

## Sulfidic Mine Wastes

### 2.1 Introduction

Sulfide minerals are common minor constituents of the Earth's crust. In some geological environments, sulfides constitute a major proportion of rocks. In particular, metallic ore deposits (Cu, Pb, Zn, Au, Ni, U, Fe), phosphate ores, coal seams, oil shales, and mineral sands may contain abundant sulfides. Mining of these resources can expose the sulfides to an oxygenated environment. In fact, large volumes of sulfide minerals can be exposed in: tailings dams; waste rock dumps; coal spoil heaps; heap leach piles; run-of-mine and low-grade ore stockpiles; waste repository embankments; open pit floors and faces; underground workings; haul roads; road cuts; quarries; and other rock excavations. When the sulfides are exposed to the atmosphere or oxygenated ground water, the sulfides will oxidize to produce an acid water laden with sulfate, heavy metals and metalloids. The mineral pyrite ( $\text{FeS}_2$ ) tends to be the most common sulfide mineral present. The weathering of this mineral at mine sites causes the largest, and most testing, environmental problem facing the industry today – *acid mine drainage* (AMD).

This chapter documents the weathering processes occurring in sulfidic wastes. An understanding of the complex chemical reactions within sulfidic wastes is essential as the reactions can cause and influence AMD. Discussions of the various techniques used to predict and monitor such acid generating wastes follow. A documentation of environmental impacts of sulfidic wastes and a review of the technologies available for the control and prevention of sulfide oxidation complete the chapter.

### 2.2 Weathering of Sulfidic Mine Wastes

Sulfidic mine wastes are in most cases polymineralic aggregates. The aggregates contain, apart from sulfides, a wide range of possible minerals including silicates, oxides, hydroxides, phosphates, halides, and carbonates. Silicates are the most common gangue minerals, and the sulfides may represent ore or gangue phases. Thus, the mineralogy of sulfidic wastes and ores is highly heterogeneous and deposit specific.

When mining exposes sulfidic materials to an oxidizing environment, the materials become chemically unstable. A series of complex chemical weathering reactions are spontaneously initiated. This occurs because the mineral assemblages contained in the waste are not in equilibrium with the oxidizing environment. Weathering of the minerals proceeds with the help of atmospheric gases, meteoric water and microorganisms.

The chemical weathering of an individual mineral within a polymineralic aggregate can be classified as an acid producing (i.e. generation of  $H^+$ ), acid buffering (i.e. consumption of  $H^+$ ), or non-acid generating or consuming reaction (i.e. no generation or consumption of  $H^+$ ). For example, the degradation of pyrite is an acid producing reaction, whereas the weathering of calcite is acid buffering, and the dissolution of quartz does not consume or generate any acid. The balance of all chemical reactions, occurring within a particular waste at any time, will determine whether the material will “turn acid” and produce AMD.

## 2.3 Acid Producing Reactions

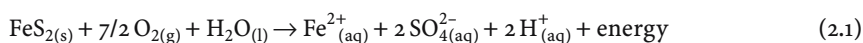
### 2.3.1 Pyrite

Sulfides are stable under strongly reducing conditions. Exposure of these minerals to oxidizing conditions will destabilize them, and the sulfides will be destroyed via various oxidation mechanisms. Pyrite is the most abundant of the sulfide minerals, occurs in nearly all types of geological environments, and is commonly associated with coal and metal ore deposits. Thus, pyrite oxidation has been studied extensively from all scientific angles, and there is a vast literature on the subject (e.g. Luther 1987; Evangelou 1995; Evangelou and Zhang 1995; Keith and Vaughan 2000). In contrast, the oxidation of other sulfides such as galena, sphalerite and chalcopyrite has received in comparison only limited attention.

Pyrite oxidation takes place when the mineral is exposed to oxygen (Rimstidt and Vaughan 2003). Oxidation which occurs in the presence of microorganisms is known as biotic. Pyrite oxidation may also occur without microorganisms as an abiotic chemical oxidation process. Biotic and abiotic degradation can be caused by oxygen (i.e. direct oxidation) or by oxygen and iron (i.e. indirect oxidation) (Evangelou and Zhang 1995). Iron, both in its divalent and trivalent state, plays a central role in the indirect oxidation of pyrite. These different pyrite oxidation mechanisms can be summarized as:

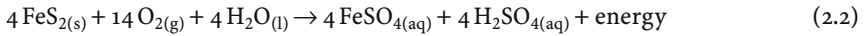
1. Oxidation by oxygen (abiotic direct oxidation)
2. Oxidation by oxygen in the presence of microorganisms (biotic direct oxidation)
3. Oxidation by oxygen and iron (abiotic indirect oxidation)
4. Oxidation by oxygen and iron in the presence of microorganisms (biotic indirect oxidation)

Stoichiometric chemical reactions are commonly used to describe these different oxidation mechanisms. In the abiotic and biotic *direct oxidation* processes (mechanisms 1 and 2), oxygen directly oxidizes pyrite:

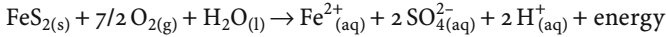


It is generally accepted, however, that pyrite oxidation is primarily accomplished by *indirect oxidation* (mechanisms 3 and 4). The indirect oxidation of pyrite involves

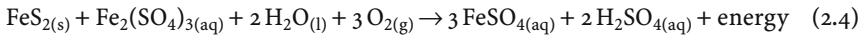
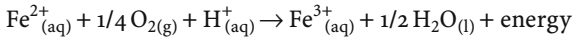
the chemical oxidation of pyrite by oxygen and ferric iron ( $\text{Fe}^{3+}$ ), which occurs in three interconnected steps. The following chemical equations show the generally accepted sequence for such indirect oxidation of pyrite:



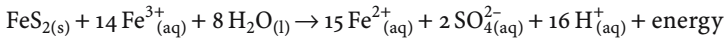
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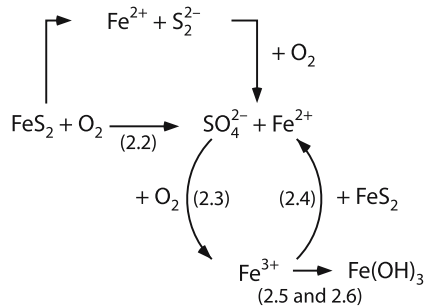


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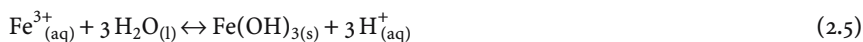
Reactions 2.2 to 2.4 release energy. Indirect pyrite oxidation is exothermic. In the initial step (Reaction 2.2), pyrite is oxidized by oxygen to produce dissolved ferrous iron ( $\text{Fe}^{2+}$ ), sulfate and hydrogen ions. The dissolved iron sulfate ions cause an increase in the total dissolved solids of the water. The release of hydrogen ions with the sulfate anions results in an acidic solution unless other reactions occur to neutralize the hydrogen ions. The second step (Reaction 2.3) represents the oxidation of ferrous iron ( $\text{Fe}^{2+}$ ) to ferric iron ( $\text{Fe}^{3+}$ ) by oxygen and occurs at a low pH. In the third reaction (Reaction 2.4) pyrite is oxidized with the help of  $\text{Fe}^{3+}$  generated in Reaction 2.3. Thus,  $\text{Fe}^{3+}$  acts as the oxidizing agent of pyrite. The oxidation of pyrite by  $\text{Fe}^{3+}$  in turn generates more  $\text{Fe}^{2+}$ . This  $\text{Fe}^{2+}$  can then be oxidized to  $\text{Fe}^{3+}$  by oxygen via Reaction 2.3. The  $\text{Fe}^{3+}$  in turn oxidizes pyrite via Reaction 2.4, which in turn produces more  $\text{Fe}^{2+}$ , and so on. Reactions 2.3 and 2.4 form a continuing cycle of  $\text{Fe}^{2+}$  conversion to  $\text{Fe}^{3+}$  and subsequent oxidation of pyrite by  $\text{Fe}^{3+}$  to produce  $\text{Fe}^{2+}$  (Fig. 2.1). This cyclic propagation of

Fig. 2.1. Simplified diagram illustrating the reaction pathways for pyrite oxidation (after Banks et al. 1997). Numbers 2.2 to 2.6 refer to Reactions 2.2 to 2.6 in the text



pyrite oxidation by  $\text{Fe}^{3+}$  continues until the supply of pyrite or  $\text{Fe}^{3+}$  to the reaction system is exhausted. While oxygen is not required for the Reaction 2.4 to occur, it is still needed to convert  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$ .

The abundance of the oxidizing agent  $\text{Fe}^{3+}$  is influenced by the pH of the weathering solution. The solubility of  $\text{Fe}^{3+}$  is very low in neutral and alkaline waters. Hence, the concentrations of  $\text{Fe}^{3+}$  are very low in these solutions, and pyrite oxidation by  $\text{Fe}^{3+}$  in neutral to alkaline waters is insignificant. Also, the concentration of dissolved  $\text{Fe}^{3+}$  decreases with increasing pH as  $\text{Fe}^{3+}$  solubility is limited by the precipitation of ferric hydroxides ( $\text{Fe}(\text{OH})_3$ ) and oxyhydroxides ( $\text{FeOOH}$ ). In other words, if the pH increases to more than approximately 3 because of partial neutralization, for example, by carbonate minerals, then the following reactions will occur:

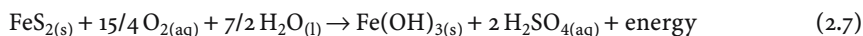


The precipitation of dissolved  $\text{Fe}^{3+}$  (Reactions 2.5, 2.6) provides significant acidity to the solution by the release of hydrogen ions into water. This reaction lowers the pH and allows more  $\text{Fe}^{3+}$  to stay in solution. The  $\text{Fe}^{3+}$  is then involved in the oxidation of pyrite (Reaction 2.4) which results in a further reduction in pH.

The chemical precipitation of iron hydroxides in Reactions 2.5 and 2.6 is termed “*hydrolysis*”. Hydrolysis is the chemical process whereby water molecules react with dissolved cations; the cations become bonded to the hydroxy group and hydrogen ions are released. Consequently, hydrolysis results in the production of hydrogen ions, thereby causing the pH to fall. As mentioned above, the hydrolysis reaction of iron is controlled by pH. Under acid conditions of less than about pH 3,  $\text{Fe}^{3+}$  remains in solution. At higher pH values, precipitation of  $\text{Fe}^{3+}$  hydroxides occurs. Such a precipitate is commonly observed as the familiar reddish-yellow to yellowish-brown stain, coating, slimy sludge, gelatinous flocculant and precipitate in AMD affected streams and seepage areas (Sec. 3.5.7).

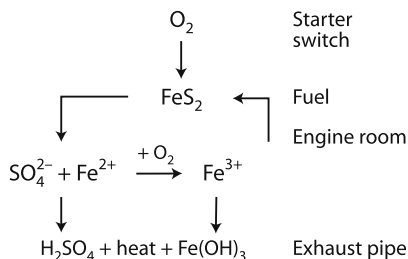
The Reactions 2.2 to 2.6 show that in the presence of molecular oxygen,  $\text{Fe}^{2+}$  and  $\text{S}^{2-}$  in pyrite are oxidized by oxygen to produce solid iron hydroxides and oxyhydroxides as well as dissolved sulfate and hydrogen ions. Clearly, oxygen and  $\text{Fe}^{3+}$  are the major oxidants of pyrite (Singer and Stumm 1970; Evangelou 1998). The oxidation of pyrite continues indefinitely unless one of the vital ingredients of pyrite oxidation is removed (i.e.  $\text{Fe}^{3+}$ , oxygen or pyrite), or the pH of the weathering solution is significantly raised.

The reaction pathways of pyrite (Reactions 2.2 to 2.6) have also been referred to as the AMD engine (Fig. 2.2). Pyrite,  $\text{Fe}^{3+}$  and oxygen represent the fuel, oxygen is also the starter engine, and  $\text{Fe}^{3+}$  hydroxides, sulfuric acid and heat come out of the exhaust pipe of the sulfidic waste. Such a simplified model of indirect oxidation of pyrite (Reactions 2.2 to 2.6) can be summarized by one overall chemical reaction:



The above reaction describes the weathering of pyrite, highlights the need for water and oxygen, and illustrates the production of acid and iron hydroxide. However,

**Fig. 2.2.** The self-sustaining, cyclic destruction of pyrite simplified as the “AMD engine”. The oxidation of pyrite is initiated through oxygen (“starter switch”). Pyrite, oxygen and iron (“fuel”) combust in the waste (“engine room”), and release  $\text{Fe}^{3+}$  hydroxides, sulfuric acid and heat into mine waters (“exhaust pipe”)



there is little consensus in the literature on the precise reaction mechanisms describing the chemical oxidation of pyrite. Also, the chemical Equations 2.2 to 2.7 are gross oversimplifications since: (a) the reactions do not explain that the  $\text{Fe}^{3+}$  hydroxides and sulfates are fictitious, idealized solid phases; (b) they do not illustrate the range of iron hydroxide, oxyhydroxide and oxyhydroxysulfate minerals formed during pyrite oxidation; (c) they do not reflect the slow oxidation of  $\text{Fe}^{2+}$  in acid waters; (d) they disregard adsorption, desorption and neutralization reactions; (e) they disregard supersaturation of waters with iron and sulfate; (f) they do not consider the precipitation of elemental sulfur ( $\text{S}^0$ ) and the formation of sulfite ( $\text{SO}_3^{2-}$ ; S: 4+), thiosulfate ( $\text{S}_2\text{O}_3^{2-}$ ; S: 2+), and polythionates ( $\text{S}_n\text{O}_6^{2-}$ ) ions; and (g) they do not describe the rate or speed (i.e. kinetics) of pyrite oxidation (Ritchie 1994b; Nordstrom and Alpers 1999a). Hence, the above reaction paths (Reactions 2.1 to 2.7) represent only approximations for actual field conditions.

How quickly pyrite weathers is influenced by its mineralogical properties and by external chemical, physical and biological factors. Mineralogical properties include the particle size, porosity, surface area, crystallography, and trace element content of pyrite. External factors are the presence of other sulfides, the presence or absence of microorganisms, as well as the oxygen and carbon dioxide concentration, temperature, pH and  $\text{Fe}^{2+}/\text{Fe}^{3+}$  ratio of the weathering solution. Therefore, the rate of pyrite oxidation (i.e. the weathering kinetics of pyrite) is influenced by the following factors:

- **Pyrite particle size, porosity and surface area.** The oxidation reactions occur on the surfaces of pyrite particles. Small particle sizes and large surface areas increase the reactivity of pyrite, and maximum oxidation of the pyrite surface occurs along pits, cracks, pores, and solid and liquid inclusions. For example, pyrite grains are exceptionally small in diameter in so-called “*framboidal pyrite*”. Framboidal pyrite refers to small-grained pyrite crystals with a grain size less than one micron. The grains are dispersed in the matrix or agglomerated to form a small spherical mass, typically several tens of micron in diameter. Such framboidal pyrite is more reactive than other pyrite morphologies – cubic pyrite crystals or coarse pyrite nodules – because of the greater surface area and porosity per volume of framboidal pyrite. Thus, pyrite oxidation is a surface controlled reaction (Evangelou 1995; Rose and Cravotta 1999).

Mining, crushing and milling of pyrite-bearing rock to fine particle sizes, for the purpose of metal extraction, vastly increase the pyrite surface area and poten-

tially expose more pyrite to oxidation and weathering. However, crushing and milling of pyritic materials do not necessarily increase the oxidation rate of pyrite in waste rock dumps. This is because coarse-grained pyritic wastes have more pore space and allow greater oxygen movement into the wastes. Consequently, acid generation in coarse-grained wastes may occur to a greater depth than in fine-grained wastes.

- *Pyrite crystallography.* Poorly crystalline pyrites or pyrites with structural defects have an imperfect or distorted crystal lattice. This leads to physical stress in the crystal structure which makes the mineral more susceptible to chemical attack (Hutchison and Ellison 1992; Rose and Cravotta 1999).
- *Trace element substitution.* Trace elements can be present in pyrite in the form of minute mineral inclusions and as chemical impurities in the crystal lattice (Table 2.1). This puts strain on the crystal structure and diminishes the sulfide's resistance to oxidation. For instance, the occurrence of arsenic in pyrite greatly decreases the resistance of pyrite to oxidation (Hutchison and Ellison 1992; Plumlee 1999).
- *Presence of other sulfides.* Sulfidic wastes commonly contain sulfides other than pyrite. If there is direct physical contact between at least two different sulfide minerals, electrons move between the sulfides and a galvanic cell is formed. During weathering the sulfide mineral with the highest electrode potential is galvanically protected from oxidation, while the mineral with the lowest electrode potential is weathered more strongly. Selective oxidation of sulfide minerals occurs as one sulfide mineral is preferentially leached over another (Evangelou and Zhang 1995; Evangelou 1995; Nordstrom and Alpers 1999a; Kwong et al. 2003; Abraitis et al. 2004). This galvanic protection process is the same as that for galvanized iron. The more electroconductive sulfide oxidizes at a slower rate than it would when not in contact with another sulfide. For example, among the three common sulfide minerals – pyrite, galena and sphalerite – pyrite has the highest electrode potential followed by galena and then sphalerite (Sato 1992). If these minerals are in contact with each other, sphalerite will be preferentially weathered and oxidation of pyrite is reduced. Hence, pyrite in direct contact with other sulfides does not react as vigorously as it does in isolation (Cruz et al. 2001a). Also, the oxidative dissolution of pyrite can be delayed, while other sulfides are preferentially oxidized (Kwong et al. 2003).
- *Temperature of the waste.* The oxidation of pyrite is exothermic and generates heat as shown by the above equations. Such elevated temperatures are also advantageous to the growth of thermophilic bacteria. These bacteria use some of the released energy for their metabolic processes. However, most of the energy is released as heat and within the physical confines of waste dumps and tailings dams, there is little dissipation of the heat due to the abundance of gangue minerals with poor heat conductivity. Thus, the pyritic waste gets warmer. Pyrite oxidation occurs faster as its oxidation rate nearly doubles with each 10 °C increase in temperature (Smith et al. 1992) (Scientific Issue 2.1).
- *Microbiological activity (bacteria, archaea, fungi, algae, yeasts, and protozoa).* AMD environments commonly contain an abundance of microorganisms. Some of these microorganisms thrive under aerobic or anaerobic conditions and favour acid or neutral pH regimes. Bacteria isolated from AMD environments are diverse and include *Acidithiobacillus thiooxidans* (previously *Thiobacillus*; Kelly and Wood 2000), *Acidithiobacillus ferrooxidans* (previously *Thiobacillus*), *Leptospirillum ferrooxidans*,

**Table 2.1.** Sulfide minerals and their chemical formula. The ability of sulfides to contain minor and trace element constituents in the form of cation substitutions is illustrated for common sulfides (after Vaughan and Craig 1978). However, some of these elements may be present as small inclusions in the host sulfides

Mineral name	Chemical formula	Minor and trace element substitution
Arsenopyrite	FeAsS	
Bornite	Cu <sub>3</sub> FeS <sub>4</sub>	
Chalcocite	Cu <sub>2</sub> S	
Chalcopyrite	CuFeS <sub>2</sub>	Ag, As, Bi, Cd, Co, Cr, In, Mn, Mo, Ni, Pb, Sb, Se, Sn, Ti, V, Zn
Cinnabar	HgS	
Cobaltite	CoAsS	
Covellite	CuS	
Cubanite	CuFe <sub>2</sub> S <sub>3</sub>	
Enargite	Cu <sub>3</sub> As <sub>4</sub>	
Galena	PbS	Ag, As, Bi, Cd, Cu, Fe, Hg, Mn, Ni, Sb, Se, Sn, Ti, Zn
Mackinawite	(Fe,Ni) <sub>9</sub> S <sub>8</sub>	
Marcasite	FeS <sub>2</sub>	As, Hg, Se, Sn, Ti, V, Pb, V
Melnikovite	Fe <sub>3</sub> S <sub>4</sub>	
Millerite	NiS	
Molybdenite	MoS <sub>2</sub>	
Orpiment	As <sub>2</sub> S <sub>3</sub>	
Pentlandite	(Ni,Fe) <sub>9</sub> S <sub>8</sub>	
Pyrite	FeS <sub>2</sub>	Ag, As, Au, Bi, Cd, Co, Ga, Ge, Hg, In, Mo, Ni, Pb, Sb, Se, Sn, Ti, V, Zn
Pyrrhotite	Fe <sub>1-x</sub> S	Ag, As, Co, Cr, Cu, Mo, Ni, Pb, Se, Sn, V, Zn
Realgar	AsS	
Stibnite	Sb <sub>2</sub> S <sub>3</sub>	
Sphalerite	ZnS	Ag, As, Ba, Cu, Cd, Co, Cr, Fe, Ga, Ge, Hg, In, Mn, Mo, Ni, Sb, Se, Sn, Ti, V
Tennantite	(Cu,Fe) <sub>12</sub> As <sub>4</sub> S <sub>13</sub>	
Tetrahedrite	(Cu,Fe) <sub>12</sub> Sb <sub>4</sub> S <sub>13</sub>	
Violarite	FeNi <sub>2</sub> S <sub>4</sub>	

and *Thiobacillus thioeparus* (e.g. Gould et al. 1994; Ledin and Pedersen 1996; Johnson 1998a,b; Schrenk et al. 1998; Blowes et al. 1998; Fowler et al. 1999; Schippers and Sand 1999; Bond et al. 2000; Gould and Kapoor 2003; Hallberg and Johnson 2005; Gleisner et al. 2006). Certain bacteria grow particularly well in pH 2 to 3 environments. These acidophilic (i.e. acid loving) bacteria participate in the conversion of Fe<sup>2+</sup> to Fe<sup>3+</sup> and the oxidation of sulfur and sulfur compounds. They utilize the oxidation of the metal component (i.e. predominantly Fe) and sulfur compounds to obtain energy for their growth. Consequently, some bacteria significantly accelerate the rate of Fe<sup>2+</sup> oxidation to Fe<sup>3+</sup>. In fact, these bacteria accelerate the rate of Fe<sup>2+</sup> oxidation, which is relatively slow under abiotic, acid (pH < 4) conditions (Reaction 2.3), by a factor of hundreds to as much as one million times (Singer and Stumm 1970). In turn, the

### Scientific Issue 2.1. Pyrite Oxidation in Permafrost Regions

#### Permafrost

Mining of sulfide ores and production of sulfidic wastes occur around the world including permafrost areas. Permafrost refers to permanently frozen rock, soil or sediment. Permafrost areas are divided into continuous and discontinuous permafrost regions whereby continuous permafrost is prevalent in the Arctic and Antarctic. Discontinuous permafrost occurs at lower latitudes where patches of permafrost alternate with unfrozen ground. In permafrost environments, the ground temperature fluctuates causing the surface layer to thaw annually. This active zone undergoes freeze-thaw cycles which promote frost wedging and frost heaving. The thickness of the active zone tends to be greater in discontinuous permafrost areas than in continuous permafrost environments. While lower plants and an organic layer may be established in the active thawing zone, an arid cold climate generally discourages the development of vegetation.

