

# Basic Concepts in Environmental Geochemistry of Sulfidic Mine-Waste Management

Bernhard Dold

*Institute of Applied Economic Geology (GEA), University of Concepción  
Chile*

## 1. Introduction

### 1.1 Mining and the environment

As minerals, which are essential to industrial economies, are presently not in short supply, nor do they seem to be for the next several generations, mining and mineral processing can no longer be presumed to be the best of all possible uses for land; it must compete with compelling demands for alternative uses. Environmental protection and rehabilitation are fast becoming high priorities throughout the world, no longer confined to industrialized countries. Environmental regulations in the developed countries are one of the main reasons for the departure of metal mining companies to less developed nations in the last few decades. Low labor costs, exploration potential, and lax or no existing environmental policies, reinforced this process (Hodges, 1995). While industrialized countries started to formulate environmental reports and to implement environmental framework laws in the 1970's (e.g., USA, Central Europe, Japan), developing countries started this process only recently in the 1990's (e.g., Chile, Peru, Korea, Nigeria), as reported in (Jänicke & Weidner, 1997). Increasing world population together with economic growth in emerging countries (e.g. China, India, Brasil etc.) is increasing constantly the demand for metals and minerals in the near future and the associated environmental assessment. Although the world economic crisis stopped this trend for one year, the newly increasing metal prices on the world market confirm that this trend will go on.

### 1.2 Mining and extraction processes

Once the exploration of an ore body is successful, exploitation begins. The extraction of the ore can take place in an open pit or underground. The ore is then transported to stockpiles or directly to the milling process, where crushing and grinding decrease the grain size for the beneficiation process. The ore grinding must be optimized with respect to the leaching, roast-leaching, or possible beneficiation circuits as tabling, flotation, high intensity magnetic separation, heavy media, and others. Liberation of the mineral by the process is governed by the grain size and the mineral complexity of the ore (Ritcey, 1989).

Flotation circuits are systems of cells and auxiliary equipment arranged to yield optimal results (about 80-90 % recovery) from an ore in creating a concentrate following grinding and reagent treatment (Fig. 1). Froth flotation involves the aggregation of air bubbles and mineral particles in an aqueous medium with subsequent levitation of the aggregates to the

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surface and transfer to a froth phase. Whether or not bubble attachment and aggregation occur is determined by the degree to which a particle's surface is wetted by water. When a solid surface shows little affinity for water, the surface is said to be hydrophobic, and an air bubble will attach to the surface. Coal and molybdenite are the most important naturally hydrophobic minerals. For sulfides except molybdenite, and possibly stibnite, as well as non-sulfide minerals, the surface condition required for flotation is obtained by specific reagents called collectors. Furthermore, complex ores require a complex combination of conditioning, collecting, and depressing necessary for optimal mineral extraction (Weiss, 1985). After the extraction of the economically interesting minerals by flotation, the residual material (in copper mines typically 95-99% of the treated material) is transported in the form of a suspension to tailings impoundments for final deposition. In practice the recovery of sulfide minerals is less than 100%, and pyrite flotation is generally suppressed by lime addition, so the tailings resulting from sulfide ores contain certain percentage of sulfides, mostly pyrite.

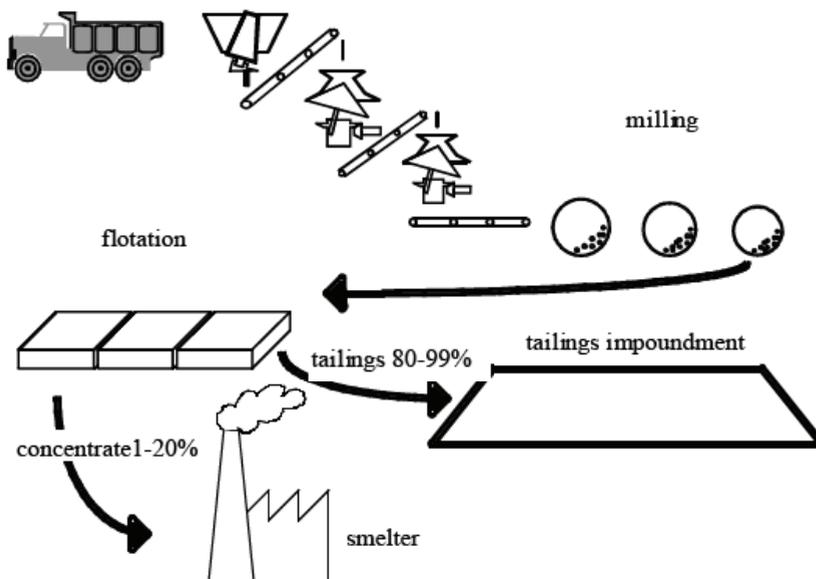


Fig. 1. The ore flow-path from the mine, through crushing and milling, to flotation. The concentrate is refined in the smelter, while the main part of the treated material will be deposited on the tailings impoundments. Tailings and concentrate proportions may differ from the given percentages.

## 2. Waste-rock dumps and tailings impoundment design and deposition techniques

The most economic and most commonly used tailings deposition technique is wet deposition nearby the mine site. In this technique, a water-sediment slurry is pumped in

nearby topographic depressions, lakes or drainage basins. An also often economic practice was sea deposition, when the mine was located close to the ocean, with sometime hazardous effects on the environment (Dold, 2006). Other techniques are a semi-dry sub-aerial method, thickened discharge, and deep-water disposal (Ritcey, 1989).

In countries with pronounced topography (e.g., Chile), most of the tailings impoundments are designed as valley dam impoundments. This type of design is provided by placing an embankment across the valley at the head end of drainage. The most common dam construction methods are the downstream and the upstream methods. In the wet deposition method, the tailings slurry is thickened to 35-40% solids and discharged by either point or line discharge. Often a discharge point is moved periodically. As a result of a periodical move of the discharge point and gravimetric grain size separation occurring in the tailings, a general trend of coarser to finer grain size from the tailings discharge point to the pond can be observed. Additionally, inhomogeneous layering of fine sand with silt and clay horizons makes the hydrological situation in the tailings material very complex. In general, it must be assumed that the coarser horizons are responsible for permeability, and that they behave as connected aquifers. This should be taken into account in sampling and the calculation of permeability coefficients. As the horizons have thickness in the range of centimeters to decimeters, frequently, bulk samples lead to too low permeability coefficients.

In case of Chile, the combination of valley dam impoundments with high potential energy, the extremely high seismic activity, and the fact that this country is very rich in mining resources makes the stability of the tailings dam construction the largest apparent problem. In addition, as the tailings material is generally fine-grain sized material, it retains well moisture also in arid climates, and the process of liquefaction during seismic activity is a very important issue (Byrne & Beaty, 1997). In contrast, the geochemical instability of tailings and waste rocks has received only recently in the last decade an increasing interest for research.

### **3. Secondary processes in sulfide mine waste - a review**

#### **3.1 Terminology**

For the description of the mine waste mineralogy the classification proposed by (Jambor, 1994) is used. The term "primary" is used to designate the complete ore mineralogy, i.e. "hypogene" and "supergene". "Secondary" minerals are minerals formed within the tailings impoundment as the products of weathering processes. "Tertiary" minerals form after the sample has been removed from the tailings environment.

