

LISBOA 90

**ENVIRONMENTAL-BIOCHEMICAL ASPECTS OF HEAVY METALS IN
ACID MINE WATER**

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ABSTRACT

Acid mine water production as well as dissolution of several metals in the same are due to an important contribution from the activity of microorganisms. The dissolution and precipitation of the metals from acid mine water seem to be especially controlled also by oxyhydroxides of Fe/Mn.

Interference of specific microorganisms can lead to dissolution and precipitation of specific metals. This ability of the microorganisms could be used to prevent pollution by acid mine water.

INTRODUCTION

Interaction between pyrite and other sulfide minerals and water and atmospheric oxygen originates acidic solutions which can cause serious problems in different aspects of metal enrichment in the environment.

This acid mine drainage is perhaps the most serious environmental impact of mining activity.

Any of the different steps in the mining process can contribute to the exposure of metal sulfides and be a source of acid mine drainage. Water passing the mine, waste rock dumps or tailing areas may generate acidification of the surrounding environment. Although efficient and modern engineering designs are now incorporated into the mines and mills, ecological problems related to acid mine water are persisting, especially after stopping the mining activity.

Biogeochemical processes seem to be very important in all the steps of acid mine drainage, beginning with its generation and until environmental damages due the mobility of metal pollutants, especially in water and soils.

LISBOA 90

MINERAL OXIDATION

The origin of acidic water can be seen in the oxidation of sulfidic minerals. Iron, both in its divalent and trivalent state, plays a key role in this mineral alteration. And a rapid oxidation of sulfide minerals occurs where such minerals are exposed to the atmosphere. The sulfidic components in pyrite are oxidized to sulfate by acidity generation and release of Fe.

TABLE 1. METAL SULFIDE MINERALS OXIDIZED BY IRON-OXIDIZING THIOBACILLI

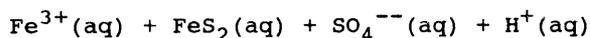
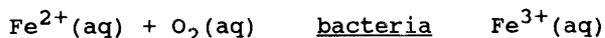
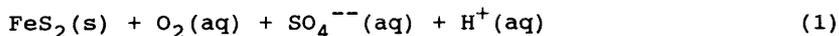
Mineral	Formula
Arsenopyrite	$\text{FeS}_2 \cdot \text{FeAs}_2$
Bornite	Cu_5FeS_4
Chalcocite	Cu_2S
Chalcopyrite	CuFeS_2
Covellite	CuS
Enargite	$3\text{Cu}_2\text{S} \cdot \text{As}_2\text{S}_5$
Galena	PbS
Marcasite	FeS_2
Millerite	NiS
Molybdenite	MoS_2
Orpiment	As_2S_3
Pyrite	FeS_2
Sphalerite	ZnS
Tetrahedrite	$\text{Cu}_8\text{Sb}_2\text{S}_7$

Adapted from Silvermann(1964)

LISBOA 90

In such processes catalytic effects of *Thiobacillus ferrooxidans* and *Ferrobacillus ferrooxidans*, in accelerating the oxidation of Fe^{2+} , seem to be much more efficient than those of sulfate, clay particles, charcoal, iron (Fe^{3+}), copper (Cu^{2+}), manganese (Mn^{3+}) or aluminium (Al^{3+}) (Singer and Stumm 1970) (Table.1). This catalytic activity of microorganisms associated with sulfide ores, forces the chemical oxidation, and *Thiobacillus ferrooxidans* seems to be the the most important bacterium involved in this process.

The following equations represent the first step of the acid generation, with the contribution of the bacterium.



In the propagation cycle, oxidation of Fe^{2+} by *Thiobacillus ferrooxidans* plays a key role. Mechanisms of thermodynamics and electron transport in this bacterium are discussed by Ingledew (1982). In this process, Fe^{2+} is admitted to be oxidized outside of the cell membrane under favorable pH conditions.

This means that by controlling the thermodynamic measurements (elimination of oxygen and maintaining reducing conditions), bacterial activity of Fe^{2+} oxidation would help to reduce the problem of acidic mine drainage.

As aerobic autotrophic bacteria require oxygen as an essential reactant, it can be admitted that the acid production rates are somehow dependent of oxygen levels (Smith and Shumate 1970).

Such an oxidation process by bacterial action seems to be connected with electrochemical processes which provide substrates for metabolism (Ralph 1979).