#### Pyrite oxidation at low temperatures

The rate of pyrite oxidation is influenced by the temperature of the environment and microbiological activity. Temperatures around 30 °C favour a faster oxidation rate of pyrite and the proliferation of iron and sulfur compound oxidizing bacteria. Hence, it may be suggested that simple freezing of sulfidic wastes to less than 0 °C would kill the microorganisms and slow down the oxidation reactions to negligible speeds.

However, studies have shown that sulfide oxidation and AMD generation are still prevalent in permafrost environments (MEND 1993a, 1997a). Here freeze-thaw cycles lead to the annual thawing of the upper permafrost layer. Atmospheric oxygen gas and water infiltrate into the active thawing zone and initiate oxidation of sulfidic wastes. Also, in continuous permafrost environments simple freezing of unsaturated sulfidic wastes does not stop the transport of oxygen into the waste since there are still enough pore spaces for the atmospheric oxygen to enter the waste material. In fact, the flux of oxygen into sulfidic waste is only slightly decreased (MEND 1997a). In addition, sulfide oxidizing bacteria still occur in permafrost regions and actively oxidize sulfides at an annual mean temperature of minus 15.6 °C (Elberling et al. 2000). Freezing of unsaturated sulfidic wastes to temperatures below 0 °C is not sufficient to stop sulfide oxidation. Therefore, in permafrost regions the rate of sulfide oxidation is slowed down but not necessarily reduced to negligible levels. Such changes are not significant enough to prevent AMD generation (MEND 1997a).

#### Tailings disposal in permafrost regions

Waste disposal and management practices can still take advantage of the low temperatures and permafrost conditions. Sulfidic tailings are commonly placed under water into a tailings dam. In continuous permafrost regions, the permanent freezing of water saturated tailings encapsulates the waste in ice. The ice layer acts as a surface barrier and reduces the transport of atmospheric oxygen into the waste (MEND 1997a). Furthermore, any frozen waste has a very low hydraulic conductivity which limits the ingress of water into the waste. However, a small but significant percentage of pore water remains unfrozen to about minus 5 °C or colder, particularly around smaller particles such as tailings (MEND 1993a). These pore waters are invariably saline, freeze only at temperatures well below 0 °C, and are able to participate in sulfide oxidation reactions. Also, ice scouring and the resultant disturbance of deposited tailings may allow oxygen transport into the waste causing sulfide oxidation (MEND 1997a). Thus, while the sulfide oxidation rate is reduced in frozen sulfidic wastes, permafrost cannot provide an absolute control on sulfide oxidation and AMD generation.

increased concentrations of  $\text{Fe}^{3+}$  oxidize the pyrite and accelerate acid formation. A so-called “self-perpetuating” or “autocatalytic” reaction develops whereby the bacteria serve as a reaction catalyst for  $\text{Fe}^{2+}$  oxidation (Reaction 2.3). Iron oxidizing bacteria such as *Acidithiobacillus ferrooxidans* and *Leptospirillum ferrooxidans* oxidize  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$  whereas sulfur oxidizing thiobacteria such as *Acidithiobacillus*



*thiooxidans* oxidize sulfides and other sulfur compounds. These aerobic bacteria speed up the chemical oxidation rate of  $\text{Fe}^{2+}$  and sulfur compounds when molecular oxygen is present.

Despite much research on microbiological oxidation of pyrite and especially on the role of *Acidithiobacillus ferrooxidans*, it has been argued that abiotic chemical oxidation of pyrite is more dominant than biotic oxidation and that 95% of bacteria associated with AMD are not *Acidithiobacillus ferrooxidans* (Ritchie 1994a; Morin and Hutt 1997). Indeed, it has been suggested that the microbial ecology rather than a particular individual microorganism is the catalyst of pyrite oxidation and responsible for extreme AMD conditions (Lopez-Archilla et al. 1993; Ritchie 1994a). Also, biological parameters – such as population density of the bacteria, rate of bacterial growth, and supply of nutrients – influence the growth and abundance of the acidophilic bacteria and hence, the rate of pyrite oxidation. Moreover, bacteria are ubiquitous, and the presence of a bacterial population in sulfidic wastes may only indicate a favourable environment for microbial growth (Ritchie 1994a). Thus, the exact role of individual bacteria and other microorganisms in sulfide oxidation is a controversy for some. Also, our knowledge of the microbiology of neutral mine waters is incomplete. A comprehensive understanding of microbial processes in mine waters may enable the development of technologies that may prevent sulfide oxidation and AMD formation (Hallberg and Johnson 2005).

- *Oxygen concentration in the gas and water phase.* Oxidation of pyrite may occur in the atmosphere or in water. A significant correlation exists between the oxidation rate of pyrite and the oxidation concentration of the medium in which oxidation takes place. Generally, the oxidation rate increases with higher oxygen concentrations. Oxygen is essential for the oxidation of sulfides and Ritchie (1994a) considers that the transport of oxygen to the oxidation sites is the rate limiting process in dumps and tailings deposits. If the oxidation takes place in water or in saturated pores under cover, the reactivity of pyrite is greatly affected by the concentration and rate of transport of oxygen in water. The concentration of dissolved oxygen in water is partly temperature-dependent and can vary from  $0 \text{ mg l}^{-1}$  to a maximum of  $8 \text{ mg l}^{-1}$  at  $25^\circ\text{C}$ . Such a concentration is significantly less than the oxygen concentration in the atmosphere (21 vol.% or  $286 \text{ mg l}^{-1}$  of  $\text{O}_2$  at  $25^\circ\text{C}$ ) (Langmuir 1997). As a result, the oxidation of pyrite in oxygenated water is much slower than the oxidation of pyrite in the atmosphere.

Changes in oxygen concentrations also influence the occurrence of aerobic iron and sulfur oxidizing bacteria which require oxygen for their survival. Above the water table, abundant atmospheric oxygen is available and oxidation rates are usually catalyzed by aerobic bacteria like *Acidithiobacillus ferrooxidans*. In contrast, oxidation rates in water saturated waste or below the water table are much slower because ground water generally has low dissolved oxygen concentrations and hence lacks catalyzing aerobic bacteria. In extreme cases such as flooded mine workings with no dissolved oxygen, the lack of dissolved oxygen and the absence of aerobic bacteria can reduce pyrite oxidation to negligible rates.

- *Carbon dioxide concentration in the gas and water phase.* Sulfide oxidizing anaerobic bacteria use carbon dioxide as their sole source of carbon in order to build up organic material for their maintenance and growth (Ledin and Pedersen 1996). Carbon dioxide is produced in sulfidic waste rock dumps as a result of carbonate disso-

lution and subsequent release of carbon dioxide into pore spaces. Thus, elevated concentrations of carbon dioxide in the pore space of waste rock dumps have been reported to increase the oxidation of pyrite as the heightened concentrations favour the growth of sulfide oxidizing anaerobic bacteria (Ritchie 1994a).

- *pH of the solution in contact with pyrite.* Acid conditions prevail in microscopic environments surrounding pyrite grains. However, the exact pH of a solution in contact with an oxidizing pyrite surface is unknown since current technologies are unable to measure the pH conditions at a submicroscopic level. The pH value of the solution in contact with pyrite influences the rate of pyrite oxidation. Under low to neutral pH conditions,  $\text{Fe}^{3+}$  acts as the oxidant of pyrite (i.e. indirect oxidation). The  $\text{Fe}^{3+}$  concentration is pH dependent. As a consequence, the oxidation rate of pyrite in  $\text{Fe}^{3+}$  saturated solutions is pH dependent. Significant dissolved concentrations of  $\text{Fe}^{3+}$  only occur at low pH values because the  $\text{Fe}^{3+}$  concentration in solution is controlled by the precipitation of insoluble  $\text{Fe}^{3+}$  precipitates (Reactions 2.5, 2.6). At pH values greater than 3,  $\text{Fe}^{3+}$  will precipitate and the oxidizing agent is removed from solution (Rose and Cravotta 1999; Ficklin and Mosier 1999). When the pH value falls below 3, sulfide oxidation becomes markedly faster.

Furthermore, the activity of some microorganisms is pH dependent with optimal conditions for *Acidithiobacillus ferrooxidans* and *Acidithiobacillus thiooxidans* below pH 3 (i.e. they are acidophilic), and for *Thiobacillus thioparus* in the neutral pH range (i.e. they are neutrophilic) (Blowes et al. 1998). Thus, low pH conditions favour the activity of acidophilic sulfide oxidizing bacteria. Once pyrite oxidation and acid production have begun, the low pH conditions allow the proliferation of acidophilic microorganisms which further accelerate the pyrite oxidation rate (Hallberg and Johnson). On the other hand, an increase in pH to more neutral values greatly affects the occurrence of iron oxidizing acidophilic bacteria. They do not contribute significantly to the oxidation process under neutral to alkaline conditions.

- *Abundance of water.* Some researchers consider water to be an essential factor and reactant in the oxidation of pyrite (Rose and Cravotta 1999; Evangelou and Zhang 1995); others consider water as a reaction medium (Stumm and Morgan 1995). Whatever the role of water in sulfide oxidation, water is an important transport medium, and alternate wetting and drying of sulfides accelerate the oxidation process. Oxidation products can be dissolved and removed by the wetting, leaving a fresh pyrite surface exposed for further oxidation.
- *$\text{Fe}^{2+}/\text{Fe}^{3+}$  ratio in the solution.* The most efficient oxidant for pyrite is dissolved  $\text{Fe}^{3+}$  and not oxygen, because  $\text{Fe}^{3+}$  oxidizes pyrite more rapidly than oxygen (Luther 1987). Therefore, the amount of  $\text{Fe}^{3+}$  produced (Reaction 2.3) controls how much pyrite can be destroyed (Reaction 2.4). As a result, the oxidation of  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$  by dissolved oxygen is considered to be the rate limiting step in the indirect abiotic oxidation of pyrite (Singer and Stumm 1970). The precipitation of dissolved  $\text{Fe}^{3+}$  (Reactions 2.5, 2.6) places a limit on available dissolved  $\text{Fe}^{3+}$  and on the rate of pyrite oxidation (Reaction 2.4).

The rate of pyrite oxidation (i.e. its destruction over a given time period) varies depending on the above parameters. The rapid destruction of pyrite can potentially

generate large amounts of acid and mobilize large amounts of metals and metalloids. Consequently, AMD generation and its impact on the environment can be severe. Alternatively, if the rate of pyrite oxidation is very slow, the production of acidity and dissolved contaminants occurs over an extended period of time, and AMD generation is negligible.

### 2.3.2

#### Other Sulfides

Pyrite is the dominant metal sulfide mineral in many ore deposits and as such plays a key role in the formation of AMD. However, other sulfide minerals commonly occur with pyrite, and their oxidation also influences the chemistry of mine waters. The weathering of these sulfides may occur via direct or indirect oxidation with the help of oxygen, iron and bacteria (Romano et al. 2001). The oxidation mechanisms of sulfides are analogous to those of pyrite but the reaction rates may be very different (Rimstidt et al. 1994; Domvile et al. 1994; Nicholson and Scharer 1994; Janzen et al. 2000; Keith and Vaughan 2000). Factors which influence the oxidation rate of pyrite such as trace element substitutions may or may not influence the oxidation rate of other sulfides (Jambor 1994; Janzen et al. 2000).

The weathering of various sulfides has been evaluated through laboratory experiments and field studies (Rimstidt et al. 1994; Jambor 1994; Domvile et al. 1994; Schmiermund 2000; Janzen et al. 2000; Jennings et al. 2000; Belzile et al. 2004; Yunmei et al. 2004; Lengke and Tempel 2005; Goh et al. 2006; Walker et al. 2006). The principal conclusion is that sulfide minerals differ in their acid production, reaction rate and degree of recalcitrance to weathering. Different sulfide minerals have different weathering behaviours. Pyrite, marcasite ( $\text{FeS}_2$ ), pyrrhotite ( $\text{Fe}_{1-x}\text{S}$ ) and mackinawite ( $(\text{Fe,Ni})_9\text{S}_8$ ) appear to be the most reactive sulfides and their oxidation generates low pH waters. Other sulfides such as covellite ( $\text{CuS}$ ), millerite ( $\text{NiS}$ ) and galena ( $\text{PbS}$ ) are generally far less reactive than pyrite. This is partly due to: (a) the greater stability of their crystal structure; (b) the lack of iron released; and (c) the formation of low solubility minerals such as cerussite ( $\text{PbCO}_3$ ) or anglesite ( $\text{PbSO}_4$ ), which may encapsulate sulfides like galena preventing further oxidation (Lin 1997; Plumlee 1999). In contrast, the persistence of minerals such as cinnabar ( $\text{HgS}$ ) and molybdenite ( $\text{MoS}_2$ ) in oxic environments indicates that they weather very slowly under aerobic conditions (Plumlee 1999). These sulfides are most resistant to oxidation and do not generate acidity.

The presence of iron in sulfide minerals or in waters in contact with sulfides appears to be important for sulfide oxidation. Indeed, the amount of iron sulfides present in an assemblage strongly influences whether and how much acid is generated during weathering (Plumlee 1999). Sulfidic wastes with high percentages of iron sulfides (e.g. pyrite, marcasite, pyrrhotite), or sulfides having iron as a major constituent (e.g. chalcopyrite, Fe-rich sphalerite), generate significantly more acidity than wastes with low percentages of iron sulfides or sulfides containing little iron (e.g. galena, Fe-poor sphalerite). Moreover, the release of  $\text{Fe}^{2+}$  by the oxidation of  $\text{Fe}^{2+}$ -bearing sulfides is important as  $\text{Fe}^{2+}$  may be oxidized to  $\text{Fe}^{3+}$  which in turn can be hydrolyzed generating acidity (Boon et al. 1998; Munroe et al. 1999). Hence, sulfide minerals which do not contain iron in their crystal lattice (e.g. covellite, galena or iron-poor sphalerite) do not have the capacity to generate significant amounts of acid (Plumlee 1999).

The reason is that  $\text{Fe}^{3+}$  is not available as the important oxidant. Consequently, iron hydrolysis, which would generate additional acidity, cannot occur.

The metal/sulfur ratio in sulfides influences how much sulfuric acid is liberated by oxidation. For example, pyrite and marcasite have a metal/sulfur ratio of 1:2 and are more sulfur-rich than galena and sphalerite which have a metal/sulfur ratio of 1:1. Consequently, pyrite and marcasite produce more acid per mole of mineral. Sulfide minerals commonly contain minor and trace elements as small solid and liquid inclusions, adsorbed films, or substitutions for major metal cations in the crystal lattice (Table 2.1). These elements are liberated and potentially mobilized during the breakdown of the host mineral. Therefore, major amounts of sulfate and metals, as well as trace amounts of other metals and metalloids are released from oxidizing sulfides.

The stability, reaction rate, and acid generating capacity vary greatly among sulfides. Sulfides like pyrite and pyrrhotite readily oxidize and generate acid, whereby

Table 2.2. Examples of simplified acid producing reactions in sulfidic wastes

Mineral undergoing weathering	Chemical reaction
<b>1. Complete oxidation of Fe-rich sulfides</b>	
Pyrite and marcasite	$\text{FeS}_{2(s)} + 15/4 \text{O}_{2(g)} + 7/2 \text{H}_2\text{O}_{(l)} \rightarrow \text{Fe}(\text{OH})_{3(s)} + 2 \text{SO}_4^{2-}_{(aq)} + 4 \text{H}^+_{(aq)}$
Pyrrhotite	$\text{Fe}_{0.9}\text{S}_{(s)} + 2.175 \text{O}_{2(g)} + 2.35 \text{H}_2\text{O}_{(l)} \rightarrow 0.9 \text{Fe}(\text{OH})_{3(s)} + \text{SO}_4^{2-}_{(aq)} + 2 \text{H}^+_{(aq)}$
Chalcopyrite	$\text{CuFeS}_{2(s)} + 15/4 \text{O}_{2(g)} + 7/2 \text{H}_2\text{O}_{(l)} \rightarrow \text{Fe}(\text{OH})_{3(s)} + 2 \text{SO}_4^{2-}_{(aq)} + \text{Cu}^{2+}_{(aq)} + 4 \text{H}^+_{(aq)}$
Bornite	$\text{Cu}_3\text{FeS}_4(s) + 31/4 \text{O}_{2(g)} + 7/2 \text{H}_2\text{O}_{(l)} \rightarrow \text{Fe}(\text{OH})_{3(s)} + 4 \text{SO}_4^{2-}_{(aq)} + 3 \text{Cu}^{2+}_{(aq)} + 4 \text{H}^+_{(aq)}$
Arsenopyrite	$\text{FeAsS}_{(s)} + 7/2 \text{O}_{2(g)} + 3 \text{H}_2\text{O}_{(l)} \rightarrow \text{FeAsO}_4 \cdot 2 \text{H}_2\text{O}_{(s)} + \text{SO}_4^{2-}_{(aq)} + 2 \text{H}^+_{(aq)}$
Fe-rich sphalerite	$(\text{Zn,Fe})\text{S}_{(s)} + 3 \text{O}_{2(g)} + \text{H}_2\text{O}_{(l)} \rightarrow \text{Fe}(\text{OH})_{3(s)} + \text{SO}_4^{2-}_{(aq)} + \text{Zn}^{2+}_{(aq)} + 2 \text{H}^+_{(aq)}$
<b>2. Precipitation of <math>\text{Fe}^{3+}</math> and <math>\text{Al}^{3+}</math> hydroxides</b>	
Iron hydroxides	$\text{Fe}^{3+}_{(aq)} + 3 \text{H}_2\text{O}_{(l)} \leftrightarrow \text{Fe}(\text{OH})_{3(s)} + 3 \text{H}^+_{(aq)}$
Aluminium hydroxides	$\text{Al}^{3+}_{(aq)} + 3 \text{H}_2\text{O}_{(l)} \leftrightarrow \text{Al}(\text{OH})_{3(s)} + 3 \text{H}^+_{(aq)}$
<b>3. Dissolution of secondary minerals (<math>\text{Fe}^{2+}</math>, <math>\text{Mn}^{2+}</math>, <math>\text{Fe}^{3+}</math>, and <math>\text{Al}^{3+}</math> sulfate and hydroxysulfate salts)</b>	
Halotrichite	$\text{FeAl}_2(\text{SO}_4)_4 \cdot 22 \text{H}_2\text{O}_{(s)} + 0.25 \text{O}_{2(g)} \rightarrow \text{Fe}(\text{OH})_{3(s)} + 2 \text{Al}(\text{OH})_{3(s)} + 13.5 \text{H}_2\text{O}_{(l)} + 4 \text{SO}_4^{2-}_{(aq)} + 8 \text{H}^+_{(aq)}$
Römerite	$\text{Fe}_3(\text{SO}_4)_4 \cdot 14 \text{H}_2\text{O}_{(s)} \leftrightarrow 2 \text{Fe}(\text{OH})_{3(s)} + \text{Fe}^{2+}_{(aq)} + 8 \text{H}_2\text{O}_{(l)} + 4 \text{SO}_4^{2-}_{(aq)} + 6 \text{H}^+_{(aq)}$
Coquimbite	$\text{Fe}_2(\text{SO}_4)_3 \cdot 9 \text{H}_2\text{O}_{(s)} \rightarrow 2 \text{Fe}(\text{OH})_{3(s)} + 3 \text{H}_2\text{O}_{(l)} + 3 \text{SO}_4^{2-}_{(aq)} + 6 \text{H}^+_{(aq)}$
Melanterite	$\text{FeSO}_4 \cdot 7 \text{H}_2\text{O}_{(s)} + 0.25 \text{O}_2 \rightarrow \text{Fe}(\text{OH})_{3(s)} + 4.5 \text{H}_2\text{O}_{(l)} + \text{SO}_4^{2-}_{(aq)} + 2 \text{H}^+_{(aq)}$
Jurbanite	$\text{Al}(\text{SO}_4)(\text{OH}) \cdot 5 \text{H}_2\text{O}_{(s)} \rightarrow \text{Al}(\text{OH})_{3(s)} + 3 \text{H}_2\text{O}_{(l)} + \text{SO}_4^{2-}_{(aq)} + \text{H}^+_{(aq)}$
Jarosite	$\text{KFe}_3(\text{SO}_4)_2(\text{OH})_{6(s)} + 3 \text{H}_2\text{O}_{(l)} \rightarrow \text{K}^+_{(aq)} + 3 \text{Fe}(\text{OH})_{3(s)} + 2 \text{SO}_4^{2-}_{(aq)} + 3 \text{H}^+_{(aq)}$
Alunite	$\text{KAl}_3(\text{SO}_4)_2(\text{OH})_{6(s)} + 3 \text{H}_2\text{O}_{(l)} \rightarrow \text{K}^+_{(aq)} + 3 \text{Al}(\text{OH})_{3(s)} + 2 \text{SO}_4^{2-}_{(aq)} + 3 \text{H}^+_{(aq)}$

pyrite generates more acid than pyrrhotite. Other sulfides like cinnabar oxidize very slowly and do not generate acid. Regardless of the oxidation rate and the acid generating capacity, weathering of sulfides contributes contaminants to mine waters. Even the relatively slow oxidation of arsenopyrite (FeAsS) can still release significant amounts of arsenic to mine waters (Craw et al. 1999; Yunmei et al. 2004).