#### **3.2 Sulfide oxidation in mine waste**

The problem of sulfide oxidation and the associated acid mine drainage (AMD), or more generally acid rock drainage (ARD), as well as the solution and precipitation processes of metals and minerals, has been a major focus of investigation over the last 50 years (Blowes et al., 1991; Jambor, 1994; Moses et al., 1987; Nordstrom, 1982; Sato, 1960). There has been less interest in the mineralogical and geochemical interactions taking place within the tailings and waste dumps itself (Dold & Fontboté, 2001; Jambor, 1994), yet this is an essential aspect to understand the parameters controlling acid mine drainage formation and to develop effective prevention methods. The primary mineralogical composition has a strong influence on the oxidation processes. This has been best illustrated by (Huminicki & Rimstidt, 2009;

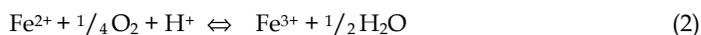
Rimstidt et al., 1994; Rimstidt & Vaughan, 2003) showing that reaction rates display significant differences depending on the sulfides being oxidized by Fe(III) and the potential Fe(III) hydroxide coating. Kinetic-type weathering experiments indicate the importance of trace element composition in the stability of individual sulfides. Where different sulfides are in contact with each other, electrochemical processes are likely to occur and influence the reactivity of sulfides (Kwong, 1993).

Most mining operations are surrounded by piles or impoundments containing pulverized material or waste from the benefaction process, which are known as tailings, waste rock dumps or stockpiles. Waste rock dumps contain generally material with low ore grade, which is mined but not milled (Run of mine). These materials can contain still large concentrations of sulfide minerals, which may undergo oxidation, producing a major source of metal and acid contamination (Dold et al., 2009). The complex microbiological, hydrological, mineralogical, and geochemical post-depositional processes and their coupled interaction in mine waste environment are not yet completely understood. In the following section the focus is on the acid producing sulfide minerals, other acid producing processes, and the acid neutralizing processes, as well as on the controlling factors for element mobility.

### 3.2.1 Acid producing sulfide minerals

#### 3.2.1.1 Pyrite (FeS<sub>2</sub>)

The most common sulfide mineral is pyrite (FeS<sub>2</sub>). Oxidation of pyrite takes place in several steps including the formation of the metastable secondary products ferrihydrite (5Fe<sub>2</sub>O<sub>3</sub>·9H<sub>2</sub>O), schwertmannite (between Fe<sub>8</sub>O<sub>8</sub>(OH)<sub>6</sub>SO<sub>4</sub> and Fe<sub>16</sub>O<sub>16</sub>(OH)<sub>10</sub>(SO<sub>4</sub>)<sub>3</sub>), and goethite (FeO(OH)), as well the more stable secondary jarosite (KFe<sub>3</sub>(SO<sub>4</sub>)<sub>2</sub>(OH)<sub>6</sub>), and hematite (Fe<sub>2</sub>O<sub>3</sub>) depending on the geochemical conditions (Bigham et al., 1996; Cornell & Schwertmann, 2003; Dutrizac et al., 2000; Jambor, 1994; Jerz & Rimstidt, 2004; Nordstrom, 1982; Rimstidt & Vaughan, 2003). Oxidation of pyrite may be considered to take place in three major steps: (1) oxidation of sulfur (equation 1); (2) oxidation of ferrous iron (equation 2); and (3) hydrolysis and precipitation of ferric complexes and minerals (equation 4). The kinetics of each reaction are different and depend on the conditions prevailing in the tailings.



reaction rates strongly increased by

microbial activity (e.g., *Acidithiobacillus spp.* or *Leptospirillum spp.*)



Equation (1) describes the initial step of pyrite oxidation in the presence of atmospheric oxygen. Once ferric iron is produced by oxidation of ferrous iron, oxidation, which may be, especially at low pH conditions, strongly accelerated by microbiological activity (equation 2), ferric iron will be the primary oxidant (equation 3) of pyrite (Ehrlich, 1996; Moses et al., 1987; Nordstrom et al., 1979). Under abiotic conditions the rate of oxidation of pyrite by

ferric iron is controlled by the rate of oxidation of ferrous iron, which decreases rapidly with decreasing pH. Below about pH 3 the oxidation of pyrite by ferric iron is about ten to a hundred times faster than by oxygen (Ritchie, 1994).

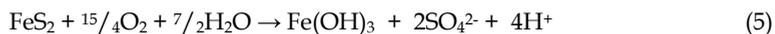
It has been known for 50 years that microorganisms like *Acidithiobacillus ferrooxidans* or *Leptospirillum ferrooxidans* obtain energy by oxidizing  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$  from sulfides by catalyzing this reaction (Bryner et al., 1967) and this may increase the rate of reaction (2) up to the factor of about 100 over abiotic oxidation (Singer & Stumm, 1970). More recent results show that a complex microorganism community is responsible for sulfide oxidation (Ehrlich, 1996; Johnson, 1998; Johnson, 1999; Johnson & Hallberg, 2003a; Norris & Johnson, 1998). Nordstrom & Southam (1997) state that the initiating step of pyrite oxidation does not require an elaborated sequence of different geochemical reactions that dominate at different pH ranges. *Acidithiobacillus* spp. form nanoenvironments to grow on sulfide mineral surfaces. These nanoenvironments can develop thin layers of acidic water that do not affect the bulk pH of the water chemistry. With progressive oxidation, the nanoenvironments may change to microenvironments. Evidence of acidic microenvironments in the presence of near neutral pH for the bulk water can be inferred from the presence of jarosite (this mineral forms at pH around 2) in certain soil horizons where the current water pH is neutral (Carson et al., 1982). Barker et al. (1998) observed microbial colonization of biotite and measured pH in microenvironments in the surroundings of living microcolonies. The solution pH decreased from near neutral at the mineral surface to 3-4 around microcolonies living within confined spaces at interior colonized cleavage planes.

When mine water, rich in ferrous and ferric iron, reaches the surface it will fully oxidize, hydrolyze and may precipitate to ferrihydrite (fh), schwertmannite (sh), goethite (gt), or jarosite (jt) depending on pH-Eh conditions, and availability of key elements such as potassium and sulfur (Fig. 2). Jarosite, schwertmannite and ferrihydrite are meta-stable with respect to goethite (Bigham et al., 1996).

The hydrolysis and precipitation of iron hydroxides (and to a lesser degree, jarosite) will produce most of the acid in this process. If pH is less than about 2, ferric hydrolysis products like  $\text{Fe}(\text{OH})_3$  are not stable and  $\text{Fe}^{3+}$  remains in solution:



Note that the net reaction of complete oxidation of pyrite, hydrolysis of  $\text{Fe}^{3+}$  and precipitation of iron hydroxide (sum of reactions 1, 2 and 4) produces 4 moles of  $\text{H}^+$  per mole of pyrite (in case of  $\text{Fe}(\text{OH})_3$  formation, see equation 5, i.e., pyrite oxidation is the most efficient producer of acid among the common sulfide minerals (net reaction 5; Table 2). Nevertheless, it is important to be aware that the hydrolysis of  $\text{Fe}(\text{OH})_3$  is the main acid producer ( $3/4$  of moles of  $\text{H}^+$  per mol pyrite).



The precipitation of these secondary Fe(III) hydroxides can form coatings (Huminicki & Rimstidt, 2009) and cemented layers (Blowes et al., 1991; Dold et al., 2009), which can decrease the oxidation rates. (Evangeliou & Zhang, 1995) reported increased oxidation rates of pyrite by addition of  $\text{HCO}_3^-$  due to the formation of pyrite surface Fe(II)- $\text{CO}_3$  complexes. This means that the frequent applied limestone treatment for mine waste management must be discussed critically, because if it is able to neutralize the acid produced, it can also increase the kinetic of pyrite oxidation.