Although pyrite is predominant in sulfide deposits, autotrophic bacteria are also acting in other metal sulfides contributing to the formation of acid mine water. Lundgren et al. (1972) reports that *Thiobacillus ferrooxidans* and *Thiobacillus thiooxidans* are active in most sulfide mineral alterations.

LISBOA 90

Temperature is probably an important factor controlling the activity of microorganisms in the production of acid mine water, since pyrite oxidation is an exothermic reaction. Harries and Ritchie (1981) admit that the oxygen distribution pattern in oxidation sites could be regulated by diffusion processes due to the temperature profile in the mine sites.

MOBILIZATION AND PRECIPITATION OF METALS

Retention of metal pollutants in acidic mine water will depend of several factors, from which pH, Fe and Mn contents, Redox and organic matter should be stressed. Chapman et al. (1983) discuss the processes controlling Pb, Cu and Zn in acidic mine water, mainly from an inorganic point of view. Mobilization of heavy metals by microbial interactions is however a well-known phenomenon.

One of the most important factor controlling biochemical metal solubility and mobility of the metals in the acid mine water (AMW) is the presence of Fe and Mn, as these elements are ubiquitously present in reducing environments. The solubilization of iron and manganese in reducing environments is a well-known phenomenon.

Changes of oxidation reduction potential and pH conditions by metabolic activities of the microorganisms, are considered one of the major processes in the mobilization of metals in acidic waters. The source metals incorporated this way into AMW can be from the orebody itself, mine tailings or dredged materials.

In mine tailings and waste material, thermophilic microbes seem to be present and contribute to chemical and biological dissolution of mineral sulfides Brierley and Murr (1973).

At elevated temperatures and in highly acidic environments (pH 1.4-2.5) similar to those found in mineral sulfide leaching operations, an chemoautotrophic microorganism of the genus *Sulfolobus* was isolated from an acid hot spring (Brierley and Brierley, 1973).

Data given by Nelson et al. (1981) suggest metal adsorption on bacteria is a function of hydrogen ion concentration. The equilibrium distribution of metals between bacterial solids and solutes, however, is mediated primarily by physical-chemical factors and is not particularly influenced by active biological transport processes.

LISBOA 90

Napier et al. (1968) establish two fundamental processes in the microbial ore leaching: 1. Mineral degradation by bacteria in the presence of dissolved oxygen. 2. Mediate leaching action of ferric ion achieved by bacterial oxidation. Special conditions for these processes are: small particle size, nutrients supply, temperature between 30 and 35 degrees Centigrade, and aeration.

Biogeochemical conditions changing of AMW can lead to the precipitation of the metals. Aeration and the degree of decomposition of organic matter can be considered relevant for the localization of the oxidation/reduction boundary in the sediments. In our case AMW would represent the reduction zone, and the metals dissolved in it would be able to precipitate as soon as they reach the oxidation level.

After contacting AMW with aerobic environment, the controlling solids may change gradually from metallic sulfides to carbonate, oxyhydroxide or silicate solids. Due to the formation of oxyhydrates of iron and manganese, or due to the change of controlling mechanisms from solubilities of sulfides to adsorption by other clay minerals, the soluble species of the metals could be scavenged.

Changes of suitable environmental conditions in the AMW, would favour biogeochemical precipitation of Fe-Mn. Neutralization of acid due carbonate minerals (e.g. in the mine waste) could be pointed out as an important factor for such environmental change. However, other geological and geochemical characteristics prevailing outside of the mining field, in the path of AMW flow, could also contribute to reducing acidification and to progressive precipitation of the different metals.

RELEVANCE OF FE-MN HYDROXIDES IN PRECIPITATION PROCESSES

Production of alkali in anoxic hypolimnia due to sedimentary reactions are connected with the neutralization of acidic precipitation, and epilimnetic sediments have also been identified as an important site of alkali production. Schiff and Anderson (1986) report that in acidic lakes, Fe^{2+} and Mn^{2+} replace Ca^{2+} as the dominant cation contributors to alkali production. Oxidation of Fe^{2+} , Mn^{2+} at the anoxic-oxic interface and biological removal of NH_4^+ in the overlying water column result in consumption of the co-diffusing alkalinity.

LISBOA 90

The model of metal adsorption by Fe-Mn hydrous oxides in aquatic environment, first proposed by Goldberg (1954) as "scavenging" process, can be considered as very important for the precipitation of metals, because of the broad dissemination of the Fe-Mn oxyhydroxides in the environment.