### 2.3.3

#### Other Minerals

While some sulfides can produce significant amounts of acid and other sulfides do not, there are non-sulfide minerals whose weathering or precipitation will also release hydrogen ions (Plumlee 1999). Firstly, the precipitation of  $\text{Fe}^{3+}$  hydroxides and aluminium hydroxides generates acid (Table 2.2). Secondly, the dissolution of soluble  $\text{Fe}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Fe}^{3+}$  and  $\text{Al}^{3+}$  sulfate salts such as jarosite ( $\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$ ), alunite ( $\text{KAl}_3(\text{SO}_4)_2(\text{OH})_6$ ), halotrichite ( $\text{FeAl}_2(\text{SO}_4)_4 \cdot 22\text{H}_2\text{O}$ ), and coquimbite ( $\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$ ) releases hydrogen ions (Table 2.2). Soluble  $\text{Fe}^{2+}$  sulfate salts are particularly common in sulfidic wastes and a source of indirect acidity. For example, the dissolution of melanterite ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ) results in the release of  $\text{Fe}^{2+}$  which can be oxidized to  $\text{Fe}^{3+}$ . This  $\text{Fe}^{3+}$  may precipitate as ferric hydroxide ( $\text{Fe}(\text{OH})_3$ ) and generate hydrogen ions, or it may oxidize any pyrite present (Table 2.2). In general, increased hydrogen concentrations and acid production in mine wastes can be the result of:

- oxidation of Fe-rich sulfides;
- precipitation of  $\text{Fe}^{3+}$  and  $\text{Al}^{3+}$  hydroxides; and
- dissolution of soluble  $\text{Fe}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Fe}^{3+}$  and  $\text{Al}^{3+}$  sulfate salts.

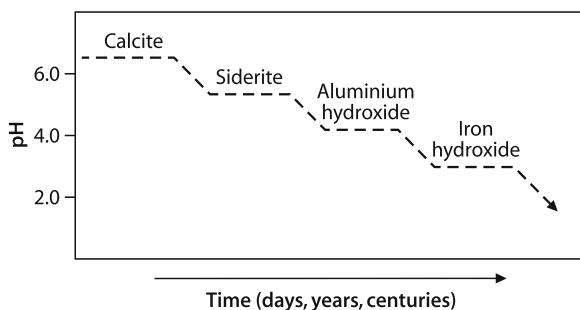
## 2.4

### Acid Buffering Reactions

The oxidation of pyrite, the precipitation of iron and aluminium hydroxides, and the dissolution of some secondary minerals release hydrogen to solution. These processes increase the solution's acidity unless the hydrogen is consumed through buffering reactions. Much of the buffering of the generated acidity is achieved through the reaction of the acid solution with rock-forming minerals in the sulfidic wastes. These gangue minerals have the capacity to buffer acid; that is, the minerals will react with and consume the hydrogen ions. Acid buffering is largely caused by the weathering of silicates, carbonates and hydroxides.

The buffering reactions occur under the same oxidizing conditions, which cause the weathering of sulfide minerals. However, unlike sulfide oxidation reactions, acid buffering reactions are independent of the oxygen concentration of the gas phase or water in which the weathering reactions take place. The individual gangue minerals dissolve at different pH values, and buffering of the solution pH by individual minerals occurs within certain pH regions (Fig. 2.3). As a consequence, depending on the type and abundance of gangue minerals within the waste (i.e. the buffering capacity of the material), not all sulfide wastes produce acidic leachates and the same environmental concerns.

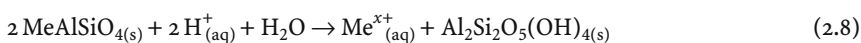
**Fig. 2.3.** Stepwise consumption of buffering capacity in a hypothetical sulfidic waste dump (Salomons 1995). (Reprinted from Salomons W (1995) Environmental impact of metals derived from mining activities: Processes, predictions, prevention. *Journal of Geochemical Exploration* 52:5–23, with permission from Elsevier Science)



### 2.4.1

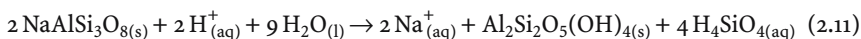
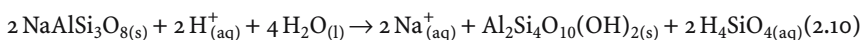
#### Silicates

The major reservoir of buffering capacity in the environment are the silicate minerals which make up the majority of the minerals in the Earth's crust. Chemical weathering of silicate minerals consumes hydrogen ions and occurs via congruent or incongruent weathering. Congruent weathering involves the complete dissolution of the silicate mineral and the production of only soluble components (Reaction 2.8). Incongruent weathering is the more common form of silicate weathering whereby the silicate mineral is altered to another phase (Reaction 2.9). The chemical composition of most silicates such as olivines, pyroxenes, amphiboles, garnets, feldspars, feldspathoids, clays and micas is restricted to a range of elements. Thus, the two types of silicate weathering can be represented by the following reactions:

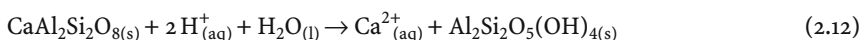


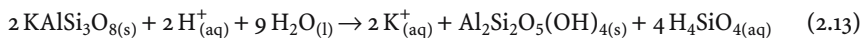
(Me = Ca, Na, K, Mg, Mn or Fe)

Chemical weathering of silicates results in the consumption of hydrogen ions, the production of dissolved cations and silicic acid, and the formation of secondary minerals (Purra and Neretnieks 2000). For example, the incongruent destruction of the sodium-rich plagioclase feldspar albite ( $\text{NaAlSi}_3\text{O}_8$ ) may produce montmorillonite (simplified as  $\text{Al}_2\text{Si}_4\text{O}_{10}(\text{OH})_2$ ) or kaolinite ( $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ ), depending on the amount of leaching:

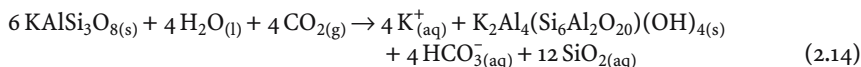


The incongruent destruction of other feldspars such as the calcium-rich plagioclase anorthite ( $\text{CaAl}_2\text{Si}_2\text{O}_8$ ), and that of orthoclase, sanidine, adularia or microcline ( $\text{KAlSi}_3\text{O}_8$ ) can be written as follows:

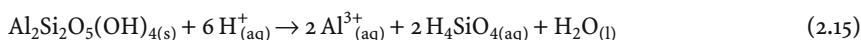




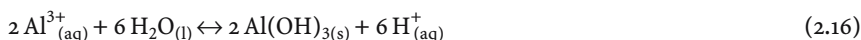
In most natural environments, the surface water contains dissolved carbon dioxide. The following reaction represents the incongruent weathering of K-feldspar under such conditions more accurately (Ollier and Pain 1997):



In the above chemical reactions (Reactions 2.10 to 2.14), plagioclase and K-feldspar consume hydrogen ions in solution or generate bicarbonate ions. In addition, the by-products of feldspar and chlorite weathering are  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ , silicic acid ( $\text{H}_4\text{SiO}_4$ ) and the clay minerals kaolinite ( $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ ), illite ( $\text{K}_2\text{Al}_4(\text{Si}_6\text{Al}_2\text{O}_{20})(\text{OH})_4$ ), or montmorillonite (simplified as  $\text{Al}_2\text{Si}_4\text{O}_{10}(\text{OH})_2$ ). The silicic acid or silica may precipitate as opaline silica or cryptocrystalline chalcedony ( $\text{SiO}_2$ ). New quartz is only rarely formed, and then it usually overgrows on pre-existing quartz grains. The clay minerals may weather further and consume hydrogen ions as they dissolve. For example, the dissolution of kaolinite can be represented by the following reaction:



If the dissolved  $\text{Al}^{3+}$  is allowed to precipitate as gibbsite ( $\text{Al}(\text{OH})_3$ ), this neutralizing mechanism is lost because an equal amount of hydrogen will be released into solution (Deutsch 1997):



On the other hand, if gibbsite already exists as a solid phase in the waste rocks, it provides additional neutralizing ability because it can consume dissolved hydrogen ions. Similarly, ferric hydroxide solids (Reaction 2.17) previously precipitated during pyrite oxidation can be redissolved in acidic waters, thereby consuming hydrogen ions:



Quartz ( $\text{SiO}_2$ ), chalcedony ( $\text{SiO}_2$ ), opal ( $\text{SiO}_2 \cdot n\text{H}_2\text{O}$ ), and other silica minerals do not consume hydrogen when they weather to form silicic acid (Reaction 2.18). Silicic acid is a very weak acid and does not contribute significant hydrogen ions to solution. The acid is unable to donate protons to a solution unless the pH is greater than 9 (Deutsch 1997).

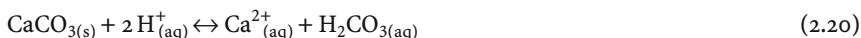


## 2.4.2

### Carbonates

Carbonate minerals play an extremely important role in acid buffering reactions. Minerals such as calcite ( $\text{CaCO}_3$ ), dolomite ( $\text{CaMg}(\text{CO}_3)_2$ ), ankerite ( $\text{Ca}(\text{Fe,Mg})(\text{CO}_3)_2$ ), or

magnesite ( $\text{MgCO}_3$ ) neutralize acid generated from sulfide oxidation. Calcite is the most important neutralizing agent, because of its common occurrence in a wide range of geological environments and its rapid rate of reaction compared to dolomite. Similarly to pyrite weathering, grain size, texture and the presence of trace elements in the crystal lattice of carbonates may increase or decrease their resistance to weathering (Plumlee 1999; Strömberg and Banwart 1999). Calcite neutralizes acid by dissolving and complexing with hydrogen ion to form bicarbonate ( $\text{HCO}_3^-$ ) and carbonic acid ( $\text{H}_2\text{CO}_3$ ) (Stumm and Morgan 1995; Blowes and Ptacek 1994; Strömberg and Banwart 1999; Al et al. 2000). Depending on the pH of the weathering solution, acidity is consumed either by the production of bicarbonate in weakly acidic to alkaline environments (Reaction 2.19) or by the production of carbonic acid in strongly acidic environments (Reaction 2.20).



Overall, the dissolution of calcite neutralizes acidity and increases pH and alkalinity in waters. A reversal of the Reactions 2.19 and 2.20 is possible when there is a change in temperature, loss of water or loss of carbon dioxide. Reprecipitation of carbonates will occur, which in turn releases hydrogen ions, causing the pH to fall.

The presence or absence of carbon dioxide strongly influences the solubility of calcite (Sherlock et al. 1995; Stumm and Morgan 1995). Calcite dissolution can occur in an open or closed system, depending on whether carbon dioxide is available for gas exchange. If water is in contact with a gas phase, then carbon dioxide can enter the solution and calcite dissolution occurs in a so-called “*open system*” (Reaction 2.21). In the open system, there is an increased solubility of calcite (Stumm and Morgan 1995). The unsaturated zones of sulfidic waste rock piles represent such open systems. In contrast, in the water saturated zone of sulfidic waste rock piles or tailings, there is no carbon dioxide gas phase. Here, calcite dissolves in a *closed system* (Reaction 2.22):



Therefore, in an open mine waste environment there is increased calcite dissolution because the calcite is exposed to a carbon dioxide gas phase. More bicarbonate is generated and more hydrogen ions are consumed than it would be the case in a closed mine waste environment (Sherlock et al. 1995).

Dissolution of other carbonates such as dolomite, ankerite or magnesite will similarly result in the consumption of hydrogen ions and in the release of bicarbonate, calcium and magnesium ions and carbonic acid. However, calcite is more easily dissolved than dolomite or ankerite. Siderite ( $\text{FeCO}_3$ ) is a common gangue mineral in coal deposits and various metal ores. The neutralizing effect of siderite depends on the redox conditions of the weathering environment. Under reducing conditions, siderite dissolves to form bicarbonate and  $\text{Fe}^{2+}$  ions. In contrast, in an open system with abundant oxygen, the dissolution of siderite has no neutralizing effect. While the gen-

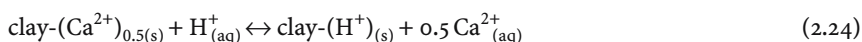


eration of bicarbonate consumes hydrogen ions, any  $\text{Fe}^{2+}$  generated will undergo hydrolysis and precipitation (Reactions 2.5, 2.6). This in turn generates as much hydrogen ions as are consumed by the generation of bicarbonate (Ptacek and Blowes 1994; Blowes and Ptacek 1994; Rose and Cravotta 1999). Hence, under well oxidized conditions, the net neutralizing effect of siderite dissolution is zero (Skousen et al. 1997).

### 2.4.3

#### Exchangeable Cations

A final neutralizing source in the subsurface are the cations ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ) present on the exchange sites of micas, clays and organic matter (Deutsch 1997; Strömberg and Banwart 1999). These exchangeable cations can be replaced by cations dissolved in weathering solutions. During sulfide oxidation, dissolved hydrogen and  $\text{Fe}^{2+}$  ions are produced which will compete for the cation exchange sites. The newly generated hydrogen and  $\text{Fe}^{2+}$  ions are removed from solution and temporarily adsorbed onto the exchange sites of the solid phases. Such reactions of clays with dissolved  $\text{Fe}^{2+}$  and hydrogen ions, respectively, can be represented as (Deutsch 1997; Rose and Cravotta 1999):



Clays may also undergo solid transformations during acid leaching whereby a potassium-bearing illite consumes hydrogen and is thereby transformed to a potassium-free smectite clay mineral (Puuru et al. 1999):



### 2.4.4

#### Reaction Rates

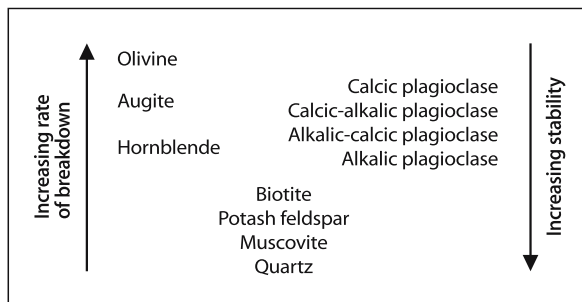
The weathering rate (i.e. weathering kinetics) of individual minerals in sulfidic wastes is influenced by: (a) the mineral's composition, crystal size, crystal shape, surface area, and crystal perfection; (b) the pH and dissolved carbon dioxide content of the weathering solution; (c) temperature; (d) redox conditions; and (e) access of weathering agent and removal of weathered products (Sherlock et al. 1995). For example, there is a large difference in weathering rates between fine-grained waste and larger waste rock particles (diameters  $>0.25$  mm). Smaller particles (diameters  $<0.25$  mm) with their larger surface areas contribute to the great majority of sulfide oxidation as well as silicate and carbonate dissolution (Strömberg and Banwart 1999).

Different minerals reacting with acidic solutions have a variable resistance to weathering (Table 2.3). Minerals such as olivine and anorthite are more reactive and less stable in the surficial environment than K-feldspar, biotite, muscovite and albite (Fig. 2.4). The rates of the different acid buffering reactions are highly variable, and the major rock-forming minerals have been classified according to their relative pH-dependent reactivity (Table 2.4). Compared with the weathering rates of even the most

**Table 2.3.** Mean lifetime of a 1 mm crystal at 25 °C and pH 5 (Lasaga and Berner 1998). (Reprinted from Lasaga AC, Berner RA (2000) Fundamental aspects of quantitative models for geochemical cycles. *Chemical Geology* 145:161–175, with permission from Elsevier Science)

Mineral	Lifetime (years)
Calcite	0.43
Wollastonite	79
Anorthite	112
Nepheline	211
Forsterite	2300
Diopside	6800
Enstatite	10 100
Gibbsite	276 000
Sanidine	291 000
Albite	575 000
Prehnite	579 000
Microcline	921 000
Epidote	923 000
Muscovite	2 600 000
Kaolinite	6 000 000
Quartz	34 000 000

**Fig. 2.4.** The stability of minerals during weathering (Sherlock et al. 1995)



reactive silicate minerals, the reaction rates of carbonates are relatively rapid, particularly that of calcite (Strömberg and Banwart 1999). Carbonates can rapidly neutralize acid. In an extreme case, calcite may even be dissolved at a faster rate than pyrite. As a consequence, drainage from a calcite-bearing waste may have a neutral pH, yet the quality of the mine drainage can eventually deteriorate and turn acid as the calcite dissolves faster than the pyrite.

Silicate minerals are abundant in sulfidic wastes, and their abundance may suggest that a waste rich in silicates has a significant buffering capacity. However, silicates do not necessarily dissolve completely, and the chemical weathering rate of silicates is very slow relative to the production rate of acid by pyrite oxidation. Therefore, rock-forming silicates do not buffer acid to a significant degree, and they only contribute token amounts of additional long-term buffering capacity to sulfidic wastes (Jambor et al. 2000). Nonetheless, silicate mineral dissolution can maintain neutral conditions if

**Table 2.4.** Grouping of minerals according to their relative reactivity at pH 5 (after Sverdrup 1990; Kwong 1993)

Mineral group	Relative reactivity at pH 5	Typical minerals
Dissolving	1.00	Calcite, aragonite, dolomite, magnesite, brucite, halite
Fast weathering	0.60	Anorthite, nepheline, olivine, garnet, jadeite, leucite, spodumene, diopside, wollastonite
Intermediate weathering	0.4	Ortho and ring silicates (epidote, zoisite), chain silicates (enstatite, hypersthene, hornblende, glaucophane, tremolite, actinolite, anthophyllite), sheet silicates (serpentine, chrysotile, chlorite, biotite, talc)
Slow weathering	0.02	Framework silicates (albite, oligoclase, labradorite), sheet silicates (vermiculite, montmorillonite, kaolinite), gibbsite
Very slow weathering	0.01	K-feldspar, muscovite
Inert	0.004	Quartz, rutile, zircon

the rate of acid production is quite slow and if abundant fine-grained, fast weathering silicates are present.

## 2.5 Coal Mine Wastes

Coal mining and processing generate the largest quantity of mine wastes (Fig. 2.5). The environmental issues related to coal wastes are attributable to the exposure of reduced earth materials (coal, sulfides, and Fe<sup>2+</sup>-bearing carbonates) to oxygen (Younger 2004). The consequences of oxidation of coal and associated strata range from the release of acid waters due to pyrite oxidation to the spontaneous combustion of the wastes.

Coals were initially deposited in reduced environments such as swamps and peat bogs. This depositional environment also resulted in the presence of fine-grained sedimentary rocks enclosing the coal seams (i.e. mudstones, sandstones). Hence, coals and their associated sediments commonly contain iron sulfides including major pyrite and possible traces of marcasite, galena, chalcopyrite and sphalerite.

Coals are readily combustible sedimentary rocks, possessing significant carbon, hydrogen and sulfur contents. The total sulfur content of coals vary, ranging from a few 0.1 wt.% to extreme examples reaching 10 wt.%. Sulfur in coal occurs in three sulfur forms, pyritic sulfur, sulfate sulfur and organic sulfur. Much of the sulfur is organically bound within solid carbonaceous materials (i.e. the coal macerals), and this form of sulfur does not contribute to the acid generation of coal wastes. Sulfate sulfur is generally the result of oxidation of pyrite in the coal and is an indicator of weathering of the coal before or after mining. Thus, it is important to determine what percentage of the total sulfur is incorporated into acid-generating pyrite. Such knowledge allows an evaluation of the acid production of coal seams and associated rock types. At coal mines, AMD is commonly brought about by the oxidation of pyrite which is finely disseminated through the coals and associated sedimentary rocks.



**Fig. 2.5.** Open cut and spoil heaps of the Moura coal mine, Australia. Spoils of the Moura coal mine are largely non-acid generating due to the lack of pyrite.

Pyrite is not the only  $\text{Fe}^{2+}$ -bearing mineral that undergoes oxidation when coal-bearing rocks are exposed to the atmosphere (Younger 2004). Carbonate minerals such as siderite ( $\text{FeCO}_3$ ) and ankerite ( $\text{Ca}(\text{Mg,Fe})(\text{CO}_3)_2$ ) are common gangue minerals of coal-bearing strata and these carbonates contain  $\text{Fe}^{2+}$ . The weathering of siderite consumes hydrogen ions as long as the released  $\text{Fe}^{2+}$  does not undergo oxidation and hydrolysis because the hydrolysis of  $\text{Fe}^{3+}$  releases hydrogen protons. Thus, siderite dissolution in an oxidizing environment has no neutralizing effect on acid waters (Sec. 2.4.2). By contrast, the dissolution of ankerite consumes more hydrogen protons than the subsequent oxidation and hydrolysis of the released iron (Younger 2004). Consequently, ankerite possesses a net neutralization potential for acid waters.

### 2.5.1 Spontaneous Combustion of Pyritic Wastes

Coal and certain base metal, uranium, iron and phosphate ore deposits are hosted by sedimentary sequences, some of which contain pyritic, carbonaceous shales and mudstones. The exothermic oxidation of sulfides and organic matter in these rock types can lead to a significant increase in temperature in pyritic, carbonaceous rocks. The elevated temperatures have the potential to cause premature detonation of explosives in a charged blasthole with catastrophic consequences (Briggs and Kelso 2003). This is particularly the case for ammonium nitrate-based explosive products.