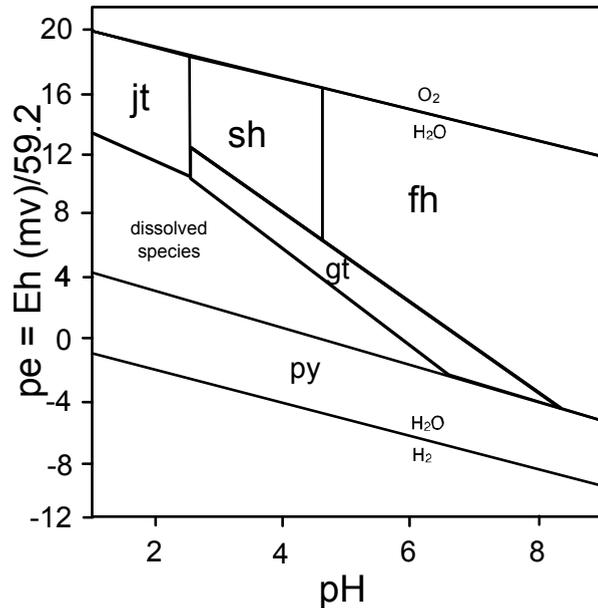
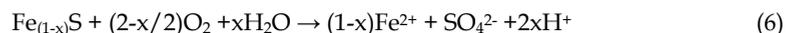


Fig. 2. pe-pH diagram for Fe-S-K-O-H system at 25°C where  $pe = Eh(mV)/59.2$ ; total log activities of  $Fe^{2+} = -3.47$ ;  $Fe^{3+} = 3.36$  or  $-2.27$ ;  $SO_4^{2-} = -2.32$ ;  $K^+ = -3.78$ ; log Kso values for solid phases for Gt = goethite, Jt = K-jarosite, Fh = ferrihydrite, Sh = schwertmannite are 1.40, -12.51, 4.5 and 18.0, respectively. Py = pyrite. Mean composition of the schwertmannites used for the development of this pe-pH diagram was  $Fe_8O_8(OH)_{4.8}(SO_4)_{1.6}$ . After Bigham et al. (1996). Note that these stability fields have to be interpreted as indicative, as the thermodynamic data published from schwertmannite and ferrihydrite show high variability (Majzlan et al., 2004).

Marcasite, the orthorhombic dimorph of pyrite, may also abundantly occur as a primary mineral in sulfidic tailings, mainly from sediment-hosted base metal deposits and as primary alteration product of pyrrhotite. Marcasite has the same formula as pyrite and leads to the same amount of acid production via oxidation. Direct observation (e.g. the Zn-Pb deposit of Reocín, Spain) suggest that its oxidation kinetics should be faster than that of pyrite, perhaps as a result of its typical twinned morphology and finer grain size, which offers more surface to oxidation than pyrite. Additional, (Jambor, 1994) reports the presence of marcasite as a secondary alteration product of pyrrhotite in zonal patterns in oxidizing mine tailings.

### 3.2.1.2 Pyrrhotite( $Fe_{(1-x)}S$ )

Wastes from sulfide ores often contain pyrrhotite associated with pyrite. The general formula of pyrrhotite is  $Fe_{(1-x)}S$ , where x can vary from 0.125 ( $Fe_7S_8$ ) to 0.0 ( $FeS$ , troilite). The oxidation rates and weathering products of pyrite are well known, but only a few investigations have focused the oxidation of pyrrhotite. (Nicholson & Scharer, 1994) propose for the oxidation of pyrrhotite the following equation:



in which the stoichiometry of the pyrrhotite affects the relative production of acid. At one extreme, if  $x = 0$  and the formula is  $\text{FeS}$ , no  $\text{H}^+$  will be produced in the oxidation reaction; at the other extreme, the maximum amount of acid will be produced by the iron-deficient  $\text{Fe}_7\text{S}_8$  phase. The main part of acid is produced by the oxidation of pyrite (equation 1) and the subsequent hydrolysis of ferric hydroxides (equation 4). In conclusion, the role of pyrrhotite in the acidifying process is similar to that of pyrite, but it is very important at early weathering stages because its oxidation rate is 20 to 100 times higher than that of pyrite in atmospheric concentrations of  $\text{O}_2$  and at  $22^\circ\text{C}$  (Nicholson & Scharer, 1994).

The oxidation of pyrrhotite can also involve the formation of elemental sulfur (Ahonen & Tuovinen, 1994), marcasite (Jambor, 1994), or the formation of pyrite. They are acid-consuming reactions.

### 3.2.1.3 Chalcopyrite ( $\text{CuFeS}_2$ )

Complete oxidation of chalcopyrite may be written as:



without acid production. Nevertheless, the combination of ferrous iron oxidation and ferrihydrate hydrolysis will be again the main acid producing process.



Chalcopyrite, together with molybdenite, is known as one of the most resistant sulfides to oxidation (Plumlee, 1999). (Rimstidt et al., 1994) reported that the oxidation rate of chalcopyrite increases with increasing ferric iron concentration, but with an oxidation rate of 1-2 orders of magnitude less than pyrite.

### 3.2.1.4 Arsenopyrite ( $\text{FeAsS}$ )

Arsenopyrite ( $\text{FeAsS}$ ) may be oxidized by the following reaction path (Mok & Wai, 1994):



Combined with ferrous iron oxidation and ferrihydrate precipitation, the overall arsenopyrite oxidation reaction can be written as follow:



If ferric iron is the oxidant, the oxidation rate of arsenopyrite is similar to the oxidation rate of pyrite. If it is oxygen, the oxidation rate of arsenopyrite is somewhat lower than that of pyrite (Mok & Wai, 1994).

## 3.3.2 Non-acid producing sulfide minerals

### 3.3.2.1 Sphalerite ( $\text{ZnS}$ ) and galena ( $\text{PbS}$ )

Sphalerite and galena are the most important base metal bearing minerals. Though Zn is toxic only at very high concentrations, sphalerite may contain environmentally dangerous amounts of Cd and Thallium (Tl). In addition, Fe may significantly substitute for Zn, in cases up to 15 mole %, in sphalerite (Baumgartner et al., 2008). If iron substitutes for zinc, sphalerite will be an acid generator in a similar way as pyrrhotite, due to hydrolysis of ferric phases. Galena is the main source of Pb contamination in mine areas. The common result of

Mineral	Mole H <sup>+</sup> /Mole Mineral	Relative wt % H <sup>+</sup> /Mole mineral	Reaction with Fe(III) <sup>1)</sup>
Pyrite	4	0.03	2.7 x 10 <sup>-7</sup>
Marcasite	4	0.03	1.5 x 10 <sup>-7</sup>
Arsenopyrite	2	0.018	1.7 x 10 <sup>-6</sup>
Chalcopyrite	2	0.011	9.6 x 10 <sup>-9</sup>
Pyrrhotite	2-0	0.022	-
Enargite	1	0.002	-

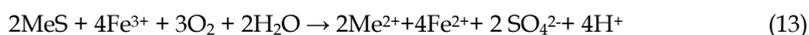
<sup>1)</sup>  $m \text{Fe}^{3+} = 10^{-3}$  and  $\text{pH} = 2.5$  at  $25^\circ\text{C}$ ;  $\text{mol m}^{-2}\text{s}^{-1}$ ; - = not studied by Rimstidt et al. (1994)

Table 1. Hydrogen ions per mole produced by oxidation via O<sub>2</sub> of some frequent minerals in mine tailings (Plumlee, 1999) and some laboratory reaction rate data from Rimstidt et al. (1994). However, Jambor (1994) suggested the relative resistance of sulfide in oxidizing tailings environment to follow the increasing order pyrrhotite → sphalerite-galena → pyrite-arsenopyrite → chalcopyrite → magnetite.

the wet oxidation of sphalerite is a leach rich in dissolved Zn, and sulfate, with variable Cd amounts, while that of galena is secondary anglesite (PbSO<sub>4</sub>) in equilibrium with a Pb<sup>2+</sup> and SO<sub>4</sub><sup>2-</sup> solution according to the following equations



Secondary anglesite coating on galena may increase the apparent resistance because anglesite has a relative low solubility and protects the sulfides from direct contact with oxidizing reagents (Jambor & Blowes, 1998). In the presence of Fe<sup>3+</sup>, the oxidation of MeS (where Me = divalent metal) produces acidity according to reaction schemes where part of the oxidation capacity of the system is derived from Fe<sup>3+</sup> as, e.g.



