

Chapter 3

Mine Water

3.1 Introduction

Water is needed at mine sites for dust suppression, mineral processing, coal washing, and hydrometallurgical extraction. For these applications, water is mined from surface water bodies and ground water aquifers, or it is a by-product of the mine dewatering process. Open pits and underground mining operations commonly extend below the regional water table and require dewatering during mining. In particular, mines intersecting significant ground water aquifers, or those located in wet climates, may have to pump more than 100,000 liters per minute to prevent underground workings from flooding. At some stage of the mining operation, water is unwanted and has no value to the operation. In fact, unwanted or used water needs to be disposed of constantly during mining, mineral processing, and metallurgical extraction.

At modern mine sites, water is collected and discharged to settling ponds and tailings dams. In contrast, at historic mine sites, uncontrolled discharge of mine water commonly occurs from adits and shafts into the environment. Generally, the volume of mine water produced, used and disposed of at mine sites is much larger than the volume of solid waste generated. At mine sites, water comes in contact with minerals and dissolves them. Hence, water at mine sites often carries dissolved and particulate matter. When such laden waters reach receiving water bodies, lakes, streams or aquifers, the waters can cause undesirable turbidity and sedimentation, they may alter temperatures, or their chemical composition may have toxic effects on plants and animals. For example, in the United States, it has been estimated that 19,300 km of streams and 72,000 ha of lakes and reservoirs have been seriously damaged by mine effluents from abandoned coal and metal mines (Kleinmann 1989).

The worst example of poor mine water quality and associated environmental impacts is acid mine drainage (AMD) water, which originates from the oxidation of sulfide minerals (Sect. 2.3). Sulfide oxidation is an autocatalytic reaction and therefore, once AMD generation has started, it can be very difficult to halt. AMD is the most severe in the first few decades after sulfide oxidation begins, and the systems then produce lower levels of contaminants (Demchak et al. 2004; Lambert et al. 2004). In extreme cases, however, AMD may continue for thousands of years (Case Study 3.1, Fig. 3.1).



Fig. 3.1 Slag heap, sulfidic waste dumps, and abandoned railway carriages at Rio Tinto, Spain. Mankind has exploited the Rio Tinto ores since the Copper Age 5000 years ago. The mining activities have left uncountable waste rock heaps, ore stockpiles, tailings dumps, slag deposits, and settling ponds, most of which do not support any vegetation. The exploitation of sulfidic ores has created a unique *mining landscape* and caused massive AMD flowing into the Rio Tinto

Case Study 3.1. Acid Mine Drainage at the Rio Tinto Mines, Spain

The Iberian Pyrite Belt

The Iberian Pyrite Belt corresponds to an area of volcanic and sedimentary rocks containing massive sulfide deposits. This area forms an arcuate belt, about 250 km long and up to 60 km wide, from Seville in southern Spain to the Atlantic coast of Portugal. The belt contains about 90 known massive sulfide deposits which have been mined for pyrite, base metals (Cu, Pb, Zn), and various trace elements (e.g. Ag, As, Au, Hg, Sn). The orebodies range from small lenses with thousands of tonnes to giant bodies with hundreds of million tonnes. Prior to erosion, these deposits contained more than 1700 Mt of massive sulfides. About 20% of this amount has been mined, and 10–15% has been lost to erosion (Barriga and Carbalho 1997). The Iberian Pyrite Belt represents the largest concentration of metals and sulfides in the world.

The Rio Tinto Mining District

The Rio Tinto district (i.e. Nerva–Minas de Riotinto) has been the most important mining district of the Iberian Pyrite Belt. Various civilizations have been living in the Rio Tinto region, exploiting its natural resources and establishing

one of the oldest mines in the world. Mining dates back to the Copper Age 5000 years ago and continued during Tartessian and Phoenician times. The mineral wealth of the region also drew Greek, Carthaginian and Roman invasions – the greatest mining activity took place during the Roman period. The mines were abandoned after the Roman era, and little mining was conducted after this time. In 1873, British mining companies began to exploit the ores on a large scale, and a significant industrial complex was established by the late 19th century. Exploitation of the mines continued into modern times.