The development of even higher temperatures may lead to the spontaneous ignition of coal and carbonaceous, pyritic shales and mudstones, which has been observed naturally (Mathews and Bustin 1984). It can also occur in underground workings, open pit faces, waste rock dumps, and slag heaps (Bullock and Bell 1997; Puura et al. 1999; Sidenko et al. 2001). It is visible as “smoke”, comprising a variety of gases such as water steam, sulfur dioxide, carbon dioxide, carbon monoxide, and methane. In particular, colliery spoil and carbonaceous, pyritic waste rock dumps have the tendency to burn and smoke.

The rocks contain abundant, often very fine-grained, micrometer sized framboidal pyrite as well as carbon and organic matter. Spontaneous combustion of this material is initiated through its exposure to atmospheric oxygen or oxygenated ground water. This leads to the slow exothermic oxidation of pyrite, carbon and organic matter which in turn results in a gradual rise in temperature of the rock. Any fine-grained rock materials will act as heat insulators, and the heat will not be able to escape. At some stage, enough heat is generated to ignite the carbon or organic matter. The oxidation reactions are significantly accelerated as soon as significant amounts of atmospheric oxygen or oxygen dissolved in water are supplied to the carbonaceous material, and large surface areas are exposed, for example, as a result of mining. Next, rapid oxidation of this hot pyritic, carbonaceous rock is initiated, and spontaneous combustion occurs. The organic carbon and sulfur begin to burn. Smoke and steam are released resembling volcanic fumaroles. The combustion of carbon and organic matter increases the heat of the rock which in turn increases the rate of sulfide oxidation. If there is sufficient oxygen during the combustion process, the pyrite is converted to hematite and sulfur oxides:



If there is not enough oxygen for complete oxidation, hydrogen sulfide is formed. In extreme cases of oxidation, temperatures reach 1200 °C and localized melting of the rocks and wastes occurs. In such cases, the outer dump layer cracks, and surface venting of gases from sulfidic materials becomes significant. The spontaneous combustion and subsequent cooling of coal spoil and pyritic waste rock dumps produce waste materials of complex mineralogical composition, including slag-type phases, thermal metamorphic minerals, and weathering related minerals (Puura et al. 1999; Sidenko et al. 2001).

If combustion has already begun in mine waste dumps, disturbing the burning heap – by excavating or reshaping it – will only provide additional atmospheric oxygen to the waste, and the rate of combustion will increase. Various methods are used to combat combustion in mine wastes, including compaction, injection of water, and water spraying (Fig. 2.6). However, compaction may eventually lead to cracking of the seal by pressurized gases. Also, the use of excessive amounts of water may generate steam and eventually cause steam explosions.

In order to prevent premature detonation of explosives or spontaneous combustion in carbonaceous, pyritic rocks, the rocks need to be characterized for their pyrite and organic carbon contents and their temperature. Such characterization should occur before or during mining. This will ensure that any high risk material will undergo special handling prior to their finite disposal. Disposal options include dumping small



**Fig. 2.6.** Water spraying of spontaneous combustion at the Blair Attoll coal mine, Australia (Photo courtesy of P. Crosdale)

heaps of wastes and leaving them to oxidize and cool prior to finite capping with benign wastes.

## 2.6

### Formation and Dissolution of Secondary Minerals

The weathering of sulfides releases sulfate, metals, metalloids and other elements into solution. This water can contact more sulfide minerals and accelerate their oxidation (i.e. acid producing reactions). Alternatively, it can contact gangue minerals, some of which react to neutralize some or all of the acid (i.e. acid buffering reactions). Above all, the reactive sulfide and gangue minerals will contribute various ionic species to the weathering solution. In fact, in many sulfidic materials the acid producing, acid buffering and non-acid generating reactions release significant amounts of dissolved cations and anions into pore waters. As a result, the waters become highly saline. Some ions will remain in solution in ionic form, where they can interact with minerals and be adsorbed. Sheet silicates such as chlorite, talc, illite and smectite are especially able to adsorb metal ions from pore solutions (Dinelli and Tateo 2001). Few ions will remain in solution indefinitely and enter ground or surface waters. Other ions will interact in the weathering solution, reach saturation levels and precipitate as secondary minerals in the waste. The formation of secondary minerals is the most common form of element fixation in pore waters of sulfidic wastes. A significant fraction of the metals released by sulfide oxidation is retained in the wastes as secondary mineral precipitates (Lin 1997; Lin and Herbert 1997). Such secondary mineral formation is not

exclusive to the wastes themselves; numerous salts approach saturation in ground waters, streams and leachates associated with the weathering of sulfidic wastes. Therefore, a wide range of secondary minerals are known to precipitate in oxidizing sulfidic wastes and AMD environments (Table 2.5). Also, the formation of secondary minerals is not exclusive to sulfidic wastes and AMD waters. It may occur in any saline water regardless of its pH.

### 2.6.1

#### Pre-Mining and Post-Mining Secondary Minerals

Secondary minerals are defined as those that form during weathering. Weathering of sulfides may occur before, during or after mining. Thus, a distinction has to be made between secondary minerals formed by natural processes prior to mining and those formed after the commencement of mining (Nordstrom and Alpers 1999a).

Sulfide oxidation prior to mining results in the formation of secondary minerals. For example, if a sulfide orebody has been exposed by erosion and weathered by surface waters descending through the unsaturated zone, a near-surface oxidized layer of secondary minerals forms (Williams 1990). Some of these secondary minerals are relatively insoluble in ground and surface waters. They effectively capture the metals and reduce the release of metals into the environment. Hence, leaching of completely oxidized wastes can produce non-acid mine waters. Nonetheless, an abundance of relatively soluble sulfates such as gypsum may still result in saline, sulfate-rich drainage waters.

Sulfide oxidation during and after mining results in the formation of secondary minerals. Post-mining secondary minerals form because waste and ore have been exposed to the atmosphere and subsequently weathered. Such post-mining oxidation products occur as cements and masses within the waste and as crusts at or near the waste's surface. The surface precipitates are commonly referred to as "*efflorescences*". They are particularly common in waste piles, underground workings, stream beds and seepage areas, and on pit faces (Figs. 2.7 and 2.8).

The distinction of pre- from post-mining secondary minerals can be a challenging task because some minerals, particularly the soluble sulfates, may have formed during the pre- and post-mining stage. The precipitation of post-mining secondary minerals takes place in response to one of these following processes (Nordstrom and Alpers 1999a):

- Oxidation and hydrolysis of the dissolved cation ( $\text{Fe}^{2+}$ )
- Hydrolysis of the dissolved cation (e.g.  $\text{Fe}^{3+}$ ,  $\text{Al}^{3+}$ )
- Reaction of acid mine waters with acid buffering minerals or alkaline waters
- Mixing of acid mine waters with neutral pH waters
- Oxidation of sulfides in humid air
- Concentration of the mine water due to evaporation

Evaporation is an important mechanism in the formation of mineral salts. This process concentrates any cations and anions in mine waters until they reach mineral saturation, forming secondary minerals. Not all precipitates are crystalline, and many solids are of a poorly crystalline or even amorphous nature. The initial minerals that

Table 2.5. Examples of post-mining secondary minerals found in sulfidic mine wastes (after Alpers et al. 1994; Nordstrom and Alpers 1999a; Jambor et al. 2000a,b; Bigham and Nordstrom 2000)

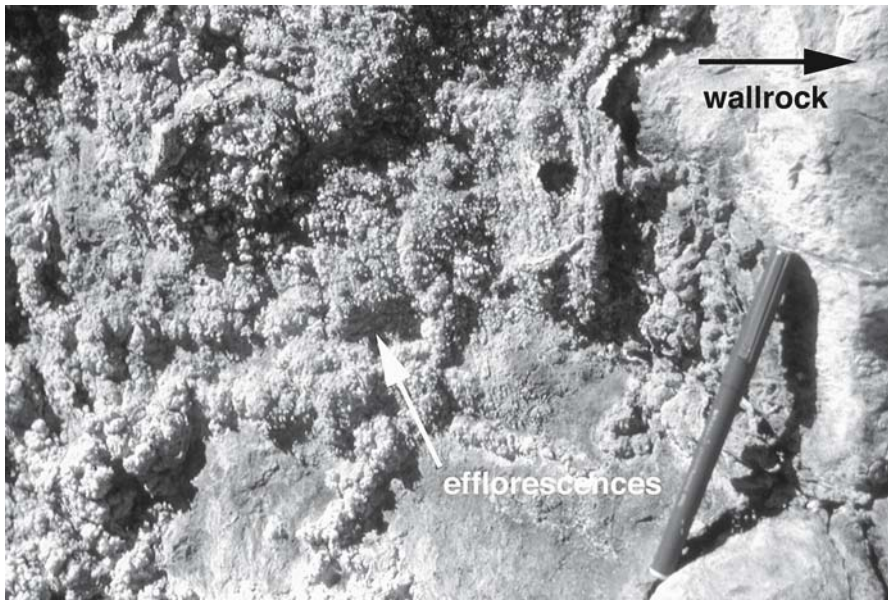
1 Sulfates		1.2 Simple hydrous metal sulfates with trivalent metal cations ( <i>continued</i> )	
1.1 Simple hydrous metal sulfates with divalent metal cations		Mineral	Formula
Mineral	Formula	Alunogen	$\text{Al}_2(\text{SO}_4)_3 \cdot 17 \text{H}_2\text{O}$
Poitevinite	$\text{CuSO}_4 \cdot \text{H}_2\text{O}$	Rhomboclase	$\text{HFe}(\text{SO}_4)_2 \cdot 4 \text{H}_2\text{O}$
Melanterite group		Butlerite	$\text{FeSO}_4(\text{OH}) \cdot 2 \text{H}_2\text{O}$
Melanterite	$\text{FeSO}_4 \cdot 7 \text{H}_2\text{O}$	1.3 Mixed divalent-trivalent hydrous metal sulfates	
Boothite	$\text{CuSO}_4 \cdot 7 \text{H}_2\text{O}$	Mineral	Formula
Bieberite	$\text{CoSO}_4 \cdot 7 \text{H}_2\text{O}$	Römerite	$\text{Fe}_3(\text{SO}_4)_4 \cdot 14 \text{H}_2\text{O}$
Mallardite	$\text{MnSO}_4 \cdot 7 \text{H}_2\text{O}$	Halotrichite group	
Epsomite group		Halotrichite	$\text{FeAl}_2(\text{SO}_4)_4 \cdot 22 \text{H}_2\text{O}$
Epsomite	$\text{MgSO}_4 \cdot 7 \text{H}_2\text{O}$	Pickeringite	$\text{MgAl}_2(\text{SO}_4)_4 \cdot 22 \text{H}_2\text{O}$
Morenosite	$\text{NiSO}_4 \cdot 7 \text{H}_2\text{O}$	Apjohnite	$\text{MnAl}_2(\text{SO}_4)_4 \cdot 22 \text{H}_2\text{O}$
Goslarite	$\text{ZnSO}_4 \cdot 7 \text{H}_2\text{O}$	Dietrichite	$(\text{Zn,Fe,Mn})\text{Al}_2(\text{SO}_4)_4 \cdot 22 \text{H}_2\text{O}$
Hexahydrate group		Bilinite	$\text{Fe}_3(\text{SO}_4)_4 \cdot 22 \text{H}_2\text{O}$
Hexahydrate	$\text{MgSO}_4 \cdot 6 \text{H}_2\text{O}$	Copiapite group	
Ferrohexahydrate	$\text{FeSO}_4 \cdot 6 \text{H}_2\text{O}$	Copiapite	$\text{Fe}_5(\text{SO}_4)_6(\text{OH})_2 \cdot 20 \text{H}_2\text{O}$
Chvaleticeite	$\text{MnSO}_4 \cdot 6 \text{H}_2\text{O}$	Ferricopiapite	$\text{Fe}_3(\text{SO}_4)_6\text{O}(\text{OH})_2 \cdot 20 \text{H}_2\text{O}$
Moorhouseite	$\text{CoSO}_4 \cdot 6 \text{H}_2\text{O}$	1.4 Fe and Al hydroxysulfates	
Bianchite	$\text{ZnSO}_4 \cdot 6 \text{H}_2\text{O}$	Mineral	Formula
Chalcanthite group		Jarosite	$\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$
Chalcanthite	$\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$	Natrojarosite	$\text{NaFe}_3(\text{SO}_4)_2(\text{OH})_6$
Pentahydrate	$\text{MgSO}_4 \cdot 5 \text{H}_2\text{O}$	Hydronium jarosite	$(\text{H}_3\text{O})\text{Fe}_3(\text{SO}_4)_2(\text{OH})_6$
Siderotil	$\text{FeSO}_4 \cdot 5 \text{H}_2\text{O}$	Plumbojarosite	$\text{PbFe}_6(\text{SO}_4)_4(\text{OH})_{12}$
Rozenite group		Alunite	$\text{KAl}_3(\text{SO}_4)_2(\text{OH})_6$
Rozenite	$\text{FeSO}_4 \cdot 4 \text{H}_2\text{O}$	Jurbanite	$\text{Al}(\text{SO}_4)(\text{OH}) \cdot 5 \text{H}_2\text{O}$
Starkeyite	$\text{MgSO}_4 \cdot 4 \text{H}_2\text{O}$	Schwertmannite	$\text{Fe}_8\text{O}_8(\text{SO}_4)(\text{OH})_6$
Boyleite	$\text{ZnSO}_4 \cdot 4 \text{H}_2\text{O}$	Aluminite	$\text{Al}_2(\text{SO}_4)(\text{OH})_4 \cdot 7 \text{H}_2\text{O}$
Kieserite group		Basaluminite	$\text{Al}_4(\text{SO}_4)(\text{OH})_{10} \cdot 4 \text{H}_2\text{O}$
Kieserite	$\text{MgSO}_4 \cdot \text{H}_2\text{O}$	1.5 Other sulfates and hydroxysulfates	
Szomolnokite	$\text{FeSO}_4 \cdot \text{H}_2\text{O}$	Mineral	Formula
Gunningite	$\text{ZnSO}_4 \cdot \text{H}_2\text{O}$	Anglesite	$\text{PbSO}_4$
1.2 Simple hydrous metal sulfates with trivalent metal cations		Barite	$\text{BaSO}_4$
Mineral	Formula	Strontianite	$\text{SrSO}_4$
Kornelite	$\text{Fe}_2(\text{SO}_4)_3 \cdot 7 \text{H}_2\text{O}$	Anhydrite	$\text{CaSO}_4$
Coquimbite	$\text{Fe}_2(\text{SO}_4)_3 \cdot 9 \text{H}_2\text{O}$	Bassanite	$\text{CaSO}_4 \cdot 0.5 \text{H}_2\text{O}$



Table 2.5. *Continued*

1.5 Other sulfates and hydroxysulfates (continued)		As minerals (continued)	
Mineral	Formula	Mineral	Formula
Gypsum	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	Arsenolite	$\text{As}_2\text{O}_3$
Thenardite	$\text{Na}_2\text{SO}_4$	Claudetite	$\text{As}_2\text{O}_3$
Aphthitalite	$\text{NaK}_3(\text{SO}_4)_2$	<b>Sb minerals</b>	
Voltaite	$\text{K}_2\text{Fe}_8\text{Al}(\text{SO}_4)_{12} \cdot 18\text{H}_2\text{O}$	Cervantite	$\text{Sb}_2\text{O}_4$
Tamarugite	$\text{NaAl}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$	Valentinite	$\text{Sb}_2\text{O}_3$
Konyaite	$\text{Na}_2\text{Mg}(\text{SO}_4)_2 \cdot 5\text{H}_2\text{O}$	Senarmontite	$\text{Sb}_2\text{O}_3$
Blödite	$\text{Na}_2\text{Mg}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$	<b>3 Carbonates</b>	
Löwite	$\text{Na}_{12}\text{Mg}_7(\text{SO}_4)_{13} \cdot 15\text{H}_2\text{O}$	Mineral	Formula
Eugsterite	$\text{Na}_4\text{Ca}(\text{SO}_4)_3 \cdot 2\text{H}_2\text{O}$	Calcite	$\text{CaCO}_3$
Syngenite	$\text{K}_2\text{Ca}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$	Magnesite	$\text{MgCO}_3$
Antlerite	$\text{Cu}_3(\text{SO}_4)(\text{OH})_4$	Siderite	$\text{FeCO}_3$
Brochantite	$\text{Cu}_4(\text{SO}_4)(\text{OH})_6 \cdot 2\text{H}_2\text{O}$	Ankerite	$\text{Ca}(\text{Fe,Mg})(\text{CO}_3)_2$
<b>2 Oxides, hydroxides and arsenates</b>		Dolomite	$\text{CaMg}(\text{CO}_3)_2$
Mineral	Formula	Smithsonite	$\text{ZnCO}_3$
<b>Fe minerals</b>		Otavite	$\text{CdCO}_3$
Goethite	$\alpha\text{-FeOOH}$	Cerussite	$\text{PbCO}_3$
Lepidocrocite	$\gamma\text{-FeOOH}$	Malachite	$\text{Cu}_2(\text{CO}_3)(\text{OH})_2$
Feroxyhyte	$\delta\text{-FeOOH}$	Azurite	$\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$
Akaganéite	$\beta\text{-FeOOH}$	Hydrozincite	$\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$
Ferrihydrite	$\text{Fe}_5\text{HO}_8 \cdot 4\text{H}_2\text{O}$	Aurichalcite	$(\text{Zn,Cu})(\text{CO}_3)_2(\text{OH})_6$
<b>Al minerals</b>		<b>4 Silicates</b>	
Gibbsite	$\gamma\text{-AlO}(\text{OH})$	Mineral	Formula
Diaspore	$\alpha\text{-AlO}(\text{OH})$	Nacrite	$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$
<b>Cu minerals</b>		Kaolinite	$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$
Tenorite	$\text{CuO}$	Chrysocolla	$\text{CuSiO}_3 \cdot 2\text{H}_2\text{O}$
Cuprite	$\text{Cu}_2\text{O}$	Plancheteite	$\text{Cu}_8\text{Si}_8\text{O}_{22} \cdot 2\text{H}_2\text{O}$
<b>As minerals</b>		Dioptase	$\text{Cu}_6\text{Si}_6\text{O}_{18} \cdot 6\text{H}_2\text{O}$
Scorodite	$\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$	<b>5 Native elements</b>	
Mansfeldite	$\text{Al}(\text{AsO}_4) \cdot 2\text{H}_2\text{O}$	Mineral	Formula
Rauenthalite	$\text{Ca}_3(\text{AsO}_4)_2 \cdot 10\text{H}_2\text{O}$	Native sulfur	S
		Native copper	Cu

precipitate tend to be poorly crystalline, metastable phases that may transform to more stable phases over time (Murad et al. 1994; Nordstrom and Alpers 1999a). Consequently, the collection and identification of metastable phases using conventional laboratory



**Fig. 2.7.** Secondary gypsum efflorescences encrusting wallrock in the Mary Kathleen open pit, Australia. Field of view 50 cm

techniques are troublesome, and materials should be collected and stored in airtight containers at temperatures resembling field conditions. By contrast, airborne and ground infrared spectrometry can be used to identify and map secondary iron minerals in the field. This approach allows the discrimination and mapping of different iron minerals in exposed outcrops, waste dumps and watersheds (Swayze et al. 2000; Dalton et al. 2000; Williams et al. 2002; Sams et al. 2003; Sams and Veloski 2003; Ackman 2003; Velasco et al. 2005). In turn, the pH value of mine drainage waters can be inferred from the colour and spectral reflectance of the precipitates because the occurrence of different iron minerals is controlled by pH as well as other parameters.

## 2.6.2

### Solubility of Secondary Minerals

Secondary minerals can be grouped into sulfates, oxides, hydroxides and arsenates, carbonates, silicates, and native elements (Table 2.5). The type of secondary minerals formed in mine wastes is primarily controlled by the composition of the waste. For example, coal spoils commonly possess iron, aluminium, calcium, magnesium, sodium, and potassium sulfates, whereas metalliferous waste rocks tend to contain abundant iron, aluminium and heavy metal sulfate salts.

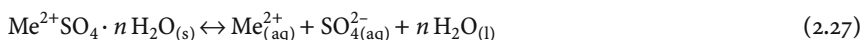
Some of the secondary minerals are susceptible to dissolution, whereby a wide range in solubility has been noted. For example, simple hydrous metal sulfates are very soluble



**Fig. 2.8.** Face of the Río Tinto smelting slag dump, Spain. Mineral efflorescences commonly occur as white sulfate salt precipitates (gypsum, epsomite, hexahydrate, bloedite, copiapite, roemerite) in protected overhangs and at seepage points at the base of the slag dump. The slags generate ephemeral drainage, which runs from the dump into the Río Tinto and contributes to its acidification and metal load

in water, whereas the iron and aluminium hydroxysulfates are relatively insoluble. In addition, there are a number of secondary sulfates and carbonates which are poorly soluble such as barite ( $\text{BaSO}_4$ ), anglesite ( $\text{PbSO}_4$ ), celestite ( $\text{SrSO}_4$ ), and cerussite ( $\text{PbCO}_3$ ). As a result, once these minerals are formed, they will effectively immobilize alkali earth elements as well as lead. The minerals act as sinks for sulfate, barium, strontium, and lead in oxidizing sulfidic wastes, and their precipitation controls the amount of sulfate, barium, strontium, and lead in AMD solutions.