Plumlee (1999) pointed out that the oxidation of sulfide minerals by aqueous ferric iron generates significantly greater quantities of acid than the oxidation by oxygen (e.g., equation 3 and 13). This is correct in the case that ferric iron is added to the system (e.g., in form of primary ferric minerals or seepage of ferric iron containing solutions). However, if we consider that the ferric iron is produced by the oxidation from ferrous iron in the system (e.g., microbologically catalyzed pyrite oxidation), for every mole of ferric iron produced one mole of protons is consumed (equation 2). This leads to the same overall produced quantity of two protons per mole pyrite oxidized as in case of pyrite oxidation via O<sub>2</sub> (compare equations 1, 2, and 3). Additionally, in case of oxidation via ferric iron no acidity can be produced via the hydrolysis of the ferric phases, the main acid producing process in sulfide oxidation (see equation 4). Thus, the sulfide oxidation by ferric iron has faster kinetics and is able to oxidize sulfide minerals in the absence of oxygen, but it does not produce more acid as the oxidation via oxygen when the ferric iron is produced in the system. However, the management of ferric iron rich solutions in mine waste environments can lead to strong exportation of acid potential and has to receive therefore special attention (Dold et al., 2009).

Table 1 shows a summary of the hydrogen ions produced by some common sulfide minerals by the oxidation via  $O_2$ . There are important differences and therefore exact knowledge of the sulfide minerals contained in waste rocks or tailings is crucial for adequate acid-base accounting (ABA).

### 3.3.3 Secondary Fe(III) hydroxides, oxyhydroxides, and oxyhydroxide sulfates

As explained in 3.2.1, the acid production processes can be split into two parts. The first is the oxidation of sulfide minerals by oxygen and ferric iron. The second is the hydrolysis of mainly Fe(III) and subsequent precipitation of ferric oxyhydroxides or oxyhydroxide sulfates.

The process of hydrolysis of Fe(III) has been reviewed by Sylva (1972), Flynn (1984), Schneider & Schwyn (1987), Stumm & Morgan (1996), and Cornell & Schwertmann (2003). Metal ions undergo hydrolysis because coordinated water is a stronger acid than free water. This result from the effect that the metal-oxygen bond weakens the O-H bonds in a way that in aqueous systems the free water molecules behave as proton acceptors. So the hydrolysis of metal ions is the result of the deprotonation of the coordinated water molecules (Sylva, 1972).

The hydrolysis, i.e. deprotonation, starts with the hexa-aquo ion (Fe(III) is hydrated by 6 water molecules), except at very low pH, where  $Fe^{3+}$  is stable. Initially, low molecular weight species such as  $Fe(OH)_2^+$  and  $Fe(OH)_2^{1+}$  form rapidly. The following dissolved species will be stable depending on pH (see also Fig. 3 and Table 2):  $Fe^{3+}$ ,  $Fe(OH)^{2+}$ ,  $Fe(OH)_2^+$ ,  $Fe(OH)_3^0$  (aq),  $Fe(OH)_4^-$ ,  $Fe_2(OH)_2^{4+}$ , and  $Fe_3(OH)_4^{5+}$  (Stumm and Morgan, 1996). By "aging" increasingly complex polymers, Fe(III) oxides, oxyhydroxides, or oxyhydroxide sulfates like ferrihydrite, schwertmannite, goethite, jarosite are formed (Fig. 2; Bigham et al., 1996). Depending on the secondary phases precipitated, considerably different amounts of protons are produced (Table 3).

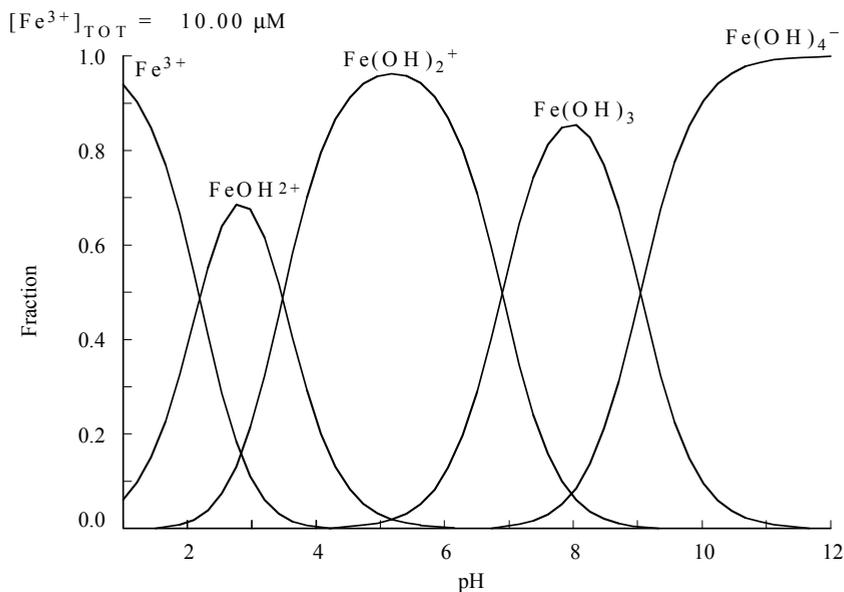


Fig. 3. Mole fraction of total dissolved Fe(III) present as  $Fe^{3+}$  and Fe(III)-OH complexes as a function of pH in pure water at 25°C (after Langmuir (1997)).

Species	Equation	Fe <sup>3+</sup>	H <sup>+</sup>	log K (I = 3 M)
Fe <sup>3+</sup>		1	0	0
Fe(OH) <sup>2+</sup>	Fe <sup>3+</sup> + H <sub>2</sub> O ⇌ Fe(OH) <sup>2+</sup> + H <sup>+</sup>	1	-1	-3.05
Fe(OH) <sub>2</sub> <sup>+</sup>	Fe <sup>3+</sup> + 2H <sub>2</sub> O ⇌ Fe(OH) <sub>2</sub> <sup>+</sup> + 2H <sup>+</sup>	1	-2	-6.31
Fe(OH) <sub>3</sub> (aq)	Fe <sup>3+</sup> + 3H <sub>2</sub> O ⇌ Fe(OH) <sub>3</sub> (aq) + 3H <sup>+</sup>	1	-3	-13.8
Fe(OH) <sub>4</sub> <sup>-</sup>	Fe <sup>3+</sup> + 4H <sub>2</sub> O ⇌ Fe(OH) <sub>4</sub> <sup>-</sup> + 4H <sup>+</sup>	1	-4	-22.7
Fe <sub>2</sub> (OH) <sub>2</sub> <sup>4+</sup>	2Fe <sup>3+</sup> + 2H <sub>2</sub> O ⇌ Fe <sub>2</sub> (OH) <sub>2</sub> <sup>4+</sup> + 2H <sup>+</sup>	2	-2	-2.91
Fe <sub>3</sub> (OH) <sub>4</sub> <sup>5+</sup>	3Fe <sup>3+</sup> + 4H <sub>2</sub> O ⇌ Fe <sub>3</sub> (OH) <sub>4</sub> <sup>5+</sup> + 4H <sup>+</sup>	3	-4	-5.77

Table 2. Hydrolysis reactions of Fe(III) species and the associated protons produced (after Stumm & Morgan, 1996).

