must be made to the appropriate Water Rights Court before they can be built. Major extensions to existing plants are subject to the same restriction. Mineral processing facilities are often planned as central plants serving several ore deposits, with long-term provision for water supply, sand disposal and water purification.

The Swedish ore deposits are situated in fairly thinly populated areas, and this is usually also the case in other countries. However, in those cases where ore exploitation has to be carried out in densely populated districts, considerable problems arise resulting in more concentrated plants, filtration of sand, secondary purification of water by precipitation, etc. In these circumstances, amenity requirements may make it a doubtful question whether a mineral industry can be operated at a profit at all.

Some measures regularly adopted by many mineral processing plants to overcome such difficulties and reduce costs are:

- (i) Recovery and recycling of as much as possible of the process water;
- (ii) control of water quality and flocculation conditions;
- (iii) use of tailings sand as filling material in the mines;
- (iv) separation of macadam and sand for processing to road and building construction materials.

In some cases the choice of mineral concentration technique may be governed by the waste water problems that the possible alternatives are likely to involve. This applies particularly if extensive neutralization or precipitation measures are judged to be necessary.

## **VII. OPTIMAL CLEANING OF WASTE WATER**

The foregoing account will have made it plain that the water pollution picture

for the mineral industry, unlike most other industrial pollution questions, is not hopelessly dark. Freshly produced mineral slime actually has a considerable water-purifying effect, and even serves to some extent as a stimulus to plant and animal life in the recipient. Mineral processing plants are usually located in the more sparsely populated parts of our country where the lakes have a low-level ecology. At the same time these regions have considerable amenity value, and the watercourses are therefore sensitive to manipulation. The extensive research conducted by the mineral industry for several decades past has aimed, among other things, at taking a responsible share in the development of optimum measures for water conservancy. The Swedish authorities have shown a most helpful attitude to these endeavours.

It is evident to us that criteria for the purity of waste water must be determined in each individual case and always set in relation to local circumstances affecting the watercourses involved and to any nuisance likely to be created. Experience shows that inflexible demands for total purification may actually lead to needlessly harmful effects. We should therefore continue as in the past to apply the principle of optimisation.