These successive mining activities have resulted in the creation of a unique *mining landscape*. The region has numerous abandoned mine workings and is littered with derelict buildings and disused mining and processing equipment. There are also uncountable waste rock heaps, ore stockpiles, tailings dumps, slag deposits, and settling ponds, most of which do not support any vegetation. The lack of vegetation on sulfidic wastes and local soils increases erosion rates into the headwaters of the Rio Tinto. Pyritic waste particulates are transported into the river tens of kilometers downstream of the mine and processing sites (Hudson-Edwards et al. 1999). The erosion processes exacerbate the *moonscape appearance* of the area affected by mining, mineral processing and smelting activities. Most importantly, the Rio Tinto mining district is characterized by uncontrolled pyrite oxidation in exposed mine workings and waste materials (Romero et al. 2006b). The oxidation of pyrite causes formation of sulfuric acid and the dissolution of many metals. Mine waters are quite acid (pH 2 or less) due to the oxidation of abundant pyrite.

The Tinto River

The Rio Tinto mining district is drained by the Odiel and Tinto rivers. The Tinto river is 90 km long and remains strongly acid (pH < 3) for its entire length (Leblanc et al. 2000; Braungardt et al. 2003). Tinto is Spanish for *red wine* and clearly refers to its turbid red, acid water. The stream's distinct turbidity is the result of abundant iron-rich suspended colloids and gelatinous flocculants. The river also carries very high dissolved sulfate, metal, and metalloid loads (As, Fe, Cu, Cd, Ni, Pb, Zn) from the headwaters to its estuary. Part of this dissolved metal load is precipitated into fluvial and estuarine sediments. Another part of the metal load enters continental shelf sediments and waters of the Gulf of Cadiz and contributes to the metal content of the Mediterranean Sea through the Strait of Gibraltar (Elbaz-Poulichet and Leblanc 1996; Nelson and Lamothe 1993). The waters and sediments of the Rio Tinto are strongly polluted with metals and metalloids. In fact, the Tinto river is one of the most polluted streams in the world. Such pollution began with the exploitation of the ores 5000 years ago (Davis et al.

2000). Despite its pollution, the Rio Tinto acts as an ecological niche for at least 1300 different microorganisms including algae, fungi, bacteria, yeast and protists (Ariza 1998; García-Moyano et al. 2008; López-Archilla et al. 1993). Some of these microorganisms actively participate in the oxidation of detrital pyrite particles present in the stream bed. The Rio Tinto is unique in the sense that the pH value of the river water does not increase downstream, nor does it change significantly during rainfall events. In general, the pH of AMD affected streams generally increases downstream due to the inflow of unpolluted surface or ground waters. The unique conditions of the Rio Tinto are likely due to a number of factors including: (a) a constant input of low pH waters from the mine workings and waste dumps into the headwaters of the river; (b) the presence of abundant detrital pyrite grains in Rio Tinto's alluvium; (c) an plethora of microorganisms which help to oxidize the pyrite grains to acid; (d) the presence of acid producing secondary minerals such as copiapite and coquimbite in the fluvial sediments; and (e) the hydrolysis of iron, precipitation of secondary iron minerals and associated production of hydrogen ions in the Rio Tinto (Buckby et al. 2003; Cánovas et al. 2007; Egal et al. 2008; Hubbard et al. 2009; Hudson-Edwards et al. 1999; Lottermoser 2005; López-Archilla et al. 1993; Olías et al. 2006; Sánchez España et al. 2006; Sarmiento et al. 2009a).

Mining may not be entirely responsible for the generation of AMD and its impact on the Rio Tinto. Historical records refer to the river's long-standing acidity. The Romans called the Rio Tinto "urbero", Phoenician for "river of fire", and the Arab name for it was "river of sulfuric acid" (Ariza 1998). There is also geological evidence that the sulfide orebodies experienced long-term weathering and erosion at some stage in their geological history. The presence of thick jarosite-rich gossans capping the pyritic ores indicates that acid weathering of outcropping sulfide ores could have produced natural ARD prior to mining. The unique red colour of the river may have attracted the very first miners to the region (Ariza 1998). Consequently, the water's conditions today could be a combination of natural ARD and mining induced AMD.

This chapter summarizes information on AMD waters and gives the principles of AMD characterization, monitoring, prediction, environmental impact, and treatment. Such aspects of AMD waters are important issues for any mining operation, regardless whether the mine waters are acid or not.