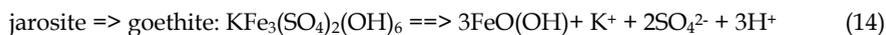
Phase	Equation	moles H <sup>+</sup> /mole Fe <sup>3+</sup> hydrolyzed
amp. Fe(OH) <sub>3</sub> (s)	Fe <sup>3+</sup> + 3H <sub>2</sub> O ⇌ Fe(OH) <sub>3</sub> (s) + 3H <sup>+</sup>	3
ferrihydrate	10 Fe <sup>3+</sup> + 60H <sub>2</sub> O ⇌ 5Fe <sub>2</sub> O <sub>3</sub> ·9H <sub>2</sub> O + 30H <sup>+</sup>	3
goethite	Fe <sup>3+</sup> + 2H <sub>2</sub> O ⇌ FeO(OH) + 3H <sup>+</sup>	3
hematite	2Fe <sup>3+</sup> + 3H <sub>2</sub> O ⇌ Fe <sub>2</sub> O <sub>3</sub> + 6H <sup>+</sup>	3
schwermannite	8Fe <sup>3+</sup> + SO <sub>4</sub> <sup>2-</sup> + 14H <sub>2</sub> O ⇌ Fe <sub>8</sub> O <sub>8</sub> (OH) <sub>6</sub> SO <sub>4</sub> + 22H <sup>+</sup>	2.75
	16Fe <sup>3+</sup> + 3SO <sub>4</sub> <sup>2-</sup> + 26H <sub>2</sub> O ⇌ Fe <sub>16</sub> O <sub>16</sub> (OH) <sub>10</sub> (SO <sub>4</sub> ) <sub>3</sub> + 42H <sup>+</sup>	2.625
jarosite	3Fe <sup>3+</sup> + K + 2SO <sub>4</sub> <sup>2-</sup> + 6H <sub>2</sub> O ⇌ KFe <sub>3</sub> (SO <sub>4</sub> ) <sub>2</sub> (OH) <sub>6</sub> + 6H <sup>+</sup>	2

Table 3. Protons produced by the hydrolysis of the different secondary Fe(III) phases.

### 3.3.4 Dissolution of sulfate minerals

#### 3.3.4.1 Iron sulfate minerals

Iron sulfate minerals are the most common secondary minerals found in the oxidizing environment of the mine waste, due to the wide distribution of pyrite and pyrrhotite as a iron and sulfur source. They are also common in the oxidized portions of weathering zones from ore deposits (e.g., gossans). They may be composed of Fe(II), Fe(II) + Fe(III), or only Fe(III). Examples are melanterite, roemerite, and coquimbite, respectively (Alpers et al., 1994; Nordstrom & Alpers, 1999). In general they have a high solubility, whereas supergene jarosite shows relatively low dissolution kinetics. Baron and Palmer, (1996) conducted a series of dissolution experiments with jarosite under 4-35°C and at pH values between 1.5 and 3. Equilibrium was established in the experiment after approximately 3 to 4 months. It is important to notice that this mineral group is meta-stable in respect to more stable iron hydroxides and oxides and may liberate acidity by this transformation (see equation 14-16). Transformation:



#### 3.3.4.2 Water-soluble sulfates (efflorescent salts)

An extended group of highly water-soluble sulfates and chlorides, as for example gypsum or chalcantite ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ) or eriochalcite ( $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ ), formed under oxidizing conditions and high evaporation rates, can release significant amounts of metals and acid with rain. This mineral group is an important factor leading to seasonal fluctuations in contamination levels of ground and surface waters, especially in semi-arid and arid climates (Alpers et al., 1994; Dold, 2006; Dold & Fontboté, 2001). Additionally, this group of water-soluble minerals expose heavy metals to aeolian transport in arid climates in a highly bioavailable form and have to receive therefore special attention in health risk evaluations (Dold, 2006).

### 3.4 Neutralization processes

The acid produced in the processes presented above may result normally in pH in the range of 1.5 - 4 in the mine waste environment. Exceptionally, pH can reach even negative values (Nordstrom et al., 2000). This acidity together with Fe(III), are able to dissolve minerals and mobilize elements in the tailings (Dold & Fontboté, 2001). In their pathway, the acid produced and the elements mobilized react with acid-neutralizing minerals such as carbonates or silicates. Acid-neutralizing reactions result in an increase in the pore-water pH. This increase in pH is frequently accompanied by precipitation of metal-bearing oxyhydroxide and oxyhydroxide sulfate minerals that remove dissolved metals from the water migrating within the tailings pore space. These secondary minerals act in a certain pH range as buffers so that a sequence of pH buffering reactions can be observed in the tailings environment (Blowes & Ptacek, 1994).

#### 3.4.1 Carbonates

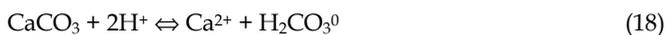
Dissolution of carbonates releases alkaline earth and metal cations, including Ca, Mg, Fe, and Mn. These cations participate in the formation of secondary solids, including simple hydroxide solids, which in some cases can later dissolve and contribute to acid neutralization. The ability of carbonates to neutralize acid by fast reaction makes them an important part of the mineralogical assemblage for ARD prediction and prevention.

##### 3.4.1.1 Calcite ( $\text{CaCO}_3$ )

Calcite is the most common carbonate mineral and the fastest reacting. Its solubility depends on the proton concentration as shown in the following equations:



This reaction will buffer at near neutral pH (6.5 - 7), while in more acidic environments the following equation can be written:



Carbonate speciation is pH dependent (Fig. 4) and the dissolution of calcite increases the amount of carbonate in solution, increasing therefore the neutralization potential of the solution. It is important to mention that calcite buffers the pH to neutral values and at pH 7  $\text{HCO}_3^-$  is the dominant specie (Fig. 4). Thus, for the neutralization of 1 mol  $\text{H}^+$  1 mol calcite is necessary as shown in equation (17). At pH below pH 6.3 carbonate can neutralize two moles of protons, as  $\text{H}_2\text{CO}_3^0$  is the dominant specie (Equation 18). When neutralization proceeds and pH increases, calcite may precipitate as a secondary mineral.

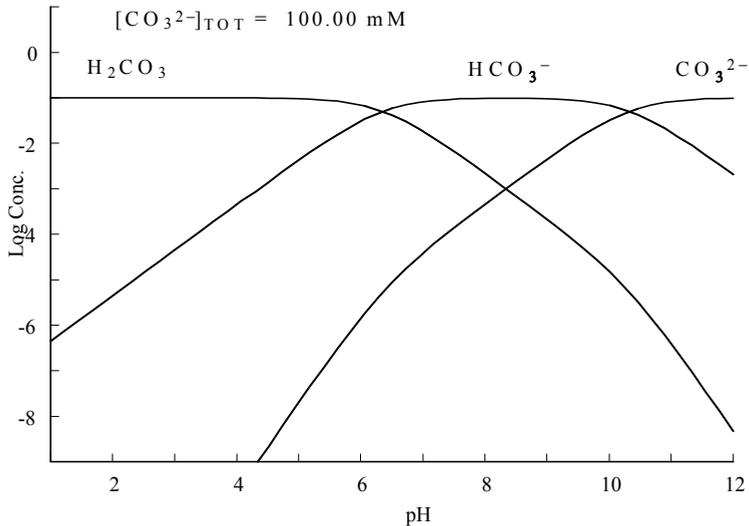
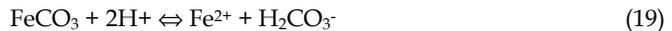


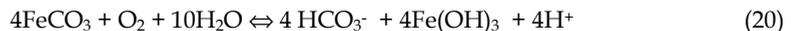
Fig. 4. Distribution of solute species in the aqueous carbonate system. Log concentration vs. pH for 100 mM  $\text{CO}_3^{2-}$ .

#### 3.4.1.2 Siderite ( $\text{FeCO}_3$ )

Siderite may act under certain conditions as a neutralizer, and under other conditions as an acid producer. The following dissolution reaction may take place and buffer the system at pH around 5:



Combined with ferrous iron oxidation and ferrihydrate precipitation, the overall siderite oxidation reaction is:



This indicates that under elevated pH, where bicarbonate is stable, the total reaction from dissolution of siderite to the precipitation of ferrihydrate gives a net acid production of one mole hydrogen ion per mol siderite dissolved. However, under more acidic conditions, where carbonic acid is stable, there will be no net acid production. However, it has to be considered that ferrous iron is liberated, which can be mobilized under neutral pH condition and, when outcropping downstream under oxidizing conditions it will oxidize and hydrolyze under the liberation of protons, producing AMD far from source.