The water soluble hydrous metal sulfates with divalent cations ( $\text{Me}^{2+}\text{SO}_4 \cdot n\text{H}_2\text{O}$ ) are the most dominant secondary mineral types (Jambor et al. 2000a,b). These hydrous sulfates may redissolve in water and release their ions back into solution:



(Me = Ca, Mg, Fe, Mn, Co, Ni, Cu, Zn;  $n = 1$  to 7)

Alternatively, the hydrous sulfates may dehydrate to less hydrous or even anhydrous compositions. For example, melanterite ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ) may precipitate first, which may

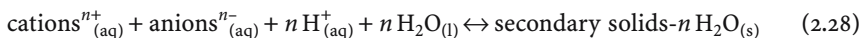
then dehydrate to rozenite ( $\text{FeSO}_4 \cdot 4 \text{H}_2\text{O}$ ) or szomolnokite ( $\text{FeSO}_4 \cdot \text{H}_2\text{O}$ ). Also, the hydrous  $\text{Fe}^{2+}$  sulfates may oxidize to  $\text{Fe}^{2+}$ - $\text{Fe}^{3+}$  or  $\text{Fe}^{3+}$  sulfate salts. For instance, the  $\text{Fe}^{2+}$  mineral melanterite ( $\text{FeSO}_4 \cdot 7 \text{H}_2\text{O}$ ) may oxidize to the mixed  $\text{Fe}^{2+}$ - $\text{Fe}^{3+}$  mineral copiapite ( $\text{Fe}_5(\text{SO}_4)_6(\text{OH})_2 \cdot 20 \text{H}_2\text{O}$ ) (Frau 2000; Jerz and Rimstidt 2003). The newly formed secondary minerals are more stable and resistant to redissolution compared to their precursors. Thus, secondary minerals may exhibit a paragenetic sequence whereby the minerals formed in a distinct order. The general trend for the simple hydrous sulfate salts is that the  $\text{Fe}^{2+}$  minerals form first, followed by the mixed  $\text{Fe}^{2+}$ - $\text{Fe}^{3+}$  minerals, and then the  $\text{Fe}^{3+}$  minerals (Jambor et al. 2000a,b).

Secondary minerals, be they relatively soluble or insoluble, possess large surface areas. Consequently, they adsorb or coprecipitate significant quantities of trace elements including metals and metalloids. The precipitates effectively immobilize elements in acid mine waters and hence provide an important natural attenuation and detoxification mechanism in mine waters (Lin 1997; Nordstrom and Alpers 1999a; Berger et al. 2000). However, this immobilization of metals is only temporary as many mineral efflorescences, particularly the simple hydrous metal sulfates, tend to be soluble and release their stored metals back into mine waters upon dissolution.

### 2.6.3

#### Acid Consumption and Production

The precipitation of some secondary minerals may influence the mine water pH as their formation generates or consumes hydrogen ions. Generally, the formation of  $\text{Fe}^{3+}$  or  $\text{Al}^{3+}$  hydroxides generates acid, whereas the precipitation of  $\text{Fe}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Fe}^{3+}$  and  $\text{Al}^{3+}$  sulfate salts such as jarosite ( $\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$ ), alunite ( $\text{KAl}_3(\text{SO}_4)_2(\text{OH})_6$ ), coquimbite ( $\text{Fe}_2(\text{SO}_4)_3 \cdot 9 \text{H}_2\text{O}$ ), jurbanite ( $\text{Al}(\text{SO}_4)(\text{OH}) \cdot 5 \text{H}_2\text{O}$ ), halotrichite ( $\text{FeAl}_2(\text{SO}_4)_4 \cdot 22 \text{H}_2\text{O}$ ), or melanterite ( $\text{FeSO}_4 \cdot 7 \text{H}_2\text{O}$ ) consumes acid. However, this consumption of acidity is only temporary as these minerals, particularly the simple hydrous metal sulfates, tend to be soluble and release their stored acidity upon dissolution (Cravotta 1994) (Table 2.2). A generalized reaction for this temporary acid consumption can be written as follows:



The precipitation and redissolution of secondary minerals in sulfidic wastes may greatly influence the acidity and chemical composition of ground, surface and pore waters (Chap. 3). As a consequence, the amounts and types of secondary salts need to be determined in sulfidic mine wastes.

### 2.6.4

#### Coatings and Hardpans

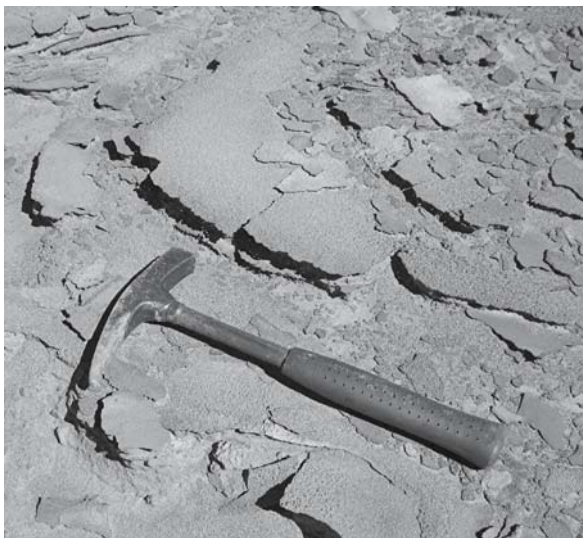
The formation of secondary minerals not only influences the mine water chemistry but also impacts on potential water-rock reactions. For example, rapid precipitation of secondary minerals – during sulfide oxidation or carbonate dissolution – may coat or even encapsulate the acid producing or buffering mineral. Such coatings will make the mineral less susceptible to continued weathering and dissolution.

Prolonged precipitation of secondary minerals may occur at the surface or at a particular depth of tailings dams and waste rock piles. Such continuous precipitation results in the formation of laterally extensive or discontinuous surface or subsurface layers (Boorman and Watson 1976; McSweeney and Madison 1988; Blowes et al. 1991; Holmström et al. 1999; McGregor and Blowes 2002; Moncour et al. 2005; Alakangas and Öhlander 2006) (Fig. 2.9). Precipitated minerals include hydroxides (e.g. goethite, ferrihydrite, lepidocrocite), sulfates (e.g. jarosite, gypsum, melanterite), or sulfides (e.g. covellite), which fill the intergranular pores and cement the waste matrices.

In waste rock piles and tailings dams, secondary minerals typically precipitate below the zone of oxidation and at the interface between oxic and anoxic layers (Fig. 2.10). A distinct vertical colour change in the waste, from reddish-brown-yellow at the top to grey below, generally indicates the transition from an oxidized layer to reduced material. If the precipitation layer dries out and cements, it forms a so-called “hardpan”. This layer acts as horizontal barrier to the vertical flow of pore waters. A hardpan may also form within the zone of oxidation at a depth where the pore water reacts with acid neutralizing carbonates. The pH of the pore water rapidly rises due to carbonate dissolution, and iron precipitates as iron hydroxides which cement the waste.

The formation of hardpans in sulfidic wastes can be induced in order to control sulfide oxidation. The addition of limestone, lime ( $\text{Ca}(\text{OH})_2$ ), magnesite ( $\text{MgCO}_3$ ), brucite ( $\text{Mg}(\text{OH})_2$ ), or other neutralizing materials, just below the surface of sulfidic waste, will help to generate artificial hardpans or so-called “chemical covers” or “chemical caps” of gypsum, jarosite and iron hydroxides (Chermak and Runnells 1996, 1997; Ettner and Braastad 1999; Shay and Cellan 2000). Regardless whether the hardpan is naturally formed or chemically induced using neutralizing materials, a hardpan protects the underlying materials from further oxidation and limits AMD generation through various processes: (a) it prevents ingress of oxygenated ground and pore water into water saturated parts of the sulfidic waste; (b) it limits the movement of atmo-

**Fig. 2.9.** Solid crusts of Fe-rich hardpans (hydrrous ferric oxide) developed on stanniferous tailings, Jumna, Australia



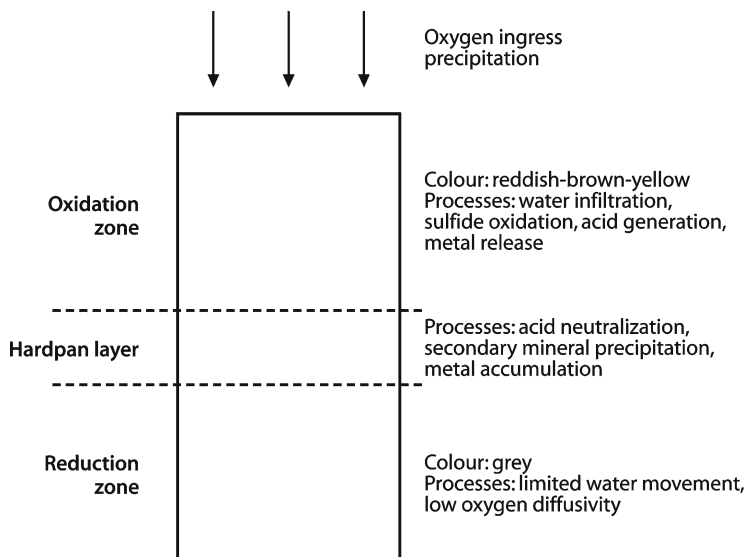


Fig. 2.10. Simplified diagram illustrating the formation of a hardpan layer in sulfidic wastes (after Jambor et al. 2000b). In this example, hardpan formation occurs at the water table between the saturated and unsaturated zone. A hardpan layer may also form within the unsaturated zone due to chemical reactions between an acidic leachate and a neutralizing layer

spheric oxygen through reactive unsaturated sulfidic wastes; (c) it reduces the waste's porosity; and (d) it accumulates heavy metals and metalloids through mineral precipitation, and adsorption and coprecipitation processes. However, elements not permanently fixed in insoluble minerals are susceptible to dissolution and mobilization back into pore waters. Such hardpans do not protect the sulfidic materials from further oxidation nor do they cause permanent sequestration of trace elements (Lottermoser and Ashley 2006).

## 2.7

### Acid Generation Prediction

AMD generation can result in surface and ground water contamination that requires expensive water treatment and involves potential liability in perpetuity. An accurate prediction of the acid producing potential of sulfidic wastes is, therefore, essential. A prediction of acid generation requires a good understanding of the physical, geological, geochemical and mineralogical characteristics of the sulfidic wastes. Data acquisition for acid generation prediction includes the completion of

- geological modeling;
- geological, geochemical, mineralogical and petrographic descriptions;
- geochemical static and kinetic tests; and
- the use of computer models for oxygen movement and geochemical processes.

### 2.7.1

#### Geological Modeling

Geological modeling is a basic technique for assessing the acid generation potential of sulfidic wastes. It involves classification of the deposit and deduction of potential acidity problems (Table 2.6). The reasoning behind this method is that ore deposits of the same type have the same ore and gangue minerals and accordingly, the same acid producing and acid buffering materials (Kwong 1993; Plumlee 1999; Seal et al. 2000). However, the method has very limited application because it assumes that factors influencing acid generation such as pyrite surface area, abundance of sulfides or waste dump characteristics are constant for the mine sites and ore deposits being compared. The comparisons are very unreliable, yet they may provide some initial insight in the overall likelihood of acid generation. The technique may be applied to stratigraphically equivalent coal mines or ore deposits in volcano-sedimentary sequences. Thus, geological modeling and classification of an ore deposit is an initial crude step in ranking the deposit in terms of its potential to produce AMD.

### 2.7.2

#### Geological, Petrographic, Geochemical and Mineralogical Descriptions

A prediction on acid generation should begin well before sulfidic wastes are produced at mine sites. Preliminary evaluations can be performed as early as the exploration drilling and early mining of an orebody. Fundamental basic data for waste characterization and acid generation prediction include: existing lithologies; structural features;

**Table 2.6.** Ranking of some ore deposit types according to their AMD potential (after Kwong 1993)

Ranking	Ore deposit type	AMD potential
1	Sedimentary exhalative massive sulfide deposits; Coal	Most AMD prone
2	Volcanogenic massive sulfide deposits	
3	Epithermal gold deposits	
4	Mesothermal gold deposits	
5	Polymetallic vein deposits	
6	Calc-alkaline porphyry copper deposits	
7	Alkalic porphyry copper deposits	
8	Orthomagmatic chromium-nickel deposits	
9	Broken Hill type lead-zinc deposits	
10	Greisen tin deposits	
11	Kimberlites and lamproite diamond deposits	
12	Mississippi Valley type lead-zinc deposits	
13	Skarn deposits	
14	Carbonatite deposits	Least AMD prone

ore and gangue textures and mineralogy; particle size distribution; depth of oxidation; and whole rock geochemistry. Geological data such as pyrite content, geochemical analyses (S, C, CO<sub>3</sub>, metals), and static test data can be used to construct a three-dimensional block model of different waste rock units prior to mining (Bennett et al. 1997).

Characterization of sulfidic waste materials involves mineralogical, mineral chemical and geochemical investigations (Lin 1997). Mineralogical observations using X-ray diffraction, optical microscopy, scanning electron microscopy, and transmission electron microscopy should note the size, shape, surface areas, degree of crystallinity, distribution, and oxidation state of sulfides, gangue minerals, and weathering products. Textural descriptions are also important as they can reveal protective encapsulation of sulfides in weathering resistant gangue minerals such as quartz.

Mineral chemical investigations using electron microprobe analyses demonstrate the abundance and siting of metals, metalloids and other elements, which may be mobilized during sulfide oxidation (Lu et al. 2005). The speciation, bioavailability and potential mobility of heavy metals in sulfidic wastes can be evaluated using partial and sequential extraction techniques (Ostergren et al. 1999; Dold 2003; Hudson-Edwards and Edwards 2005). Heavy metals may be present as cations: (a) on exchangeable sites; (b) incorporated in carbonates; (c) incorporated in easily reducible iron and manganese oxides and hydroxides; (d) incorporated in moderately reducible iron and manganese oxides and hydroxides; (e) incorporated in sulfides and organic matter; and (f) incorporated in residual silicate and oxide minerals. Thus, geological, petrographic, geochemical and mineralogical descriptions of sulfidic wastes provide important information on the nature and distribution of acid producing and acid buffering minerals, and on the mineralogical siting of metals and metalloids.

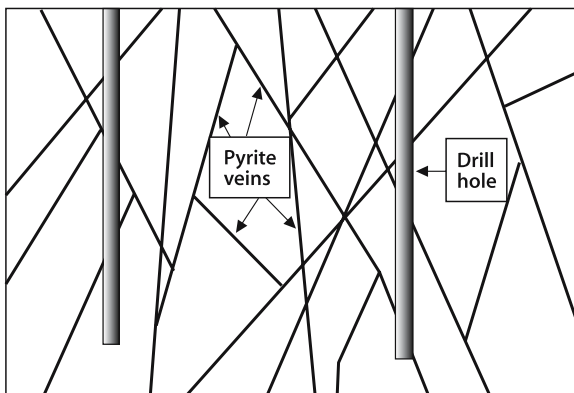
### 2.7.3 Sampling

The distribution of acid producing and acid consuming minerals is generally heterogeneous on micro- to macroscopic scales. Different ore lenses, coal seams and waste materials may represent acid producing or acid buffering units. Sulfidic wastes cannot be treated as a homogenous mass.

Waste samples can be obtained during exploration drilling and mining. However, representative sampling from drill cores is very difficult to achieve. The properties of vein deposits highlight the problems of sampling from drill cores for acid generation prediction (Dobos 2000). For example, a mesothermal gold vein deposit comprises of a rock mass, which is non-acid generating, and a series of acid generating veins with abundant pyrite (Fig. 2.11). Drilling and sampling of a composite over the entire drill section will yield a sample, largely comprising of the non-acid generating host rock. In contrast, blasting of this material will cause the rock to break along the veins, resulting in the exposure of a disproportionate amount of pyrite veins. If this mined material is dumped, it will generate more acid than the initially drilled and geochemically tested material. Therefore, geologically controlled sampling is most important in order to ensure that the analyzed samples are representative of the type and distribution of acid producing and acid buffering minerals (Dobos 2000). Otherwise, significant errors may occur when averages of static or kinetic test data are used: (a) to



**Fig. 2.11.** Schematic diagram showing a macroscopic ore texture of a mesothermal gold deposit (after Dobos 2000). Acid producing pyrite veins are hosted by non-acid producing country rocks. The traces of drill holes into the veined rock are also indicated



predict the likelihood of acid generation from a particular waste pile; or (b) to forecast the composition of seepage waters emanating from waste dumps.

Waste rock piles and coal spoil heaps of historic mining operations commonly require characterization and acid prediction. It has been suggested that the most economic sampling strategy to adequately characterize existing waste rock piles is a homogeneous composite of 15 to 30 samples (Munroe et al. 1999; Smith et al. 2000). However, sulfidic waste piles, particularly those dumped some time ago, may have developed a vertical mineralogical and chemical zonation. Sampling restricted to dump surfaces will disregard sulfidic, partly oxidized or secondary mineral enriched wastes at depth. Hence, drilling may be required to obtain sample materials representative of the entire waste dump.

#### 2.7.4 Geochemical Tests

Geochemical tests should not be conducted without detailed mineralogical and geochemical investigations of the material. Particularly, the acquisition of pure static and kinetic test data without a detailed knowledge of the mineralogical composition of the waste represents a waste by itself. Detailed procedures for various static and kinetic tests, and instructions on how to interpret them, are found in Morin and Hutt (1997) and Lapakko (2002). Laboratory methods for the geochemical analysis of environmental samples, including sulfidic wastes, are given by Crock et al. (1999).

##### 2.7.4.1 Static Tests

Static tests are geochemical analyses of sulfidic waste which are used to predict the potential of a waste sample to produce acid. Details of these tests are documented in the literature (Sobek et al. 1978; Smith et al. 1992; Morin and Hutt 1997; White et al. 1999; Mitchell 2000; Jambor 2003). Static tests are empirical procedures, and there is a confusing array of tests to measure and to document acid production and acid neutral-

ization. In addition, static tests and reporting conventions vary (North America: AP, NP, NNP, NPR; Australia and the Asia Pacific region: MPA, ANC, NAPP). Fortunately, static tests can be assigned to three major categories:

- *Saturated paste pH and electrical conductivity.* A representative crushed waste sample is saturated with distilled water to form a paste. The pH and electrical conductivity (EC) of the paste are determined after a period of equilibration (12 to 24 hours) (Morin and Hutt 1997). A pH value of less than 4 generally indicates that the sample is acid generating, and an EC value of greater than  $20 \mu\text{S cm}^{-1}$  indicates a high level of total dissolved solids in the waste's leachate. Paste pH and EC values of wastes and soils forming on waste rock dumps may change over time because sulfide minerals within the materials weather and release ions into solution and the materials are flushed by infiltration and runoff waters (Borden 2001).
- *Acid Base Accounting (ABA).* Acid Base Accounting refers to the numerical data used to predict acid generation. The three components of the ABA are: (1) determination of acid production; (2) determination of acid consumption; and (3) calculation of net acid production or consumption using the data from (1) and (2).
  1. *Determination of acid production.* The Acid Potential (AP), Acid Production Potential (APP), or Maximum Potential Acidity (MPA) tests establish the maximum amount of sulfuric acid produced from sulfidic wastes. This is measured by analyzing the sample for its sulfur content. For the MPA and APP, the weight per cent sulfur is then converted to kilograms of sulfuric acid per tonne of waste (MPA value in  $\text{kg H}_2\text{SO}_4 \text{ t}^{-1} = \text{wt.}\% \text{ S} \times 30.625$ ). For the AP, the weight per cent sulfur is converted to kilograms of calcium carbonate per tonne of waste that would be required to neutralize the acidity (AP value in  $\text{kg CaCO}_3 \text{ t}^{-1} = \text{wt.}\% \text{ S} \times 31.25$ ).
  2. *Determination of acid consumption.* The Neutralization Potential (NP), Acid Neutralizing Capacity (ANC) or Acid Consumption (AC) tests measure the amount of acid the sample can neutralize. This is determined by analyzing the acidity consumption of a sample in acid ( $\text{HCl}$  or  $\text{H}_2\text{SO}_4$ ). Consequently, the tests establish the buffering capacity of a sample due to dissolution and weathering of gangue minerals, or in other words, the ability of a sample to neutralize acid generated from sulfide oxidation. The NP and ANC are determined by adding acid to a sample, and then back titrating with hydroxide to determine the amount of acid the sample has consumed. The ANC value is reported in the form of kilograms of sulfuric acid consumption per tonne of waste ( $\text{kg H}_2\text{SO}_4 \text{ t}^{-1}$ ), whereas the NP value is given in the form of kilograms of calcium carbonate consumption per tonne of waste ( $\text{kg CaCO}_3 \text{ t}^{-1}$ ).
  3. *Calculation of net acid production or consumption.* The Net Acid Production Potential (NAPP) represents the theoretical balance of a sample's capacity to generate acid. In contrast, the Net Neutralization Potential (NNP) gives the waste's capacity to neutralize any acid generated.
    - 3.1 *NAPP calculations* are based on the net acidity of samples (i.e. kilograms of  $\text{H}_2\text{SO}_4$  per tonne of waste) (Environment Australia 1997). The NAPP is defined as being the difference between the Maximum Potential Acidity (MPA) and the Acid Neutralizing Capacity (ANC), whereby the MPA value is subtracted from the ANC value. A positive NAPP value indicates the sample should generate acid, whereas a negative value indicates the potential for acid neutralization.

$$\text{NAPP} = \text{MPA} - \text{ANC}$$

or

$$\text{NAPP (kg H}_2\text{SO}_4 \text{ t}^{-1}) = S \text{ (wt.\%)} \times 30.625 - \text{ANC (kg H}_2\text{SO}_4 \text{ t}^{-1}) \quad (2.29)$$

3.2 *NNP calculations* are based on the net neutralizing potential available in the samples (i.e. kilograms of  $\text{CaCO}_3$  per tonne of waste) (Mitchell 2000; White et al. 1999; Skousen et al. 2002). The NNP or ABA is defined as being the difference between the Acid Potential (AP) and the Neutralization Potential (NP). In theory, the NNP value is the net amount of limestone required to exactly neutralize the potential acid-forming rock.

$$\text{NNP or ABA} = \text{NP} - \text{AP}$$

or

$$\text{NNP or ABA (kg CaCO}_3 \text{ t}^{-1}) = \text{NP (kg CaCO}_3 \text{ t}^{-1}) - \text{AP (kg CaCO}_3 \text{ t}^{-1}) \quad (2.30)$$

Theoretically, rocks with positive NNP values have no potential for acidification whereas rocks with negative NNP values do. In practice, a safety factor is applied and rocks with a significant positive NNP value are generally regarded as having no acidification potential ( $>+20$  or  $+30 \text{ kg CaCO}_3 \text{ t}^{-1}$ ). Rocks with a significant negative NNP value ( $<-20$  or  $-30 \text{ kg CaCO}_3 \text{ t}^{-1}$ ) are potentially acid generating. Materials with intermediate NNP values have uncertain acid generation potentials ( $-20$  or  $-30 \text{ kg CaCO}_3 \text{ t}^{-1} < \text{NNP} < +20$  or  $+30 \text{ kg CaCO}_3 \text{ t}^{-1}$ ).