3.2 Sources of AMD

Mining of metallic ore deposits (e.g. Cu, Pb, Zn, Au, Ni, U, Fe), phosphate ores, coal seams, oil shales, and mineral sands has the potential to expose sulfide minerals to oxidation and generate AMD water. Coal and ore stockpiles, tailings storage

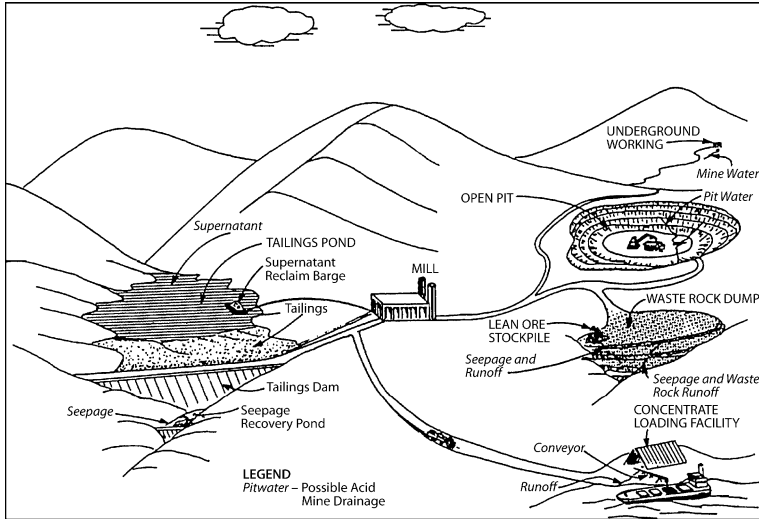


Fig. 3.2 Sources of AMD at a metal mine (Ferguson and Erickson 1988)

facilities, as well as waste rock and heap leach piles are all potential sources for acid generation as are underground workings, mine adits, shafts, pit walls, and pit floors (Figs. 3.2, 3.3, 3.4 and 3.5). At these sites, mine waters can become acidic through reactions of meteoric water or ground water with exposed sulfides. Consequently, AMD water can form as the result of numerous processes such as:

- Ground water enters underground workings located above the water table and exits via surface openings or is pumped to the surface (i.e. mining water) (Fig. 3.3);
- Ground water enters pits and surface excavations;
- Meteoric precipitation comes in contact with pit faces (Fig. 3.4);
- Meteoric precipitation infiltrates coal and ore stockpiles, heap leach piles, coal spoil heaps, and waste rock dumps (Fig. 3.5);
- Meteoric precipitation and flood inflow enter tailings disposal facilities;
- Run-off from rainfall interacts with mining, mineral processing, and metallurgical operations;
- Surface water and pore fluids of tailings, heap leach piles, ore stockpiles, coal spoil heaps, and waste rock dumps may surface as seepage waters or migrate into ground water aquifers; and
- Uncontrolled or controlled discharge of spent process waters occurs from tailings dams, stacks, ponds, and heap leach piles.

AMD waters can form rapidly, with evidence such as iron staining or low pH run-off often appearing within months or even weeks. AMD generation is thereby independent of climate and is encountered at mine sites in arid to tropical climates

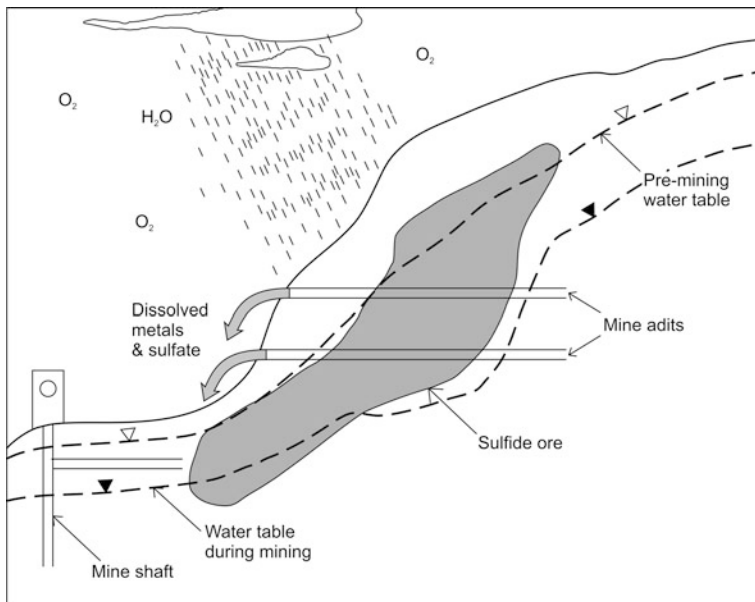


Fig. 3.3 Conceptual process of sulfide oxidation and AMD development in an underground mine