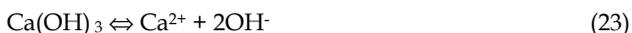
If ferrous iron is present in a solution containing bicarbonate, the formation of siderite may occur by the following reaction:



This reaction buffers the pH at around 5 - 5.5. This reaction path may be an alternative to ferrous to ferric iron oxidation and the consecutive precipitation of Fe(III)oxyhydroxides. Geochemical studies by several authors have shown that in tailings impoundments and AMD affected aquifers the waters are frequently close to saturation or even oversaturated with respect to siderite (Blowes et al., 1994; Blowes et al., 1991; Morin & Cherry, 1986).

### 3.4.2 Lime (Ca(OH)<sub>2</sub>)

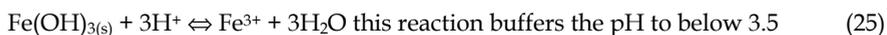
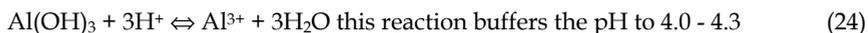
Lime is a common agent in the flotation circuit to depress the flotation of pyrite by the increase of the pH to 10.5.



Lime is used in hydrometallurgical processes due to its high solubility in water and fast neutralization reaction. It may be washed out from tailings impoundments. In this case, the role in neutralizing the acid produced in the tailings may be minor. Therefore, for pH buffering in mine wastes (tailings and waste dumps) carbonates should be preferred.

### 3.4.3 Metal hydroxides dissolution

As a result of neutralization and pH increase, the precipitation of metal hydroxides or hydroxide sulfates is favored, as gibbsite, amorphous Al(OH)<sub>3</sub>, amorphous Fe(OH)<sub>3</sub>, ferrihydrite, goethite, or schwertmannite. Some of the reactions can be described as follows:



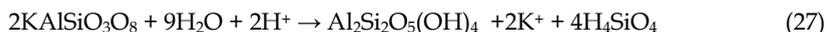
These reactions complement an ideal neutralization sequence, which starts with calcite (pH 6.5 - 7.5) followed by siderite (pH 5.0 - 5.5). When all carbonates are consumed the next buffer is gibbsite (pH 4.0 - 4.3), followed by Fe(III)hydroxides as goethite (pH below 3.5). In the oxidation zone itself the pH range commonly between pH 2 and 3 depending on the amount of goethite, schwertmannite and jarosite (Dold & Fontboté, 2001).

### 3.4.4 Silicates

Dissolution of most aluminosilicate minerals also consumes H<sup>+</sup> ions and contribute base cations (Ca, Mg, Fe(II)), alkali elements (Na, K) and dissolved Si and Al to the tailings pore water (Blowes & Ptacek, 1994). Though, dissolution of aluminosilicate minerals is slower than of metal hydroxides and much slower than that of carbonates (Table 4). Feldspar weathering is mainly controlled by pH, silica, Na, K, and Ca concentrations. One possible reactions path is:



Reactions 27 and 28 illustrate this path.

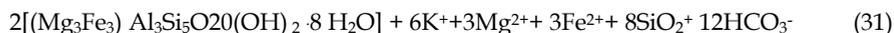
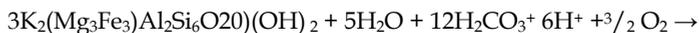


K-feldspar

kaolinite

In this reaction, K and Si enter the solution, while protons are consumed. The solubility of feldspar increases when proton activity increases or the removal of K or Si is fast, e.g. by secondary mineral formation. Secondary kaolinite may dissolve to form gibbsite, a reaction that does not neutralize acid:





Malmström & Banwart (1997) studied the pH dependence of dissolution rate and stoichiometry of biotite at 25°C. They found that the release of the interlayer K is relatively fast and becomes diffusion controlled within a few days. The release of framework ions (Mg, Al, Fe, Si) is much slower. Strömberg & Banwart (1994) suggested that, in the absence of carbonates, primary minerals, particularly biotite, provide the major sink for acidity in drainage from mine waste rock (see equation 31). However, this statement has to be taken with care, as in the neutralization via biotite also Fe(II) is liberated (equation 31) and may so produce acidity via hydrolysis.

### 3.5 Dissolution

Dissolution is mainly controlled by surface complexation of protons or organic ligands such as the organic acids acetate, oxalate, or citrate. Organic acids are widely used in studies of dissolution kinetics and the solubility of secondary oxides and hydroxides, especially in soil science and acid mine drainage (Cornell & Schwertmann, 2003; Dold, 2003a). For example, the dissolution rates of Fe(III)hydroxides by oxalate are increased photochemically, by higher acidity and temperature, and by the presence of Fe(II) in the system (Suter et al., 1988). Reduction also increases dissolution kinetics because Fe(II) has a greater atomic radius (0.76 Å) than Fe(III) (0.64 Å), so Fe(II) does not fit any more in the crystalline system of the ferric minerals and the detachment of the ferrous ion is facilitated (Stumm & Sulzberger, 1992).

### 3.6 Prediction - Acid-Base Accounting (ABA)

It has been shown in the above sections that there are minerals able of producing acid (Acid Potential - AP) and those, which are able to neutralize acid (Neutralizing Potential - NP) in mine waste. Understanding the relative influence of these two parameters can lead to an estimation of the net acid-producing potential (NAPP) or net neutralizing potential (NNP). It is important to be able to predict if or if not a geological unit has the capacity of generating acid, and is a deciding factor for further treatment strategies of the material. Depending on the complexity of the mineral assemblage, it is a major task to understand all the interactions and processes taking place and to calculate the acid-base accounting (ABA). An ABA can be seen as an intent to quantify these two relevant mineral groups (Sulfides and carbonates), in order to predict if a rock-unit will or will not produce an acid environment. A review of the used static and kinetic test procedures is given in White III et al. (1999). A simple ABA would be to measure the total sulfur and total carbon contents in a sample and assume that the total sulfur value represents the pyrite content and the total carbon the calcite content. More elaborated methods try to take into account the different sulfur-bearing phases and to record the complexity of the acid-neutralizing mineral assemblage. For example sequential extraction procedures can be used as high-resolution ABA method (Dold, 2003b).

However, there remain mayor problem in the calculation of standard ABA. Most acid-base accounting procedures (ABA) assume that  $\text{H}_2\text{CO}_3$  (equation 18) is the dominant specie, resulting in a conversion factor for the acid potential (AP) of 31.25 based on the sulfur concentration. This is correct at lower pH (below pH 6.3) and doubles the buffer capacity of

calcite (equation 18). However, if the system should be buffered at neutral pH, equation 17 has to be considered, where one mol of calcite can neutralize only one mol of protons, leading to a conversion factor for the acid potential of 62.5. The factor 31.25 leads to an overestimation of 100% of the neutralization potential at neutral pH. Additionally, the standard ABA does not consider the specific mineralogy present in the sample (e.g. acid producing Fe(III) oxyhydroxide sulfates, like jarosite and schwertmannite).

### 3.7 Mobility and sorption processes

The liberation of elements from minerals depends mainly on the solubility of minerals, which act as hosts of the metals or other elements. Once the element is liberated, its mobility is controlled by the complex-species stability at the existing pH, redox and other geochemical conditions, and the surface charge of the adsorbents, which is also pH dependent. The hydroxides and clay minerals are characterized by their small grain size and high surface area combined with a net surface charge; they are therefore effective adsorbents.