Alternatively, the ratio NP/AP, known as the *Neutralization Potential Ratio (NPR)*, or the ratio NP/MPA can be used as the criterion to evaluate the capacity of the material to generate AMD (Price et al. 1997; Skousen et al. 2002). Theoretically, a NP/AP ratio less than 1 generally implies that the sample will eventually lead to acidic conditions (Sherlock et al. 1995). A ratio greater than 1 is indicative that the sample will not produce acid upon weathering. In practice, a safety factor is applied and rocks with a NP/AP ratio greater than 2, 3 or 4 are non-acid generating, whereas samples with a NP/AP ratio less than 1 have a likely acidification potential (Price et al. 1997).

- *Net Acid Generation (NAG) or Net Acid Production (NAP)*. The NAG test directly evaluates the generation of sulfuric acid in sulfidic wastes. It is based on the principle that a strong oxidizing agent accelerates the oxidation of sulfides. The test simply involves the addition of hydrogen peroxide to a pulverized sample and the measurement of the solution pH after 24 hours, when the oxidation reaction is thought to be complete (final NAG pH). If the NAG pH is below a critical value, then the sample has the potential to generate acid in the field (Schafer 2000). Variations of the NAG test procedure include the static, sequential and kinetic NAG test (Miller 1996, 1998a). A final NAG pH greater than or equal to 4.5 classifies the sample as non-acid forming. A final NAG pH result of less than 4.5 confirms that sulfide oxidation generates an excess of acidity and classifies the material as higher risk. The NAP test is similar to the NAG test and involves the addition of hydrogen peroxide and titration of the per-

oxide-sample slurry to a neutral pH using hydroxide. The amount of acidity consumed is reported in kilograms of calcium carbonate per tonne of waste ( $\text{kg CaCO}_3 \text{ t}^{-1}$ ).

Results of NAG and NAPP tests will place a waste material into one of several categories including acid consuming (ACM), non-acid forming low sulfur (NAF-LS), non-acid forming high sulfur (NAF-HS), potentially acid forming low capacity (PAF-LC), and potentially acid forming high capacity (PAF-HC) (Table 2.7) (Miller 1996, 1998a). If a site contains PAF-HC or PAF-LC material, then kinetic test data need to be acquired, and AMD management practices have to be established (Miller 1996, 1998a). However, attention must also be given to NAF-HS and ACM material if they host soluble secondary minerals such as gypsum. Drainage from such materials may be neutral to alkaline but exceptionally saline, thereby exceeding water quality guidelines for sulfate. In addition, neutral to alkaline drainage waters may carry exceptionally high contents of metals such as zinc, molybdenum or cadmium and metalloids such as arsenic, antimony or selenium (Sec. 3.4.3).

The main advantage of these static tests is their simplicity, and most static tests can be performed at mine sites. However, the determination of the acid generating potential is not standardized. Also, the static tests are based on several assumptions and are, therefore, associated with many problems (Miller 1996; Morin and Hutt 1997; White et al. 1999; Paktunc 1999; Jambor 2000, 2003; Jambor et al. 2003; Weber et al. 2004):

- The tests use powdered or crushed samples for analysis which artificially increase the grain size and expose more mineral grains to reactions.
- Total sulfur analyses are not representative of the AP, APP or MPA because sulfur may also be present in non acid-producing sulfides or non-reactive or non acid-producing sulfates such as gypsum, anhydrite, barite or even organic material. It is possible to analyze for sulfidic sulfur contained in sulfides and for sulfate sulfur contained in secondary sulfate minerals (e.g. Yin and Catalan 2003). However, current bulk geochemical analytical techniques are not capable of distinguishing pyritic sulfur from sulfur present in acid-producing sulfates or in other sulfides that may or

**Table 2.7.** Typical classification criteria for sulfidic waste types (after Miller 1996, 1998a)

Waste type	Final NAG pH	Static NAG value [ $\text{kg H}_2\text{SO}_4 \text{ t}^{-1}$ ]	NAPP [ $\text{kg H}_2\text{SO}_4 \text{ t}^{-1}$ ]
Potentially acid forming high capacity (PAF-HC)	<4.5	>5	positive
Potentially acid forming low capacity (PAF-LC)	<4.5	$\leq 5$	positive
Non-acid forming (NAF)	$\geq 4.5$	0	negative
Acid consuming (AC)	$\geq 4.5$	0	<-100
Uncertain <sup>a</sup>	$\geq 4.5$	0	positive
Uncertain <sup>a</sup>	<4.5	>0	negative

<sup>a</sup> Samples which have conflicting NAPP and NAG results need further testing using mineralogical characterization and kinetic tests.

may not generate acid. Sulfur present in organic matter does not participate in acid generation (Casagrande et al. 1989).

- Framboidal pyrite is more reactive than euhedral forms due to the greater specific surface area (Weber et al. 2004). As a result, NAPP testing is biased by the rapid acid generating oxidation of framboidal pyrite prior to and during the ANC test.
- The possible coating of acid producing sulfides by secondary minerals is not taken into account, and it is assumed that the acid producing and acid consuming minerals will react completely.
- Organic carbon is oxidized by hydrogen peroxide during NAG testing which interferes with the acidity of the solution.
- The static tests do not allow the much slower acid buffering reactions of silicates to take place which, however, contribute only very minor amounts to the neutralization potential of sulfidic wastes (Jambor et al. 2000c).

Overall, static tests may under- or overestimate the acid production of a particular sample. As a result, numerous authors have proposed improvements and alternatives to existing static tests (e.g. Morin and Hutt 1997; Lawrence and Scheske 1997). Regardless of these modifications, static tests only predict the acid potential of individual samples and not of entire waste dumps. The tests are best used as rapid screening tools to assess the likelihood of acid generation from particular sulfidic wastes (Miller 1996, 1998a).

#### 2.7.4.2

##### *Kinetic Tests*

Kinetic tests simulate the weathering and oxidation of sulfidic waste samples. They are generally used to follow up the findings of static testing. Kinetic tests expose the sulfidic waste over time, from several months to two to three years, to moisture and air (Smith et al. 1992; Morin and Hutt 1997; Mitchell 2000; Younger et al. 2002; Lapakko 2002; Munk et al. 2006). The experiments can be accelerated to simulate long-term weathering of waste materials in a shorter time frame. Water is thereby added to the waste more frequently than it would occur under normal field conditions.

Generally, kinetic tests involve the addition of water to a known quantity of waste. Leach columns and humidity cells are the most frequently used laboratory test techniques, whereby water is dripped or trickled onto one kilogram to one tonne of sample. The acid producing and acid buffering reactions are allowed to proceed, and the leachate is periodically collected and analyzed for its composition including pH and EC as well as sulfate, metal and metalloid concentrations. Mineralogical and geochemical characterization of the sulfidic waste has to be carried out prior to and after experimentation. In laboratory kinetic tests, relatively small samples are monitored under controlled conditions, whereas field kinetic tests monitor relatively large samples under less controlled conditions in large bins or drums (Fig. 2.12).

The main advantage of these simulated weathering techniques is that they consider the weathering rates of sulfides and gangue minerals. The tests can provide an indication of the oxidation rate, lag period for the onset of acid generation, and effectiveness of blending or layering of different wastes. The tests also provide data on the load of metals, metalloids and other elements in leachates and seepage waters from waste



**Fig. 2.12.** Drums used for the kinetic testing of sulfidic mine wastes at the Misima Island gold mine, Papua New Guinea. The tubes enable meteoric water and atmospheric gases to interact with the waste, and leachate can be collected from the drum base

disposal facilities. They thereby indicate the water quality in the short and long term.

Kinetic tests are not standardized, and a great number of kinetic test designs have been developed. Any interpretation of kinetic analytical results has to scrutinize experimental design, analytical techniques and local environmental conditions. Furthermore, the interpretation of kinetic data has to consider that the data can be in great contrast to the actual field data. The reason for such discrepancies may be due to the experimental designs which hardly resemble actual waste profiles where numerous variables such as oxygen diffusion, water infiltration, microbial populations, secondary mineral formation, changes in mineralogical composition, evolution of the surface state of sulfides, and other environmental conditions control AMD generation. Hence, several authors have evaluated laboratory kinetic tests for measuring rates of weathering and have proposed improvements and alternatives to existing kinetic tests (Cruz et al. 2001b; Hollings et al. 2001; Frostad et al. 2002; Kargbo and He 2004; Benzaazoua et al. 2004).

Kinetic field trials at the mine site have distinct advantages over laboratory tests. Most importantly, the tests permit accurate replication of the local climate and selection of appropriate sample material and volume (Smith et al. 1992; Morin and Hutt 1997; Bethune et al. 1997). In particular, field-based trial dumps allow the determination of acid generation parameters under actual field conditions. Small waste piles are constructed with an appropriate liner, and piezometers and lysimeters may be installed. Leachate, run-off and pore water compositions and volumes can then be investigated.

The trials reduce the inaccuracies resulting from small test samples and allow a more realistic assessment of the AMD processes and potential.

### 2.7.5

#### Modeling the Oxidation of Sulfidic Waste Dumps

Oxygen is essential for the oxidation of sulfides in waste dumps. Simple calculations can demonstrate that the availability of oxygen controls the oxidation rate of sulfidic waste (Gibson and Ritchie 1991). For example, a 50 t sulfidic waste rock pile has a sulfur concentration of 2 wt.%. The waste dump, therefore, contains 1 t of sulfur which will require, based on the stoichiometric ratio, 1.75 t of oxygen for its oxidation to sulfate. A 50 t waste pile with a porosity of 0.3 contains approximately  $8 \times 10^{-3}$  t of oxygen, which is only 1/200 of the 1.75 t needed for complete oxidation (Gibson and Ritchie 1991). Consequently, in order to accomplish complete oxidation of the waste, oxygen must travel into the heap from the atmosphere.

Indeed, the transport of oxygen to the oxidation sites is considered the rate limiting process in dumps and tailings deposits (Ritchie 1994a–c). The gas-phase transport of oxygen in waste dumps from the surface to the oxidation sites at depth occurs by: (a) diffusion (i.e. flow of oxygen induced by a gas concentration gradient); (b) convection (i.e. flow of air induced by wind action, barometric pressure changes, or thermal convection driven by the heat generated from the exothermic pyrite reaction); and (c) advection (i.e. flow of air induced by a thermal or pressure gradient) (Ritchie 1994a–c; Rose and Cravotta 1999). Minor amounts of oxygen may also be transported into the dump via liquid-phase diffusion and advection (i.e. flow of oxygen via infiltrating precipitation).

The relative contribution of diffusion, convection or advection to overall gas transport is dependent on a variety of parameters including the position of the waste within the dump, the component materials and minerals, and the way in which the dump has been constructed. Diffuse transport of oxygen through the gas-filled pore spaces is thought to dominate in unsaturated, newly built waste dumps (Ritchie 1994b; Aachib et al. 2004; Kim and Benson 2004). Uniform diffusion into such waste materials will result in oxygen profiles with horizontally flat oxygen concentration contours. Gas convection is limited to the edges of waste dumps, and since dump edges are a small fraction of the total dump volume, convection is disregarded in the modeling of the oxidation rate of pyritic waste dumps (Ritchie 1994b). However, convective gas flux has been reported from newly constructed waste dumps (Cathles 1994). In addition, localized convections have been observed in aged waste dumps, as indicated by high oxygen concentrations at depth and complex oxygen concentration profiles. The advective and convective modes of oxygen transport appear to predominate in porous waste dumps containing abundant coarse-grained rock fragments (Rose and Cravotta 1999). The diffuse mode of oxygen transport predominates in less permeable waste materials composed of small fragments.

The reactivity of a sulfidic waste pile and its oxidation behaviour in the long term can be described using the intrinsic oxidation rate (Ritchie 1994a–c). The intrinsic oxidation rate is calculated through a series of mathematical equations. These equations quantify the physical mechanisms which control the oxidation of a pyritic waste heap. For instance, the oxygen consumption rate represents the rate at which oxygen

is consumed by the dump material (in units of kilograms of oxygen per cubic meter of waste per second;  $\text{kg}^{-1} \text{m}^{-3} \text{s}^{-1}$  or  $\text{mol kg}^{-1} \text{s}^{-1}$ ). The term quantifies the loss of oxygen from the pore space by oxidation reactions in the waste. A typical oxygen consumption rate value calculated for waste rock dumps is in the order of  $10^{-8}$  to  $10^{-11} \text{kg}^{-1} \text{m}^{-3} \text{s}^{-1}$  (Bennett et al. 1994; Ritchie 1995; Hollings et al. 2001). In this model, it is assumed that oxygen is only consumed by pyrite. However, oxygen may also be consumed by the oxidation of other sulfides, native elements and organic matter. Furthermore, the sulfide oxidation rate is dependent on a large number of variables including temperature, pH,  $\text{Fe}^{3+}$  concentration, particle size distribution, mineral surface area, bacterial population, trace element substitution, degree of pyrite crystallinity and so forth. Finally, sulfide oxidation rates within a single dump appear to be variable; a dump may contain pockets of more highly oxidizing materials, particularly toward the dump edges (Linklater et al. 2005). Thus, these weathering models will need further refinement.

## 2.8 Monitoring Sulfidic Wastes

The recognition of sulfide oxidation does not necessarily require sophisticated equipment and measurements. In fact, some of the common indicators of sulfide oxidation can be recognized in the field:

- Abundant yellow to red staining on rocks and flocculants in seepage points, streams and ponds due to the formation of secondary iron minerals and colloids
- Sulfurous odours
- Unsuccessful colonization of waste materials by vegetation
- Abundant mineral efflorescences within and on exposed waste materials
- Increasing magnetic susceptibility due to the abundance of magnetic secondary iron oxides and carbonates
- Increasing waste temperature due to exothermic pyrite oxidation
- Decreasing oxygen concentration in pore gases due to oxygen consumption; and most importantly
- Decreasing pH, increasing EC, and increasing sulfate, metal (Cu, Zn etc) and major cation (Na, K, Ca, Mg) concentrations in drainage waters with time (Miller 1995)

The latter three indicators of sulfide oxidation are used to monitor sulfidic wastes. Sulfidic waste rock dumps, tailings dams and heap leach piles need monitoring in order to detect at the earliest point in time whether the waste material will “turn acid” and generate AMD. Also, rehabilitated waste repositories need monitoring to establish the effectiveness of the control technique used to curtail sulfide oxidation. The monitoring techniques are designed to identify the early presence of, or the changes to, any products of the acid producing reactions in sulfidic wastes. The products of the acid producing reactions are usually quantified by one or more of the following parameters (Hutchison and Ellison 1992):

- Water analyses of dissolved contaminant concentrations and loads (Sec. 3.8)
- *Temperature profiles.* Pyrite oxidation is an exothermic reaction, and the effects of heat generation can be assessed by remote or in situ sensing. Remote sensing using



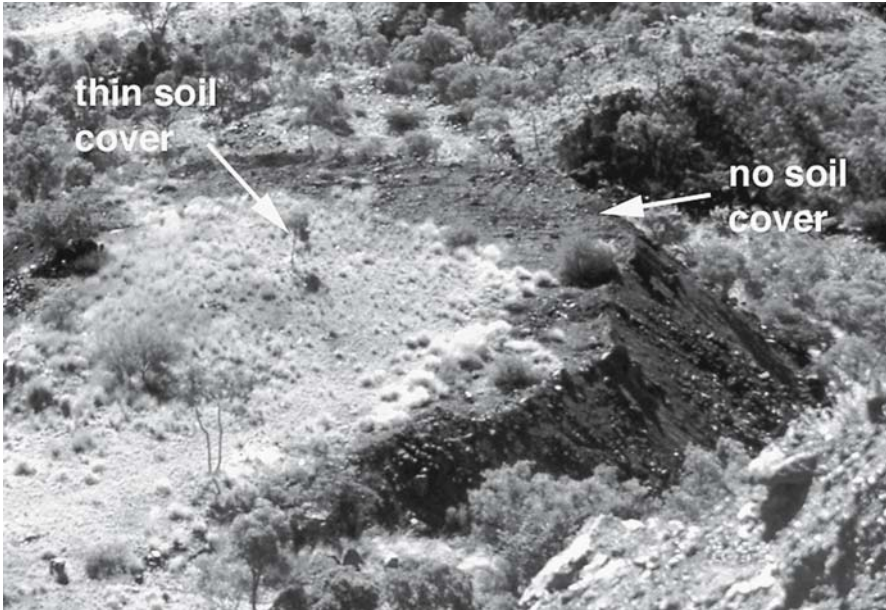
thermal infrared spectrometry is best suited for identifying zones of high acid generation of exposed sulfidic materials such as open pits (Hutchison and Ellison 1992). However, remote sensing or airborne geophysical techniques are not appropriate for detecting the onset of acid generating conditions in covered or piled sulfidic wastes. In situ temperature sensing is used to detect temperatures and temperature gradients in sulfidic waste rock piles or tailings. Temperature sensitive electrical probes (thermistors) or thermocouples are placed into a series and lowered down installed PVC pipes. Rapid increases in temperature profiles are symptomatic of the exothermic oxidation reactions of pyrite.

- *Oxygen concentration within gas pores.* Sulfide oxidation reactions in the unsaturated zone of sulfidic waste piles and tailings are oxygen consuming. Hence, the depletion of oxygen within the gas phase can be indicative of sulfide oxidation, and a knowledge of pore gas compositions will allow an evaluation of sulfide oxidation reactions within the waste pile. First, pore gas sampling using appropriately constructed probe holes is performed (Lundgren 2001). Next, oxygen analyzers determine the oxygen concentration and finally, oxygen concentration profiles are acquired. Oxygen is generally supplied to the interior of a fine-grained waste rock pile by diffusion, which is induced by concentration differential from the atmosphere. The concentration profile within such a pile will show decreasing oxygen with increasing depth below the surface. Under these conditions, active oxidation zones associated with acid generation can be detected as they result in sharp oxygen partial pressure gradients.

## 2.9 Environmental Impacts

The visible environmental impacts of sulfidic waste dumps and spoil heaps include waste erosion and a depauperate or even absent flora. For example, the surface of coal spoil heaps with their inherent salt content, sodicity of the waste and pronounced salt crust commonly does not support any vegetation (Bullock and Bell 1997). The sparse or non-existent vegetation is also caused by a lack of soil nutrients (N, P) and organic matter, as well as the potentially high salinity and acidity and high metal content in the surface layers of metalliferous wastes (Fig. 2.13). The lack of vegetation on sulfidic wastes increases erosion rates. The erosion processes exacerbate the “moonscape appearance” of these wastes and increase the areas affected by waste particles. Reactive and unreactive waste particles are transported into soils and streams and may affect areas many kilometers downstream of the mine site (Pirrie et al. 1997; Hudson-Edwards et al. 1999; Loredó et al. 1999; Cidu and Fanfani 2002) (Case Study 2.1; Scientific Issue 2.2). The area impacted by mine wastes is then no longer confined to the immediate environments of the waste.

If no rehabilitation of waste dumps occurs, it may be several decades before slow natural revegetation of adapted local flora will eventuate, with grasses often appearing to have a pioneer function in such successions (Ashley and Lottermoser 1999a). The voluntary colonization of sulfidic wastes by native vegetation is inhibited by the harsh chemical and physical conditions in the substrate (Bordon and Black 2005). Bioaccumulation of metals and metalloids may occur in plants growing on metal and metalloid enriched substrates. Grazing animals may consume such contaminated grasses and soils (Ashley and Lottermoser 1999b; Loredó et al. 1999). This may lead to



**Fig. 2.13.** Partly revegetated sulfidic waste rock dump. A thin soil layer placed on the sulfidic waste has encouraged natural revegetation. In contrast, vegetation did not develop on that part of the dump without a soil cover

potential health problems for humans from the long-term exposure to contaminants in locally farmed food products. Bioaccumulation of metals and metalloids can be pronounced in certain plant species. Such plants are genetically tolerant to metal-rich substrates and have various strategies to cope with the high metal concentrations in these environments. The strategies include the preferential accumulation of heavy metals and metalloids in the plant tissue. Plants with particular capabilities to accumulate large amounts of metals in their tissue are referred to as “hyperaccumulators”. They may be of possible use in the extraction of metals from low-grade ores and wastes (Scientific Issue 4.1; Sec. 4.8).