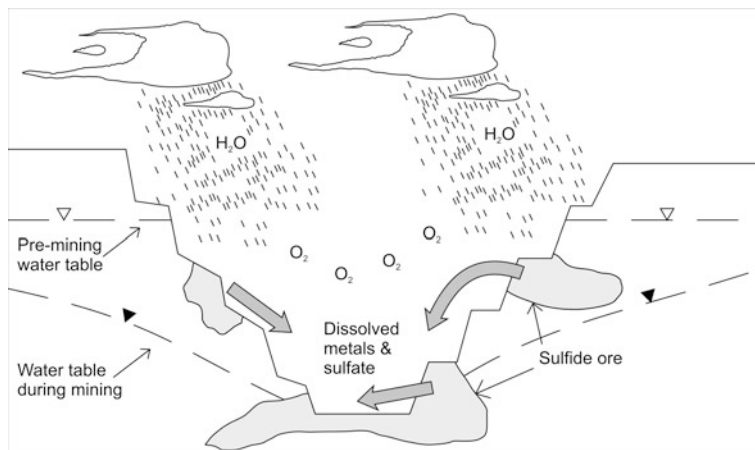


Fig. 3.4 Conceptual process of sulfide oxidation and AMD development in an open pit mine

from the Arctic Circle to the equator (Scientific Issue 2.2). However, not all mining operations that expose sulfide-bearing rock will cause AMD. In addition, contaminant generation and release are not exclusive to AMD environments. They also occur in neutral and alkaline drainage environments as shown in the following sections.

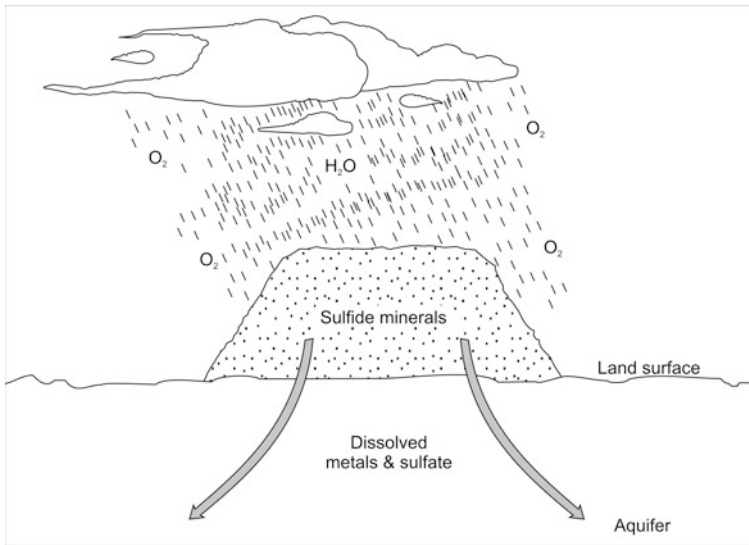


Fig. 3.5 Conceptual process of sulfide oxidation and AMD development in a waste rock dump

3.3 Characterization

Constituents dissolved in mine waters are numerous, and mine waters are highly variable in their composition (Table 3.1). Some waters contain nitrogen compounds (nitrite, NO_2^- ; nitrate, NO_3^- ; ammonia, NH_3) from explosives used in blasting operations and from cyanide heap leach solutions used for the extraction of gold (Sect. 5.4). Other mine waters possess chemical additives from mineral processing and hydrometallurgical operations (Sect. 4.2.1). For instance, metallurgical processing of many uranium ores is based on leaching the ore with sulfuric acid (Sect. 6.5.1). Spent process waters are commonly released to tailings repositories, so the liquids of uranium tailings dams are acid and sulfate rich. Also, coal mining may result in the disturbance of the local aquifers and the dissolution of chloride and sulfate salts that are contained in the marine sedimentary rocks present between the coal seams. As a result, coal mine waters can be exceptionally saline.

Therefore, depending on the mined ore and the chemical additives used in mineral processing and hydrometallurgical extraction, different elements and compounds may need to be determined in waters of individual mine sites. Regardless of the commodity extracted and the mineral processing and hydrometallurgical techniques applied, major cations (i.e. Al^{3+} , Si^{4+} , Ca^{2+} , Mg^{2+} , Na^+ and K^+) and anions (i.e. Cl^- , SO_4^{2-} , CO_3^{2-} , HCO_3^-) are important constituents of any mine water. Other constituents such as nitrogen or cyanide compounds, or dissolved and total organic carbon concentrations, should be determined depending on site specific conditions. Additional parameters analyzed and used for the study of mine waters are given in Table 3.2.