#### 3.7.1 Complexation

Stumm and Morgan (1996) define complex formation as follows: Coordination or complex formation is referred to as any combination of cations with molecules or anions containing free pairs of electrons (bases). This combination can be electrostatic, covalent, or a mixture of both. The metal cation will be called the central atom, and the anions are ligands. Two types of complex species can be distinguished: the ion pairs and the complexes. Ions of opposite charge that approach within a critical distance effectively form an ion pair and are no longer electrostatically effective. In contrast, most stable entities that result from the formation of largely covalent bonds between a metal ion and an electron-donating ligand are called complexes (Parks, 1990).

#### 3.7.2 Stability of complex species

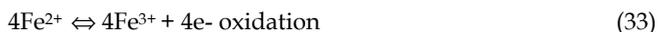
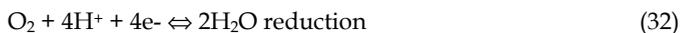
Chemical speciation and species refer to the actual form in which a molecule or ion is present in solution. If a metal cation is liberated into solution it will be on the search for a partner. As a result, metal cations will tend to form in water aquo- or hydroxo-complexes. This process is called hydrolysis and was discussed in the example of ferric hydroxide formation (3.2.1). Fig. 3 illustrates the predominant complex species of Fe(III) depending on the pH of the oxidation state of the central atom and of the solution.

Equilibrium in hydrolysis reactions is usually established fast, as the hydrolysis species are simple. The "aging" of the solution and the associated formation of polynuclear complexes is a slower process and can be seen as the intermediate state to the solid precipitate. Hence, hydrolysis species are thermodynamically unstable or meta-stable (Stumm & Morgan, 1996). Complexes with monodenate ligands are usually less stable than those with multidentate ligands. More important is the fact that the degree of complexation decreases more strongly with dilution for monodenate complexes than for multidentate complexes (chelates).

#### 3.7.3 Redox reactions

The stability of species depends strongly on the reduction-oxidation (redox) reaction taking place between the ions. In a similar way that acids and bases are interpreted as proton donors and proton acceptors, reductants and oxidants are defined as electron donors and

electron acceptors. Because there are no free electrons in nature, every oxidation is accompanied by a reduction, or in other words, an oxidant is a substance that causes oxidation to occur while being reduced itself.



The combination of redox condition (expressed as Eh or pe) and pH makes it possible to predict which species are dominant under the specific geochemical conditions. These stability fields are made visible in the Eh-pH diagrams largely used in geochemistry (e.g., Fig. 3 and (Brookins, 1988)).

### 3.7.4 Sorption

Sorption is a general name for adsorption, absorption, and ion exchange. Sorption also includes surface precipitation and element diffusion. The sorption processes take place at the mineral-water interface and are controlled by the reactivity of surface functional groups. Surface functional groups are the surface mineral atoms that may form chemical reactions with species in solution, forming mineral-species complexes.

Whether or not a mobilized element will be adsorbed depends on the redox conditions resulting from specific speciation of the metal complexes and on the pH dependent reactivity of the surface functional groups of the adsorbent. Oxides, oxyhydroxides and silicates surfaces in contact with water typically are electrically charged because of ionization of the functional groups. The magnitude and sign of this surface charge vary with the solution pH (Parks, 1990).

Adsorption and absorption processes of metal ions on iron hydroxides, clay minerals, and calcite have been well investigated in laboratory research (Dzombak & Morel, 1990). Adsorption of metal ions on Fe(III)hydroxides is a function of pH, temperature, surface area of sorbent, dissolved metal concentrations, and reaction time (Dzombak & Morel, 1990; Stumm & Morgan, 1996). Long-term studies show that metal ions may be incorporated by diffusion into the crystalline systems of secondary ferric hydroxides (Davis & Ritchie, 1986; Donnert et al., 1990). This process, where the adsorbate becomes incorporated in the crystal structure of the adsorbent, including the formation of solid solution by co-precipitation or solid-state diffusion, is referred to as absorption (Brown et al., 1995). Adsorption can be differentiated into two processes. First, the specific adsorption or chemisorption, where the sorption at the mineral-water interface may involve further reactions of some ions, results in the loss of one or more waters of hydration from the adsorbate ion and the formation of a relatively strong chemical bond between adsorbate and adsorbent (ligand exchange). The adsorbed species is referred to as an inner-sphere adsorption complex. A weaker interaction may occur between the hydrated ion and the mineral surface in which waters of hydration are retained (Fig. 5). Adsorption of this type is termed non-specific, and the adsorbed species is referred to as an outer-sphere adsorption complex (Brown et al., 1995).

The resulting adsorption is a function of the species stable at each pH and the net surface charge of the adsorbent at the relevant pH, e.g. for goethite is the "zero point of charge" (ZPC) at pH 8. In Fig. 6 adsorption of metal cations and oxyanions are shown with the net surface charge of the adsorbent, in this case goethite.

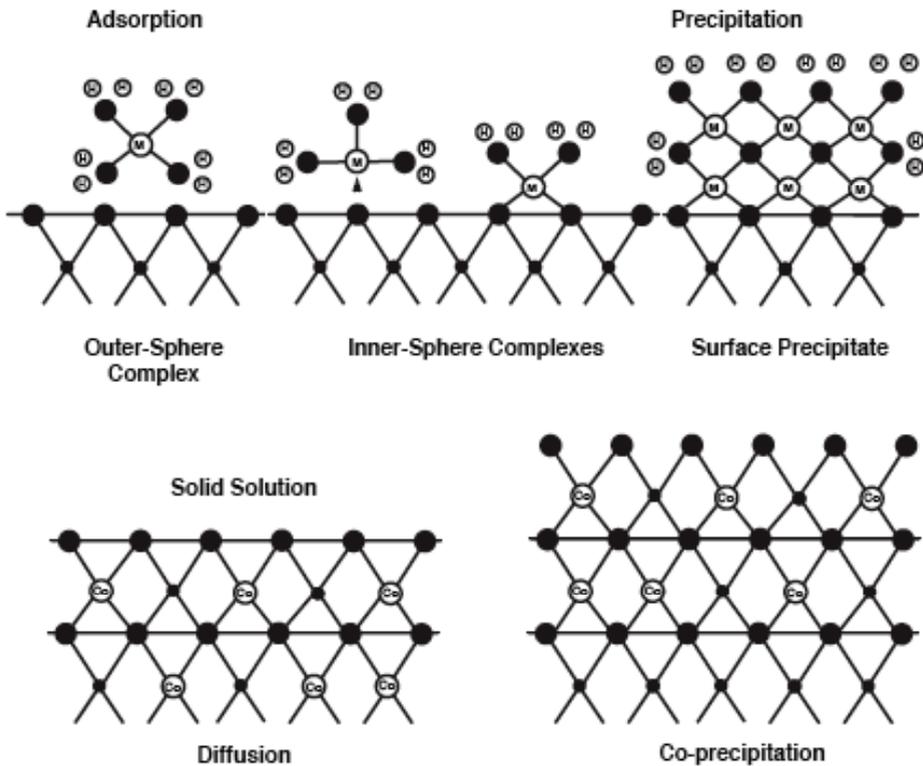


Fig. 5. Possible sorption complexes at the mineral-water interface. M represents aqueous metal ions, and H represents protons. The figures representing diffusion and co-precipitation show two possible modes of Cobalt (Co) absorption in calcite (after Brown et al., 1995).

The underlying material of the oxidation zone in mine tailings has the function of a buffer for the acid and metal bearing solution through sorption and neutralization processes. Once the adsorption and acid-neutralization capacity of the underlying tailings material is exceeded, the mobilized elements may lead to formation of highly metal-bearing acid mine drainage (AMD).

### 3.8 Microbiological activity

As mentioned before, microbiological activity acts as a catalyst for the oxidation of ferrous to ferric iron, a key process of the acid rock drainage (ARD) problem. Increasing awareness about the role of microorganism in geological processes has lead recently to a new scientific direction called geomicrobiology, e.g. (Banfield & Nealson, 1997; Ehrlich, 1996). The role of microorganisms in the formation of acid mine drainage associated to tailings impoundments and mine waste environments are increasingly a new subject of investigation (Diaby et al., 2007; Johnson & Hallberg, 2003b; Nordstrom & Southam, 1997).