Thermodynamically metastable phases, which exhibit extensive isomorphic substitution (Calmano and Forstner, 1983) are known to be the more important sites for the sorption of heavy metals and for the Fe-Mn oxyhydrates. Formation of such hydrous oxides can occur at the point where neutralization of AMW takes place, as for example at the junction of AMW with water exhibiting different pH values.

Experimental hydrochemical studies (Cameron and Ballantine, 1975) reveal the influence of the formation of Fe/Mn precipitation on metal contents in river water. In areas of absence of an oxide scavenger, dispersion of metals was significant, whereas in drainage areas with a pH in excess of 7, the levels of the same metals decrease very rapidly.

Differentiations under changing redox conditions determine the relative accumulation of trace metals in Fe/Mn concretions in both marine and freshwaters. Callender and Bowser (1976) concluded that specific sorption effects on hydrous oxides are responsible for metal accumulation in freshwater concretions.

Precipitation of metals associated with iron or manganese could also take place by changing geochemical conditions in soils where water containing these metals percolated. Vasari et al (1972) describe precipitation of iron and manganese in water percolating podsol soils. The ground water containing much organic, fulvic and humic acid has a low pH value. The dissolved cations are in reduced form and can migrate with percolating waters as ions, fulvates, humates and organic compounds. When the environment changes from anaerobic conditions to aerobic and more oxidizing ones, the organic acids become neutralized and metallic ions and organic compounds are precipitated.

There are indications that microorganisms are active in precipitation of oxyhydrates of Fe-Mn in natural waters. Subsequently other metals, probably due to the scavenging effect, would contribute to the deposition of other metals like copper, cobalt and nickel. Both processes, inorganic and biogeochemical precipitation, have been suggested for the genesis of the marine ferromanganese nodules. (Xavier 1982, Xavier 1976).

LISBOA 90

Participation of the microorganisms in the precipitation of iron and manganese was reported for the first time by Ehrenberg in the last century (1836).

Since then a lot of work has been done in this area (Silvermann, M.P. and Ehrlich, H.L. 1964, Trudinger and Bubella 1967, Zajik 1969, Ehrlich, 1971), and different models of interaction microorganisms-Fe, Mn have been proposed. Different kinds of microorganisms contribute to dissolution and precipitation of iron and manganese minerals (Table. 2)

Ehrlich (1968) describes microbial Mn^{2+} oxidation and MnO_2 reduction. Such bacterial activity, has also an affinity with certain other cations like Fe^{2+} , Cu^{2+} , Ni^{2+} and Co^{2+} .

Microbial processes connected with stagnant waters can also be relevant for metal deposition of AMW under special circumstances.

Metal-staining is one of the mechanisms by which heavy metals are enriched in anoxic sediments. In stagnant basins, where water circulation is very restricted, anoxic sediments are rich in organic material and heavy metals. Due to biogeochemical processes metals act with organic matter, conducting to metal fixation. Fenchel and Blackburn (1979) discuss the molecular aspects of the biomineralization. Degens et al. (1970), found structures similar to bacterial cell walls in the Black Sea sediments. Temple and Leroux (1964), determined the effect of copper toxicity on sulfate reducing bacteria and show that metal concentration in the environment prevent their action leading to the precipitation of copper sulfide. Interaction of the metal with chemical groups in the wall, and, after that, deposition of large quantities of the metals seem to be the principal phases of the metal deposition in the cell walls of microorganisms.

LISBOA 90

Table 2. BIOGEOCHEMISTRY OF SOME IRON AND MANGANESE MINERALS

Name (Formula)	Source	Ore-building organism	Ore-dissolving organism
<u>Carbonates</u>			
Rhodochrosite (MnCO ₃)	Sed.	Sulfate red. bacteria	Bacteria, fungi
Siderite (FeCO ₃)	Sed. Hydr.	Bacteria	Bacteria, fungi
<u>Oxides</u>			
(For all oxides)		Bacteria, algae	Bacteria, fungi, protozoa
Pyrolusite (MnO ₂ .H ₂ O)	Sed.		
Manganite (Mn ₂ O ₃ .H ₂ O)	Sed.		
Hausmannite (Mn ₃ O ₄)	Sed.		
Goethite (Fe ₂ O ₃ .H ₂ O)	Sed.		
Hematite (Fe ₂ O ₃)	Sed.		
Magnetite (Fe ₃ O ₄)	Sed.		
Limonite (2Fe ₂ O ₃ .3H ₂ O)	Sed.		
<u>Sulfides</u>			
Alabandite (MnS)	Igneous, hydr., sed.	NA	NA
Pyrite (FeS ₂)	Igneous, hydr., sed.	Sulfate red. bacteria	Thiobacilli, ferrobacilli
Pyrrhotite (FeS _{n+1})	Igneous, hydr., sed	Sulfate red. bacteria	Thiobacilli, ferrobacilli

NA = no specific microbial action known, but such action is deemed possible.