## 2.10 Control of Sulfide Oxidation

Uncontrolled sulfide oxidation can lead to the generation of AMD. In order to prevent sulfide oxidation and the generation of AMD, appropriate control strategies are needed. Strategies for the control of sulfide oxidation require the exclusion of one or more of the factors that cause and accompany oxidation, that is, sulfide minerals, bacteria, water, iron and oxygen. The aim of these methods is to reduce the interaction between the waste and the other reactants. Established control strategies include barriers (i.e. wet and dry covers), selective handling and isolation, co-disposal and blending with other materials, addition of organic wastes, and bacterial inhibition (Environment Austra-

lia 1997; Miller 1998b; Evangelou 1998; SMME 1998; Parker 1999; Brown et al. 2002). More technologically advanced and innovative strategies involve induced hardpan formation, grouting or mineral surface treatments (Scientific Issue 2.3, Fig. 2.14). Both established and innovative sulfide oxidation control strategies are generally designed to induce one or more of the following:

- Exclusion of water
- Exclusion of oxygen
- pH control
- Control of  $\text{Fe}^{3+}$  generation
- Control of bacterial action
- Removal and/or isolation of sulfides

No single technology is appropriate to all mine site situations, and in many cases a combination of technologies offers the best chance of success; that is, a “tool box” of technologies should be applied. Reducing oxygen availability, which is generally achieved using dry or wet covers, is the most effective control on the oxidation rate. These covers are surface barriers designed to limit the influx of oxygen and surface water to the waste body.

Alternatively, depending on the mineralogical characteristics of the tailings at a mine site, the best environmental result would be to separate different fractions of the sulfidic waste during mineral processing (Mitchell 2000). Selective concentration of pyrite or pyrrhotite during mineral processing would produce a high-sulfide concentrate. The sulfides could then be properly disposed of or used for the production of sulfuric acid.

Finally, the methods currently applied to control sulfide oxidation are not yet proven to securely prevent AMD development in the long term. Global climate change will lead to changing rainfall patterns and weathering processes at individual mine sites. In some cases, the applied control technique may only delay the onset of acid generation. Therefore, the following control techniques may only represent the first step to more sophisticated acid prevention techniques.

### 2.10.1

#### Wet Covers

Submerging sulfidic waste (i.e. tailings or waste rocks) under water is an effective counter to acid generation. The maximum concentration of dissolved oxygen in water is three orders of magnitude lower than that found in the atmosphere. The low solubility of oxygen in water and the slow transport of oxygen in water (i.e. its diffusivity) also reduces the transport of oxygen into a mass of sulfidic waste. Once the available oxygen in water is consumed, an anoxic environment is established, and the rate of sulfide oxidation is reduced because the rate of oxygen replacement is relatively slow. In addition, erosion is reduced, and the formation of reducing conditions fosters the growth of sulfate reducing bacteria which will immobilize dissolved metals as sulfides. However, oxygen can enter surface waters via vertical mixing due to the orbital motions of wind-induced waves and the turbulent mixing caused by breaking waves. Hence, the water cover has to be of substantial depth since surface waters are in constant contact and exchange with atmospheric oxygen.

### Case Study 2.1. Sulfidic Mine Wastes and Their Environmental Impacts at Historical Metalliferous Mine Sites in the New England Area, Australia

#### Introduction

Metalliferous mine sites can represent important sources of acidity and metal pollutants in watercourses and soils, with consequent degradation of local ecosystems. This case study reports AMD caused by mining carried out during the late 19th and early 20th centuries at metalliferous mine sites in the New England area of northern New South Wales, Australia (Ashley and Lottermoser 1999a,b; Lottermoser et al. 1999). Six abandoned base metal mine sites with differing geologic, physiographic, climatic and floral regimes were investigated to provide information on the environmental behaviour of heavy metals and metalloids originating from different primary metal and acid-producing sources. Each site has the common characteristics of decomposing sulfidic waste material, acid mine drainage (AMD), limited acid buffering capacity of host rocks, and degraded soils, streams and vegetation.

#### Sulfidic Ore and Waste Dumps

Largely unconsolidated and unvegetated dumps of sulfidic ore and waste material occur at each mine site. They have high heavy metal contents (wt.% levels As, Cu, Fe, Pb, Zn) and are the major point sources of AMD. Ore heaps, waste dumps and tailings deposits consist of mixtures of weakly to strongly sulfidic rock and non-mineralized host rock material. Exposure of sulfide-bearing material to contemporary weathering processes has led to the dissolution of sulfide and gangue minerals, formation of post-mine oxidation minerals as efflorescences and crusts, as well as AMD with pH values as low as 2.2. Heavy metal values in the AMD leachates are largely derived from sulfide oxidation. Many post-mine oxidation minerals, particularly sulfates and arsenates, also influence the mine water chemistry. These minerals dissolve during rain events and subsequently re-form on drying.

#### Drainage Systems

Where AMD enters streams, there is a drop in pH, and most aquatic and bankside plant communities disappear. Green filamentous algae are common colonizing species in AMD-affected streams. Chemical mobilization from ore/waste/tailings dumps is most pronounced for arsenic, cadmium, copper and zinc, whereas lead remains largely immobile. Physical dispersion of secondary metal-bearing minerals (e.g. jarosite-bearing phases, scorodite, Fe oxides) and chemical precipitation of metals into stream sediments in the form of clays, iron and manganese oxides and organic matter are significant. Consequently, many stream sediments have metal concentrations exceeding background values by one to four orders of magnitude. Upon entering larger drainage systems the metal concentrations of waters and stream sediments may be diluted to background values, although at some locations, anomalous metal concentrations can be traced for several kilometres downstream.

#### Soils

Soil samples taken close to mine waste dumps and processing sites have grossly higher average heavy metal and metalloid values than background samples, commonly by two to three orders of magnitude. Highly contaminated soils may contain heavy metals incorporated into jarosite-type phases, scorodite, iron oxides, manganese oxides, clays, and organic material.

Deep-water disposal of sulfidic waste has been popular and successful in Canada for some time. Possible disposal sites are numerous and readily available there, and annual precipitation exceeds evaporation (Pedersen et al. 1998). The sulfidic wastes are thereby placed in natural or engineered water covers, including former open pits (i.e. in-pit disposal) (Mitchell 2000).

**Case Study 2.1. Continued****Vegetation and Algae**

The contaminated sites are commonly devoid of vegetation or support a depauperate assemblage, with consequent marked erosion. At mine and smelter sites, bioaccumulation and biomagnification processes of heavy metals occur in grasses and other plants but patchy recolonization of contaminated sites by metal-tolerant species is evident. Ashed plant material from contaminated sites shows heavy metal accumulation of one to three orders of magnitude compared to the same plants on background sites. Filamentous green algae flourish in AMD emanating from ore and waste dumps, shafts and adits and in drainage systems affected by acidic waters. The algae are tolerant of low pH waters with high metal, metalloid and sulfate concentrations. They have the capacity for heavy metal and metalloid accumulation, and dried material has been found to contain wt.% levels of heavy metals and metalloids.

**Pollution**

Environmental impacts common to all sites include: (a) unconstrained weathering of sulfidic mine waste with the production of AMD; (b) local disappearance of aquatic life and vegetation; (c) locally confined heavy metal pollution and acidification of streams and soils; (d) downstream heavy metal pollution of local drainage systems; and (e) bioaccumulation and biomagnification of heavy metals in aquatic algae and terrestrial plants. Bioaccumulation processes of heavy metals indicate a potential for heavy metal accumulation in the food chain of the surrounding terrestrial ecosystems, including grazing animals.

Although mining ceased many decades ago at all investigated sites, contamination of local streams by AMD remains and will continue due to the high sulfide and metal content of the exposed ore and waste dumps. In addition, the presence of post-mine oxidation minerals in topsoils, stream sediments, and ore and waste dumps creates additional contamination problems because some of the phases act as temporary storage for acidity and heavy metals and may release these upon dissolution.

The heavy metal abundances of many soils and stream sediments exceed soil quality criteria and contaminated site guidelines at certain sites by up to several orders of magnitude. Mine seepage waters contain heavy metal values well in excess of recommended concentrations in drinking waters for domestic and stock use. However, there is no significant contamination to major river systems due to massive dilution of AMD effluents.

The major concerns with subaqueous disposal are to achieve stagnant anoxic conditions and to maintain complete and continuous water saturation. Sulfidic waste should not be exposed to water containing oxygen. Such water can be moved physically to the bottom of the water layer, as a result of temperature differences or wind. In arid and semi-arid regions, the wet cover control technique is not an option because deep water bodies are rare, and there is no sufficient year-round supply of water that would ensure that the waste remains in a permanently saturated condition. Drying out of a saturated waste will lead to sulfide oxidation and AMD generation. Therefore, wet covers are unsuitable for arid and semi-arid regions. Moreover, the subaqueous deposition of partially or completely oxidized sulfidic materials is not an option. These wastes contain soluble secondary minerals which will dissolve and release sulfate, metals and metalloids when immersed in water (Li and St-Arnaud 1997).

Rapid flooding can be applied to prevent AMD from developing in underground mines and open pits. In fact, flooding has been successful for mine workings where

## Scientific Issue 2.2. Trace Metal Release from Historical Smelting Slags

### Characteristics of Smelting Slags

Historical copper and lead smelters, particularly those operating during the late 19th and early 20th century, produced large volumes of slag dumps. Most slag dumps are largely in the same form as it existed when smelting stopped (Fig. 2.6). The slags are known to be highly heterogeneous and mineralogically diverse materials. They may contain relict ore, gangue and flux minerals and comprise of variable amounts of glass and crystallized minerals. The composition of slag depends on the composition of the ore and the fluxes used. Thus, historical base metal smelting slags display a range in bulk chemical composition with major concentrations (wt.%) of  $\text{SiO}_2$  and  $\text{Fe}_2\text{O}_{3(\text{Total})}$  and lesser amounts of  $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{MnO}$ ,  $\text{CaO}$ ,  $\text{MgO}$ ,  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$ ,  $\text{P}_2\text{O}_5$ , and  $\text{S}$  (e.g. Lottermoser 2002; Piatak et al. 2004). In addition, historical base metal smelting slags are commonly characterized by elevated metal and metalloid contents as a result of inefficient metal recovery technologies (wt.% levels of  $\text{Cu}$ ,  $\text{Pb}$  and  $\text{Zn}$ ; Parsons et al. 2001; Lottermoser 2002). The metals are thereby tied up within the silicate glass and various slag phases and minerals, including native elements, sulfides, oxides, hydroxides, chlorides, carbonates, sulfates, arsenates, and silicates (Ettler et al. 2001).

### Weathering of Slags

The presence of secondary minerals on slag deposits and laboratory experiments have shown that these historical slags are not chemically inert but undergo weathering and leaching processes, thereby releasing metals to pore and seepage waters (e.g. Parsons et al. 2001; Piatak et al. 2004; Ganne et al. 2006). The slags are undergoing contemporaneous reaction with air and rainwater. The weathering results in the release of metals and metalloids from the different slag phases. The released elements either exit from the dumps into surface seepages and ground waters, or precipitate as an array of weathering related secondary minerals (Lottermoser 2005). The release of metals from slag depends on the chemical and physical properties of the pyrometallurgical wastes. Initially, the stability of the slag phases and minerals to weathering processes determines whether elements can be released. The mobility of metals from slag is also a function of the texture, for example, the degree to which reactive glass or minerals such as sulfides are exposed or encapsulated. Furthermore, coprecipitation and adsorption/desorption reactions as well as solubility equilibrium with secondary minerals will control dissolved metal concentrations in the porewaters of slag dumps (e.g. Parsons et al. 2001; Ettler et al. 2003; Piatak et al. 2004). Prevailing porewater compositions (e.g. Eh, pH of fluids present in the pore network of the slag dumps) will also affect the rate of weathering and therefore the rate of metal release. Also higher proportions of sulfides to carbonates in slag wastes favour lower pH conditions in pore and seepage waters, the more acid fluids leaching sulfides and silicates and mobilizing trace metals (Kucha et al. 1996). The abundance of sulfides and carbonate minerals in smelting slags and the texture of individual slag phases (e.g. the possible encapsulation of sulfides in other primary slag phases) will determine acid generation and the pH of leachates emanating from slag dumps. Hence, seepage waters of slag deposits are known to possess near-neutral to acid pH values.

Weathering and leaching of metalliferous smelting slags are accompanied by the mobilization of metals, metalloids, alkali earth elements and sulfate into pore and seepage waters. Evaporation of the seepage waters emanating from slag dumps may cause the precipitation of mobilized elements and compounds and leads to their temporary fixation in secondary soluble sulfate minerals (Fig. 2.8). Dissolution of these efflorescences during the next rainfall and flushing event and associated  $\text{Al}^{3+}$  and  $\text{Fe}^{3+}$  hydrolysis contributes to the acidification and metal and sulfate contamination of local waterways. Thus, historical smelting slag dumps represent long-term sources of metal pollutants to local ground and surface waters.

they are located below the water table. The submergence of underground workings and filling of open pits can eliminate atmospheric oxygen and curtail acid generation reactions.

### Scientific Issue 2.3. Coating Technologies for Sulfidic Wastes

#### Coating Technologies

The reaction of pyrite with atmospheric oxygen is the main cause of AMD. Thus, if one can place a barrier between the two reactants, pyrite oxidation is halted. Coating sulfide grains with relatively insoluble precipitates would protect the sulfides from further oxidation and dissolution. Such natural coating has been observed during the oxidation of pyrite in carbonate buffered solutions whereby ferric hydroxides formed on pyrite surfaces (Nicholson et al. 1990). The hydroxides formed a barrier between pyrite and oxygen and limited pyrite oxidation.

Coating technologies are based on the natural encapsulation of sulfides by insoluble mineral precipitates. The techniques allow chemical reactions to take place between reagents and the sulfide minerals. Various chemical reagents such as sodium acetate, sodium metasilicate or potassium orthophosphate have been evaluated for the coating of pure pyrite and pyrrhotite samples and pyritic coal waste (Huang and Evangelou 1994; Georgopoulou et al. 1996; Zhang and Evangelou 1998; Fytas and Evangelou 1998; Evangelou 2001). The coating technology aims to produce relatively insoluble phases on sulfide surfaces. The coatings have to be insoluble and stable in order to protect the sulfides from further oxidation and acid production.

#### Phosphate Stabilization

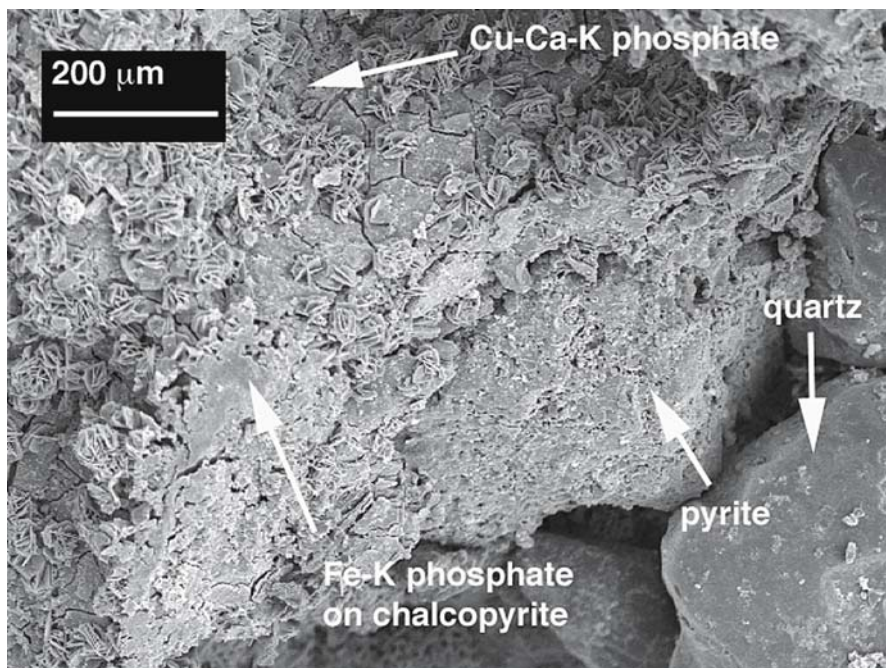
Phosphate induced stabilization is an emerging technology that uses solid or liquid phosphate products to decrease the mobility and bioavailability of metals and radionuclides in contaminated soils, ground waters and sulfidic mine wastes. The principle of phosphate stabilization is based on the fact that the addition of phosphate compounds such as apatite results in the formation of new phosphate phases. These phases have low solubilities and remain stable on a geological time scale (Hodson et al. 2000). In particular, liquid phosphate stabilizers such as potassium orthophosphate are known to create stable iron phosphate coatings around pyrite and pyrrhotite grains. These coatings armour and encapsulate the sulfides and prevent them from further oxidation. Phosphate is the preferred choice of chemical because phosphate minerals of many metals (Cd, Cu, Ni, Pb, U, Zn) have exceptionally low solubilities. In addition, the minerals are stable over a wide range of Eh and pH conditions found in the natural surface environment. Therefore, the formation of phosphate minerals in metal contaminated soils, sediments, waters and wastes immobilizes metals. The metals are prevented from leaching into waters and interacting with the biosphere.

In the phosphate coating technique, sulfides are treated with a weak hydrogen peroxide solution (Georgopoulou et al. 1996; Fytas and Evangelou 1998). The role of hydrogen peroxide is to induce oxidation of a small quantity of  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$ . Soluble phosphate ions are added in the form of orthophosphate or soluble phosphate fertilizers which results in the formation of  $\text{Fe}^{3+}$  phosphate phases on the surface of the oxidizing sulfides. These phosphates are relatively insoluble, protecting the sulfide from reactions with oxygen. The phosphate coating technology appears to be cost effective and feasible in preventing pyrite oxidation. However, these innovative techniques are still at the exploratory stage, are based on laboratory experiments (Harris and Lottermoser 2006a,b). Field trials on polymineralic and partly oxidized sulfidic mine wastes remain to be conducted in order to prove that phosphate stabilization is a viable control strategy for sulfide oxidation.

## 2.10.2

### Dry Covers

Capping the sulfidic wastes with a thick layer of solid material is another effective counter to acid generation. Such dry covers reduce the oxygen flux and water flow into the underlying sulfidic waste. By limiting the amount of oxygen entering the waste, the oxidation reaction can be slowed (Harries and Ritchie 1987). Likewise, by reducing the flow of water into the waste rock, the quantity of contaminated drainage can be reduced.



**Fig. 2.14.** Scanning electron microphotograph of phosphate coatings on pyrite and chalcopyrite. In a laboratory experiment, soluble phosphate ions were added to a polysulfidic waste. Formation of phosphate phases occurred, coating the surfaces of pyrite and chalcopyrite. These phosphates protect the sulfides from further oxidation (Photo courtesy of D. Harris)

Dry covers are constructed from low hydraulic conductivity solids. Materials used for dry covers include low-sulfide waste rock, oxide waste, clay subsoils, soils, organic wastes, and neutralizing materials (e.g. limestone, lime, dolomite, brucite, kiln dust). The solid materials are placed on the crown and sides of sulfidic waste repositories. Prior to their use, the cover materials have to be characterized for their hydraulic conductivity and evaluated for their capacity to minimize oxygen and water transfer into the waste. At their simplest, a dry cover usually consists of a layer of clay (~1 m thick), which has been compacted to give low hydraulic conductivity that allows very little infiltration. At sites, where the supply of clay limited, compaction of coarser-grained cover materials or benign mine wastes may result in the formation of a low permeability seal.

Dry covers range from simple clay barriers to complex, composite covers. The latter types have a number of layers. A possible design may have the following sequence from top to bottom:

- A soil/rock layer – which retains moisture, acts as a substrate for vegetation, and prevents erosion
- A coarse-grained layer – which provides lateral drainage for any infiltration



- A compacted clay layer (at least 30 mm thick) – which creates a low air void content, reduces the cover’s permeability to water, and lowers the diffusion rate of oxygen into the waste
- A coarse-grained layer – which reduces the contact of capillary saline waste waters with the protective cover, and prevents the precipitation of secondary salts at or near the surface of the dry cover
- A compacted layer of acid buffering materials such as lime – which minimizes reaction of the waste with the overlying layers, and promotes the development of a chemical cap

In an arid region with little vegetation, the top soil layer acting as a substrate for vegetation may be replaced with either a rock cover (so-called “riprap”) or a layer of coarse-grained material that will reduce erosion.

Non-conventional dry capping solutions include the use of epoxy resins, chemical caps (i.e. chemically induced surficial hardpan layers), wood chips, bark, municipal solid waste compost, sewage sludge, peat, pulp and paper mill residues, grouts, fly ash mixtures, and non-acid generating or low-sulfides tailings, some of which have been applied with variable success (Elliott et al. 1997; SMME 1998; Xenidis et al. 2002; Bussi re et al. 2004; Forsberg and Ledin 2003, 2006; Pond et al. 2005; Hulshof et al. 2006). In addition, permafrost has been used in cold climates as a sulfide oxidation control strategy (Scientific Issue 2.1).

The construction of effective dry covers has to consider the climatic conditions at the mine site. Depending on the prevailing climate, dry covers are either designed: (a) to maximize run-off using *unsaturated covers*; (b) to store relatively large volumes of infiltrating water for long periods of time using *saturated covers*; or (c) to store relatively large volumes of infiltrating water for short periods of time using *sponge covers*.