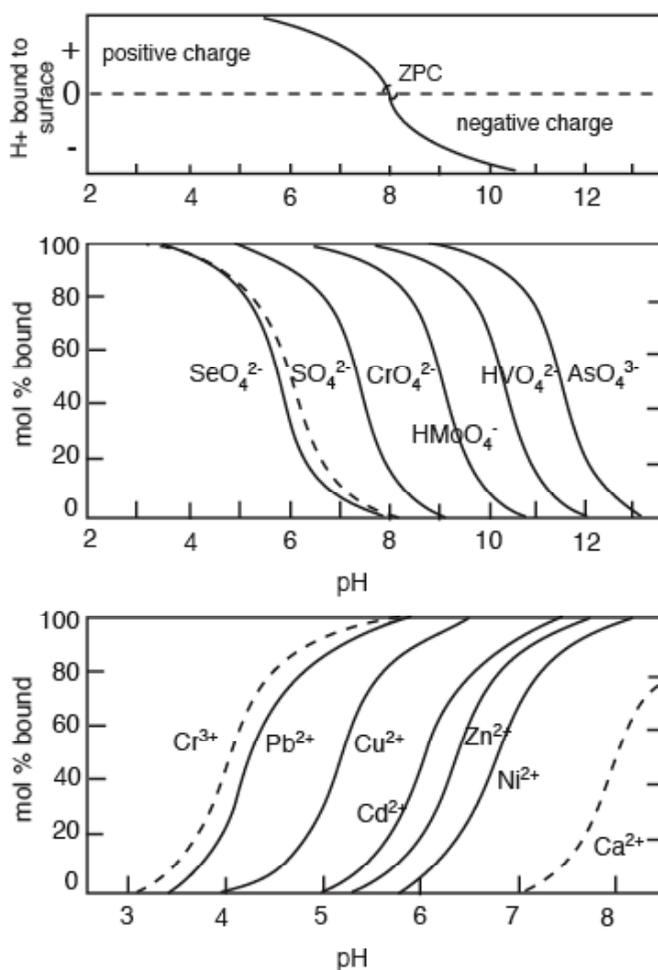


Fig. 6. Adsorption of oxyanions and bivalent cations to Fe(III)hydroxides. With decreasing pH the net surface charge becomes positive due to proton adsorption at the surface. Elements, which are stable at acidic condition as oxyanions become preferentially adsorbed. The adsorption of metals stable as cations increases with pH due to the increasing negative surface charge of the adsorbent. The dashed curves have been calculated (based on data from Dzombak and Morel, 1990; from Stumm and Morgan, 1996).

As mentioned in section 2.4.2.1, *Acidithiobacillus ferrooxidans* has been known to play a key role in sulfide oxidation for 40 years (Singer & Stumm, 1970). These acidophilic chemolithotroph and autotroph bacteria derives cellular carbon from atmospheric  $\text{CO}_2$  fixation via the Calvin cycle and obtains energy from the oxidation of Fe(II) or reduced S compounds ( $\text{H}_2\text{S}$ ,  $\text{HS}^-$ ,  $\text{S}^0$ ,  $\text{S}_2\text{O}_3^{2-}$ ,  $\text{SO}_3^-$ ). This microbe is also reported to be a facultative  $\text{H}_2$ -oxidizer and is capable of surviving under anaerobic conditions by utilizing reduced S compounds as an electron donor

and Fe(III) as an electron sink (Davis, 1997). *Acidithiobacillus ferrooxidans* is the longest known and most studied organism in acid mine drainage and mine waste environments. Nevertheless, a diverse microbial population of metal-tolerant, neutrophilic to acidophilic sulfide and sulfur-oxidizing Thiobacilli are known so far (Johnson & Hallberg, 2003b; Schippers et al., 1995). *Leptospirillum ferrooxidans* seems to be the dominant genus in some acid environments as reported from Iron Mountain, California (Edwards et al., 1998), mine tailings (Diaby et al., 2007), or leach piles (Rawlings & Johnson, 2007). Also heterotrophic bacteria, green algae, fungi, yeasts, mycoplasma, and amoebae have all been reported from acid mine waters. (Wichlacz & Unz, 1981) isolated 37 acidophilic heterotrophs from acid mine drainage. (Davis, 1997) reports the highest *Acidithiobacillus ferrooxidans* population at the oxidation front, while its heterophobic counterpart *Acidiphilum* spp. show higher population in the upper part of an aged oxidation zone of a mine tailings. (Diaby et al., 2007) have shown that in a porphyry copper tailings impoundment *Leptospirillum ferrooxidans* is the dominant specie at the oxidation front and also with the highest population. Recent data show complex communities structures in pyrite oxidation and bioleaching operation (Halinen et al., 2009; Ziegler et al., 2009). Ehrlich (1996) reported several satellite microorganisms live in close association with *Acidithiobacillus ferrooxidans*. It is nowadays recongnized that an complex ecological interactions control the biogeochemical element cycles in acid environments like the Rio Tinto River, Spain (Gonzalez-Toril et al., 2003). (Barker et al., 1998) reported the increased release of cations from biotite (Si, Fe, Al) and plagioclase (Si, Al) by up to two orders of magnitude by microbial activity compared to abiotic controls. The authors also report the formation of a low pH (3-4) microenvironment associated with microcolonies of bacteria on biotite. These results suggest that in acid rock drainage, tailings and mine waste environments, a complex microbial ecosystem exists, of which the controlling parameters and interactions are poorly understood. This knowledge is not only needed to prevent acid mine drainage and to minimize its hazardous environmental impact, but also to increase metal release in bioleaching operations for more effective metal recovery methods, important aspects for a more sustainable mining approach (Dold, 2008).

### 3.9 Conclusions

Geochemical conditions in mine waste environments change with time by the exposure of sulfide minerals to atmospheric oxygen and water. Sulfide oxidation is mainly controlled by oxygen and water flux, type of sulfide minerals, type of neutralizing minerals, and the microbial activity. The relation of acid producing processes and neutralizing processes determinates the geochemical Eh-pH conditions and so the mobility of the liberated elements. Thus, it is crucial to determinate the acid producing minerals (primary and secondary) and the acid neutralizing minerals in mine waste in order to predict future geochemical behaviour and the hazardous potential of the material.

Summarizing, it can be stated that for accurate mine waste management assessment, a combination of detailed mineralogical, geochemical, and microbiological studies has to be performed in order to understand and predict the complex geomicrobiological interactions in acid rock drainage formation.

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## **Waste Management**

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Solid Waste Management is one of the essential obligatory functions of the Urban Local Bodies/Municipal Corporation. This service is falling too short of the desired level of efficiency and satisfaction resulting in problems of health, sanitation and environmental degradation. Due to lack of serious efforts by town/city authorities, garbage and its management has become a tenacious problem. Moreover, unsafe disposal of garbage and wastewater, coupled with poor hygiene, is creating opportunities for transmission of diseases. Solutions to problems of waste management are available. However, a general lack of awareness of the impact of unattended waste on people's health and lives, and the widespread perception that the solutions are not affordable have made communities and local authorities apathetic towards the problems. The aim of this Book is to bring together experiences reported from different geographical regions and local contexts. It consolidates the experiences of the experts from different geographical locations viz., Japan, Portugal, Columbia, Greece, India, Brazil, Chile, Australia and others.

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51000 Rijeka, Croatia  
Phone: +385 (51) 770 447  
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### **InTech China**

Unit 405, Office Block, Hotel Equatorial Shanghai  
No.65, Yan An Road (West), Shanghai, 200040, China  
中国上海市延安西路65号上海国际贵都大饭店办公楼405单元  
Phone: +86-21-62489820  
Fax: +86-21-62489821

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