Adapted from Silverman(1964)

LISBOA 90

ENVIRONMENTAL ASPECTS

The AMW produced has serious environmental effects on the water quality of the surrounding rivers and lakes as well as on the soil, due to metal concentrations.

The effects of mine effluents on the aquatic system, as well as on the soils is a well known problem. Harvey (1976) gives several examples of acid pollution problems from Brunswick mines where waste water had accumulated high concentrations of the metals zinc, copper and iron. Tyler and Buckney (1973) report that in Tin and Tungsten mines in Tasmania, the coarse tailings contributed to the accumulation of lead, copper, cadmium, zinc and sulfuric acid enrichment in larger areas surrounding the mine area, contaminating the aquatic system of the region.

Models predicting how far metals of mining effluents will be transported, in order to evaluate the intensity of their environmental impact in the aquatic system, are unfortunately rare. Artificial acidification of rivers for a long period and injection of toxic chemicals into freshwater systems have been carried out in different regions. Kuwabara et al. (1984) added a mixture of NaCl and CuSO₄ into a stream. The modelling of the results show that the biological system of the river influenced the concentration of the metals dispersed in the water. In many countries legal problems hinder the realization of such an experimental work, even in a controlled area and small metal quantities.

Infiltration of AMW in sediments or soil near mining sites and a secondary migration towards the surface can lead to specific dissolution/precipitation of metals on the reduction/oxidation boundary, similar to those observed in many sedimentary environments.

Trace metals exist in different forms in the sediment-water interface and may occur in interstitial waters as free or complexed ions or loosely adsorbed on solids. Some may incorporate with insoluble organic or inorganic matters of authigenic solids. The migration of metals between the interface of water and sediments or within the sediments under different redox conditions, will particularly affect the environmental contamination of AMW flowing through sedimentary formations.

Concerning bioavailability and toxicity of metals in waters, trace element speciation plays an important role (Batley, 1989). These specific aspects of contamination can also be considered relevant for the AMW. Particles may be very important in the distribution of metals between the dissolved and solid phases, as they offer sites for adsorption. These interactions are complicated

LISBOA 90

because sedimentary surfaces, organic and inorganic ligands all compete for complexation of the metals.

Four interactions concerning speciation are pointed out by Forstner and Salomons (1983):

1. speciation of metals may enhance or prevent adsorption depending on the adsorption onto the mineral surfaces
2. speciation of solid phase determines the extent of the sorption although mineral particles themselves are able to adsorb trace metals
3. aging effects and other diagenetic processes taking place after deposition cause a redistribution of trace metals over the various components of the sediments
4. sediments influence the speciation of dissolved metals indirectly, because they are a substrate for biogeochemical transformations which result in the formation of methylated species of some trace metals.

One of the most important applications of the interaction microorganisms/metals in solution are the biological processes in the treatment of effluents of mines. Michaelis (1988) discusses an integrated biological concept in the treatment of mine tailings. According to this concept, different kinds of organisms are able to remove metals and other contaminants from effluent solutions. Possible applications of the biological systems are:

1. Heavy metals polishing in mine drainage and tailings decant solutions
2. Passive primary treatment in conjunction with limestone/lime addition
3. Detoxification of cyanide, heavy metals, and ammonia-containing effluents, before or after natural degradation.

Nonbiological recovery of metals from solid wastes is referred to by Ball et al. (1987). A pilot test developed by the Montana College of Mineral Science and Technology stresses the following major unit processes:

1. metal hydroxide dissolution by sulfuric acid leaching
2. iron removal by jarosite precipitation
3. solid/liquid separation by filter pressing
4. copper and zinc recovery by solvent extraction
5. chromium recovery by oxidation to dichromate
6. nickel recovery by Ni-sulfate crystallization.

LISBOA 90

Organic membranes are associated in several cases with heavy metals, either in cellular or extracellular way (Degens and Stoffers, 1977). In cellular systems there are a number of heavy metals which are detrimental to life, and organisms can often protect themselves against metal "poisoning" by forming chelating compounds which they excrete into the environment or use internally for the efficient removal or neutralization of heavy metals.

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LISBOA 90

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LISBOA 90

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