### 2.10.2.1

#### *Unsaturated Covers*

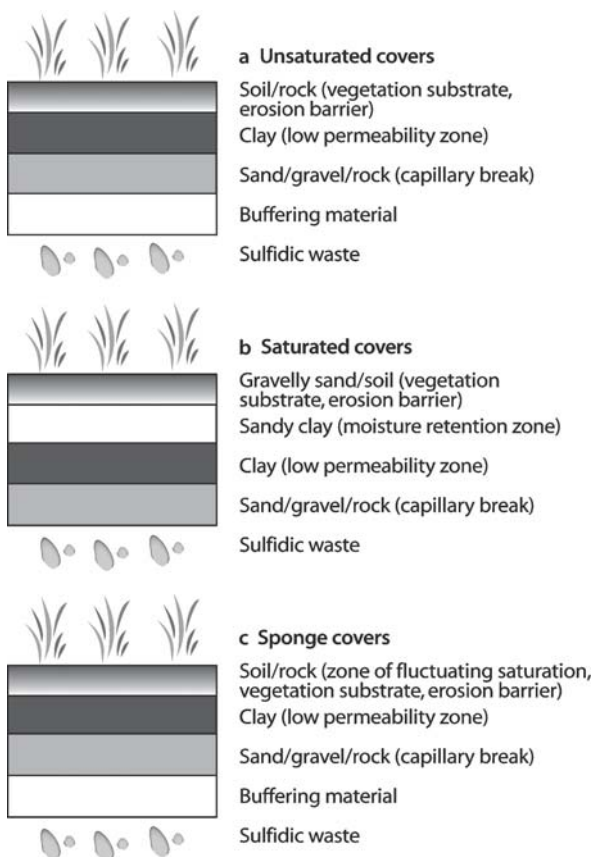
In areas where evaporation exceeds rainfall (semi-arid to arid), only unsaturated dry covers can be used. Unsaturated covers comprise a variety of geological materials (e.g. alluvium, topsoil, oxide waste). They contain a compacted fine-grained layer or low permeability clay seal, and they may have a capillary break of coarse-grained material and a layer of acid buffering materials (Fig. 2.15a). The covers are designed to maximize rainfall run-off and to minimize water infiltration and oxygen diffusion into the waste. The cover is topped with a loose soil or benign waste layer, needed to promote the establishment of vegetation. However, a relatively thin top layer means that trees need to be removed regularly to prevent roots penetrating and damaging the layer design and allowing access of oxygen to the sulfidic waste.

### 2.10.2.2

#### *Saturated Covers*

For mine sites with a wet climate, water saturated covers prevent infiltration of oxygen to potentially acid generating materials. The capping consists of carefully designed

**Fig. 2.15.** Schematic cross-sections illustrating complex dry cover designs; **a** unsaturated covers; **b** saturated covers; **c** sponge covers



layers of soil and clay, which maintain a saturated layer throughout the year, with the water being provided by natural rainfall. The basic design involves a medium-grained material such as sandy clay with medium hydraulic conductivity underlain by fine-grained materials such as clay with low hydraulic conductivity (Fig. 2.15b). The layer of sandy clay is designed to hold water from infiltrating rainfall and to act as a water reservoir keeping the pores close to saturation; that is, the layer acts as a moisture retention layer. The clay layer may be compacted or uncompacted. Capillary suction forces prevent drainage of this layer with low hydraulic conductivity. A coarse-grained layer of rock, below the clay and at the base of the cover, drains first, and provides a capillary break to the movement of any AMD waters rising from the sulfidic material below. An additional coarse-grained layer may also be installed above the clay layer in order to reduce evaporation of the clay layer. At the surface, a layer of gravelly sand/soil is placed above the sandy clay zone. The soil is not only substrate for the vegetation but also protects the underlying cover from erosion.

A good saturated cover promotes run-off and maintains a high degree of water saturation within the sandy clay layer (Taylor et al. 1998). Transport of oxygen in the pores of this saturated layer is then governed by the low solubility and slow transport of oxygen in water rather than air. This in turn limits the movement of oxygen into the sulfidic waste.

Saturated covers are used in humid, wet climates where the cover remains saturated due to the high rainfall. The Rum Jungle uranium mine is an example where the application of a saturated cover system on sulfidic waste rocks has had limited success (Harries and Ritchie 1988; Bennett et al. 1999). The cover system was particularly effective in reducing the oxygen flux during the wet season; however, during the dry season the clay seal cracks resulting in AMD release and environmental impacts downstream (Figs. 2.16, 2.17). Thus, clay as part of a cover design may work well in wet climates but not necessarily in dry climates or seasonal climates due to drying, shrinking and cracking of the clay seal. Also, in many mining districts, the soil profiles can be notably deficient in clays. Consequently, the lack of suitable cover materials such as clays makes the construction of saturated covers as oxygen diffusion barriers impossible.

### 2.10.2.3

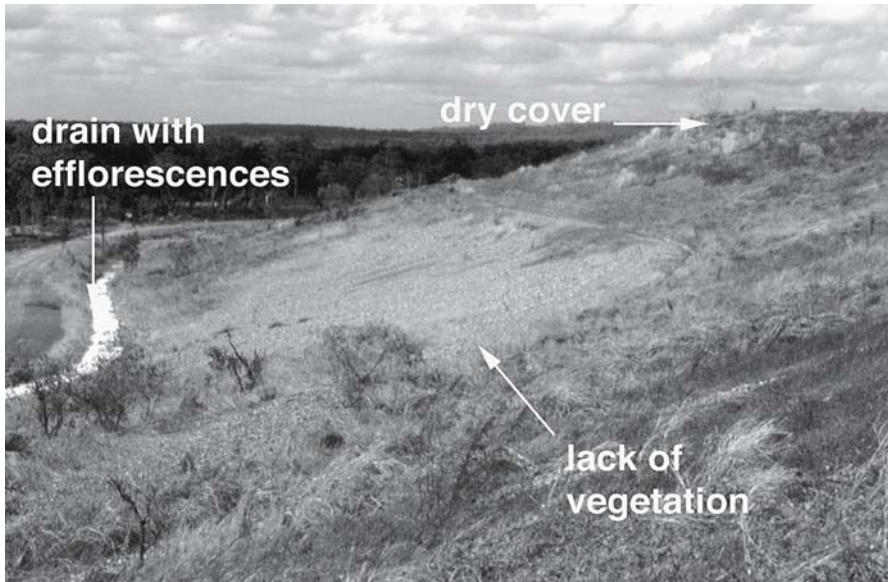
#### *Sponge Covers*

Sponge covers or so-called “store-release” covers are suitable for climates with distinctly seasonal rainfall (Williams et al. 1997; Currey et al. 1999). The covers are designed to store water in an upper cover layer (Fig. 2.15c). An irregular topography prevents surface run-off, and much of the drainage flows into the waste. The porous, loose top layer becomes saturated with water during a precipitation event. It then functions as an oxygen ingress barrier for the underlying sulfidic waste. The barrier uses the low solubility and slow transport of oxygen in water, reducing oxygen ingress in the same manner as a water cover does. Percolation of water into the waste is limited because the majority of the stored water is removed through evapotranspiration. In fact, vegetation plays a significant role in using and pumping water from these covers (Williams et al. 1997; Currey et al. 1999). The pumping action of plants prevents the stored water from infiltrating the underlying sulfidic waste. Nonetheless, cover failures may still be possible. Prolonged droughts or bushfires may cause significant die-off to plants, and subsequent infiltration would lead to a significant flow through and out of the waste materials (Dobos 2000).

### 2.10.3

#### **Encapsulation, In-Pit Disposal and Mixing**

Mining of sulfidic ores generally produces wastes with different acid generation potential. Selective handling of these different waste types allows the construction of waste rock dumps according to their acid generation potential (Cravotta et al. 1994; Environment Australia 1997). The disposal practice may utilize the buffering capacity of any benign waste to control acid production. Potentially acid generating material

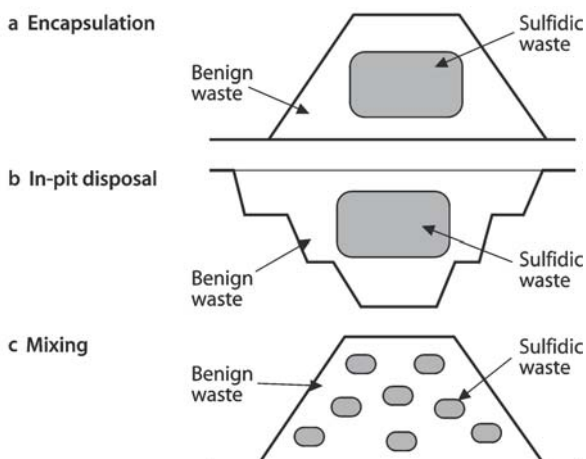


**Fig. 2.16.** White's waste heap, Rum Jungle uranium mine, Australia. The sulfidic waste rock dump has a saturated cover design which comprises compacted clay, sandy clay loam and gravelly sand on top. The crown of the waste cover is covered with grass while the sides of the waste pile did not develop a complete vegetation cover



**Fig. 2.17.** Scalded seepage area at the base of White's waste heap (Fig. 2.16). The clay seal has cracked, and water infiltration into the dump has increased since the installation of the cover in 1984. Saline, acid seepages emanate from the base of the dump and precipitate abundant sulfate and iron oxyhydroxide efflorescences

**Fig. 2.18.** Control of sulfide oxidation in mine waste using **a** encapsulation, **b** in-pit disposal, and **c** mixing techniques (after Environment Australia 1997)



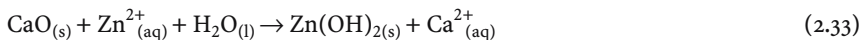
is thereby enclosed in non-reactive benign material such as oxide waste or even neutralizing material (Fig. 2.18a) (i.e. encapsulation method). Alternatively, the waste is backfilled into open pits (Fig. 2.18b) (i.e. in-pit disposal method) (cf. Sec. 4.5). The sulfidic waste needs to be placed below the post-mining ground water table (cf. Fig. 4.6). Mixing highly sulfidic and benign wastes represents an additional disposal option (Fig. 2.18c). Encapsulation and mixing practices do not usually prevent sulfide oxidation and acid generation unless additional control measures are applied. However, the techniques may reduce AMD intensity substantially.

#### 2.10.4

##### Co-Disposal and Blending

Sulfidic waste may also be blended and/or co-disposed with benign or alkaline material. Co-disposal refers to the mixing of coarse-grained waste rock with fine-grained tailings or coal washery wastes (Williams 1997; Wilson et al. 2000; Rensburg et al. 2004). Such a disposal practice has distinct advantages. It allows filling of the large pores of waste rock with fine tailings. As a result, the hydraulic properties of the wastes are altered, the water retention and saturation is increased, and the oxygen transfer into the waste rock is decreased. Sulfide oxidation can be curtailed.

Blending is generally conducted in conjunction with other control measures such as dry covers. Blending refers to the addition of alkaline material, which is used to raise the neutralization potential of the mine waste. The objectives are: (a) to balance the acid neutralization and acid generation potentials; (b) to minimize the risk of AMD; and (c) to immobilize any soluble or potentially soluble metals and metalloids as insoluble or sparingly soluble sulfates, carbonates and hydroxides. Neutralizing materials are mixed with acid producing waste. The neutralizing materials may be limestone ( $\text{CaCO}_3$ ) or lime ( $\text{CaO}$ ) as well as any acid buffering waste produced at the mine site. The alkaline materials are applied to ensure that the metals are immobilized permanently by converting them into sparingly soluble minerals such as sulfates, carbonates and hydroxides:



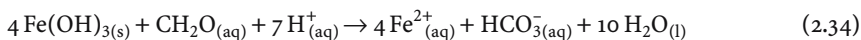
Surface applications of some alkaline materials or applications under thin soil cover have not been successful (Smith and Brady 1999). Possible explanations may include: (a) the dissolution of calcite at surface conditions is limited by the partial pressure of carbon dioxide; and (b) preferential flow of water occurs through the waste dump, bypassing much of the near surface alkaline material. Thus, uniform mixing of acid buffering waste or neutralizing materials with sulfidic waste is of paramount importance in order to achieve consumption of acidity (Smith and Brady 1999). In an already established sulfidic waste dump, the use of neutralizing agents is limited by the difficulty of blending them through waste layers. Thorough mixing is usually difficult, inefficient and expensive. In addition, a treatment relying on deep disturbance of the waste has the risk of exposure of additional unoxidized sulfidic mine waste. Therefore, blending has to occur while the waste materials are being dumped at their disposal sites.

The major disadvantage of blending is that it does not prevent sulfide oxidation. While blending helps to immobilize dissolved metals such iron, aluminium, copper and lead as insoluble minerals in sulfidic wastes, it may not prevent the release of sulfate as well as other metals and metalloids (e.g. As, Cd, Mo, Zn) into pore waters. These elements are potentially mobile under neutral to alkaline pore water conditions.

### 2.10.5

#### Addition of Organic Wastes

The addition of organic wastes may also prevent sulfide oxidation. The wastes can be used as a compacted subsurface layer in dry cover designs or as amendments to create reactive, low permeability biomass surfaces. Tried organic materials include sewage sludge, wood chips, sawdust, manure, peat, pulp and paper mill residues, and municipal solid waste compost (Cabral et al. 1997; Elliott et al. 1997; SMME 1998; Hulshof et al. 2006). The wastes inhibit pyrite oxidation via various mechanisms. Firstly, organic wastes provide a pH buffer and create reducing conditions which inhibit sulfide oxidizing bacteria, reduce sulfate to sulfide, and immobilize metals as sulfides. Secondly, dissolved organic compounds form stable iron-organic complexes or combine with iron to form stable precipitates. Thirdly, the organic compounds are adsorbed on pyrite surfaces, preventing oxidation (Evangelou 1995, 1998). However, if organic waste such as sewage sludge is part of a dry cover design, organic acids (simplified stoichiometrically as the molecules  $\text{CH}_2\text{O}$  and  $\text{H}^+$ ) may dissolve iron hydroxide phases (Blowes et al. 1994):



Adsorbed and coprecipitated metals, originally present in the iron precipitates, are also released into the aqueous phase. The iron and other metals can form stable or-

ganic complexes which may migrate into ground and surface waters. Therefore, it is possible that the use of organic material enhances the migration of contaminants from sulfidic wastes (Mitchell 2000).

Organic waste placed at the surface of waste repositories is in constant contact with the atmosphere and will decompose over time. Such oxidation ensures that the added organic material is eventually used up. Consequently, the addition of organic waste, unless regularly done, is a short-term fix to a long-term waste problem.

### 2.10.6

#### Bactericides

Certain bacteria are known to increase the rate of pyrite oxidation. Hence, anti-bacterial agents, so-called “*bactericides*”, have been used to inhibit the growth of these microorganisms (Ledin and Pedersen 1996; Kleinmann 1997, 1999). Many compounds including anionic surfactants, cleaning detergents, organic acids, and food preservatives have been screened as selective bactericides. The anionic surfactants sodium lauryl sulfate and alkyl benzene sulfonate are considered the most reliable and cost effective inhibitors (Kleinmann 1997, 1999). In the presence of such compounds, hydrogen ions in the acidic environment move freely into or through bacteria cell membranes, causing their deterioration.

While there are clear advantages in the use of bactericides including decreased pyrite oxidation and metal mobility, there are also disadvantages and potential risks. The applied compound may cause toxicity to other organisms; there is the possibility of resistance development; and it is difficult to reach all zones of the sulfidic waste (Kleinmann 1999). Bactericides are generally water soluble and leach from the waste, and they may be adsorbed on the surfaces of other minerals. As a result, repetitive treatments are necessary to prevent repopulation of the waste by bacteria when the bactericide is depleted (Kleinmann 1999). Alternatively, slow-release pellets may help to provide long-term bacterial inhibition (Kleinmann 1999). Thus, bactericides are another short-term solution to a long-term waste problem, and if applied, they should be part of other control measures (Environment Australia 1997).

## 2.11

### Summary

Sulfidic mine wastes, especially those which contain high concentrations of pyrite, are the major sources of AMD. Pyrite oxidation may occur via biotic or abiotic and direct or indirect oxidation processes. Biotic indirect oxidation of pyrite is an important acid generating process whereby pyrite is oxidized by oxygen and  $\text{Fe}^{3+}$  in the presence of microorganisms. Pyrite oxidation is a complex process because it not only involves chemical, electrochemical and biochemical reactions, but it also varies with environmental conditions. The following factors all work to enhance the speed of pyrite oxidation: large surface area; small particle size; high porosity; poor crystallinity; significant trace element substitutions of and solid inclusions within the pyrite; acidic pH values of the solution in contact with pyrite; no direct physical contact with other sulfides; high oxygen and high  $\text{Fe}^{3+}$  concentrations in the oxidizing medium; high temperature; abundant microbial activity; and alternate wetting and drying of the sulfide grain.

Sulfides other than pyrite have different acid production potentials, stabilities and rates of reaction. The metal/sulfur ratio in sulfides influences how much sulfuric acid is liberated by oxidation. Also, the amount of iron sulfides present strongly influences whether and how much acid is generated during weathering. Iron sulfides (e.g. pyrite, marcasite, pyrrhotite) or sulfides having iron as a major constituent (e.g. chalcopyrite, iron-rich sphalerite) generate the most acidity. In contrast, sulfide minerals which do not contain iron in their crystal lattice (e.g. covellite, galena or iron-poor sphalerite) do not have the capacity to generate significant amounts of acid. This is because  $\text{Fe}^{3+}$  is not available as the important oxidant, and iron hydrolysis cannot occur which would generate additional hydrogen ions. The production of acid also occurs through the dissolution of secondary soluble  $\text{Fe}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Fe}^{3+}$  and  $\text{Al}^{3+}$  sulfate salts, and the precipitation of secondary  $\text{Fe}^{3+}$  and  $\text{Al}^{3+}$  hydroxides.

Any acid generated can be consumed through the reaction of the hydrogen ions with gangue minerals. The weathering of silicates results in the consumption of hydrogen ions, formation of secondary minerals, and release of dissolved cations and silicic acid. The dissolution of hydroxides and carbonates as well as cation exchange processes on clay minerals also consume acid. The gangue minerals reacting with the acidic solutions have a variable resistance to weathering and therefore, exhibit different reaction rates. Carbonate minerals show the highest reactivity and highest acid consumption, whereas silicates have significantly slower reaction rates and provide only token amounts of additional long-term buffering capacity to sulfidic wastes.

Weathering of sulfidic wastes produces mine waters laden with dissolved salts. The dissolved salts may approach saturation in pore waters, ground waters, streams and leachates associated with the oxidation and leaching of sulfidic wastes. In fact, numerous secondary minerals are known to precipitate in AMD environments. Some secondary minerals may redissolve in AMD waters thereby influencing the mine water chemistry; others may precipitate and coat acid buffering or acid producing minerals. Massive precipitation of secondary minerals in wastes results in the formation of laterally extensive or discontinuous subsurface or surface layers which act as horizontal barriers to vertical water movements. Thus, the secondary mineralogy of sulfidic wastes plays an important role in controlling how readily and how much acid, metals and sulfate are liberated to drainage waters.

The prediction of AMD generation from sulfidic wastes is possible using geological and petrographic descriptions, geological modeling, static and kinetic tests, and mathematical models. These tools may be used to estimate potential sulfide oxidation and dissolved metal mobility. Sulfidic waste dumps are major sources of AMD. Oxygen advection, convection and diffusion occur in such wastes, which can result in the production of acid. Fine-grained wastes have much greater surface areas and hence, a greater acid generation potential than coarse-grained wastes, yet the fine grain size limits oxygen diffusion, water ingress and acid generation.

Monitoring techniques of sulfidic wastes are designed to identify the early presence of or the changes to any products of the acid producing reactions. The products can be identified by obtaining waste temperature measurements, oxygen pore gas concentration profiles, and leachate analyses for dissolved contaminant concentrations and loads. Rapid increases in temperature profiles of waste dumps indicate the exothermic oxidation of sulfides, whereas the depletion of oxygen concentration within gas pores is also indicative of sulfide oxidation.



Control techniques of sulfide oxidation are based on the exclusion of one or more of the factors that cause and accompany oxidation; that is, sulfide minerals, bacteria, water, iron and oxygen. Controlling sulfide oxidation may reduce or even eliminate the possibility of AMD generation. The destructive sulfide oxidation processes are driven by the ready exchange of oxygen with the atmosphere. Hence, reducing oxygen availability is the most effective control on the oxidation rate. This is generally achieved using dry or wet covers. The advantage of wet covers is that oxygen diffuses very slowly and has limited solubility in water. In contrast, a dry cover with a low oxygen permeability restricts water and oxygen movement into and through the waste. The dry cover reduces both the oxidation rate of sulfides and the transport of leachates from the waste. Other established and experimental methods for the prevention of sulfide oxidation and AMD development include selective handling and isolation, co-disposal and blending, mineral surface treatments, addition of organic wastes, and bacterial inhibition.

Further information on sulfidic wastes can be obtained from web sites shown in Table 2.8.

**Table 2.8.** Web sites covering aspects of sulfidic wastes

Organization	Web address and description
The International Network for Acid Prevention (INAP)	<a href="http://www.inap.com.au">http://www.inap.com.au</a> Industry based initiative to coordinate research and development into the management of sulfidic wastes
US Environmental Protection Agency (EPA)	<a href="http://www.epa.gov/epaoswer/other/mining/techdocs/amd.pdf">http://www.epa.gov/epaoswer/other/mining/techdocs/amd.pdf</a> Technical report on AMD prediction
US Geological Survey (USGS)	<a href="http://crustal.usgs.gov/projects/minewaste/index.html">http://crustal.usgs.gov/projects/minewaste/index.html</a> Mine waste characterization
Mine Environment Neutral Drainage Program (MEND), Canada	<a href="http://www.nrcan.gc.ca/mms/canmet-mtb/mmsl-lmsm/mend">http://www.nrcan.gc.ca/mms/canmet-mtb/mmsl-lmsm/mend</a> Extensive technical reports on sulfide oxidation prevention techniques
Department of Environmental Protection, Pennsylvania	<a href="http://www.dep.state.pa.us/dep/deputate/minres/Districts/homepage/Default.htm">http://www.dep.state.pa.us/dep/deputate/minres/Districts/homepage/Default.htm</a> AMD and coal mine drainage prediction and pollution prevention
Mining Information Service EnviroMine	<a href="http://technology.infomine.com/enviromine">http://technology.infomine.com/enviromine</a> News and information on sulfidic wastes including static and kinetic tests