Table 3.1 Chemical composition of some mine waters from metal mine sites in Australia (Lottermoser unpublished data; Lottermoser and Ashley 2006a). World Health Organization's drinking water guideline values are also listed (WHO 2008)

	Tailings pond water, Jumna tin mill	Mine site drainage water, Montalbion silver mine	Tailings dam seepage water, Mary Kathleen uranium mine	WHO guidelines
<i>General parameters</i>				
pH	2.57	3.59	5.55	
Conductivity (mS cm ⁻¹)	2.74	1.39	5.11	
TDS (mg l ⁻¹)	1860	1091	4550	
<i>Major ions (mg l⁻¹)</i>				
Ca	27	85	503	
Mg	23	34	465	
Na	1	13	204	
K	<1	3.8	10	
Al	129	47	0.01	
Fe	148	1.63	302	
Mn	7.2	11	219	0.4
HCO ₃	<1	<0.1	13	
SO ₄	1530	780	4110	
Cl	<1	14	147	
F	1.9	na	na	1.5
<i>Trace elements (μg l⁻¹)</i>				
As	772	50	3	10
Ba	6	50	17	700
Cd	291	623	na	3
Co	192	289	na	
Cr	68	3	na	50
Cu	30,800	21,700	4	2000
Mo	2	0.2	na	70
Ni	257	236	93	70
Pb	607	36	<1	10
Se	20	22	na	10
U	36	na	319	15
Zn	63,700	79,000	17	

na: not analyzed

3.3.1 Sampling and Analysis

Detailed procedures for water sampling, preparation and analysis are found in manuals and publications (e.g. Appelo and Postma 1999; Ficklin and Mosier 1999). Laboratory methods for the geochemical analysis of environmental samples including mine waters are given by Crock et al. (1999). Quality assurance/quality control of the analytical results must be ensured using established procedures. The submission of duplicates or even triplicates of the same sample will allow an evaluation

Table 3.2 Selected parameters important to mine waters (after Appelo and Postma 1999; Brownlow 1996; Drever 1997; Ficklin and Mosier 1999)

Parameter	Explanation
Eh	Reduction-oxidation potential of a solution. The redox state of mine waters is best analyzed by determining the concentrations of multiple redox species such as Fe^{2+} and Fe^{3+} in the sample. Expressed as volts (V)
pH	Negative logarithm of hydrogen activity; $-\log[\text{H}^+]$
Electrical conductivity (EC)	Ability to conduct electrical current, depending on the amount of charged ions in solution. Expressed as μScm^{-1} . For freshwater, the conductivity is approximately related to the quantity of total dissolved solids by the expression: $\text{EC } 0.65^{-1} = \text{mg l}^{-1}\text{TDS}$
Hardness	Sum of the ions which can precipitate as “hard particles” from water. It is expressed as $\text{mg CaCO}_3 \text{ l}^{-1}$ and related to the sum of calcium and magnesium ions by the equation: $\text{mg CaCO}_3 \text{ l}^{-1} = 2.5 (\text{mg Ca l}^{-1}) + 4.1 (\text{mg Mg l}^{-1})$
Alkalinity	Capacity of a solution to neutralize acid. Determined by titrating with acid down to a specific pH, e.g. pH 4.5. In most natural waters, alkalinity is equal to the molality concentrations of bicarbonate and carbonate ions. Other ions such as ammonia, borate, silicic acid, bisulfides, organic anions, and hydroxide ions can combine with hydrogen and contribute to alkalinity. Expressed as mg CaCO_3 or $\text{HCO}_3^- \text{ l}^{-1}$
Acidity	Capacity of a solution to donate protons. Determined by titrating with a base up to a specific pH value, e.g. pH 8.3. A number of dissolved ions (H^+ , Fe^{2+} , HSO_4^-), gases (CO_2 , H_2S), humic and fulvic acids, and suspended matter (metal hydroxides, clays) may contribute to an acidity value. Mine waters generally have very low organic acid contents. Expressed as mg CaCO_3 or $\text{HCO}_3^- \text{ l}^{-1}$
Total dissolved solids (TDS)	Amount of dissolved solids. Determined by evaporating and weighing the dry residue. Expressed as mg l^{-1}
Dissolved oxygen (DO)	Amount of dissolved oxygen. Expressed as mg l^{-1}
Turbidity	Macroscopic, visual evidence of suspended matter in water. Expressed by using an empirical number scale
Temperature	$^{\circ}\text{C}$
Salinity	Amount of total dissolved solids. Freshwater has <1000 or 1500 mg l^{-1} TDS, brackish waters have $1000\text{--}10,000 \text{ mg l}^{-1}$ TDS, saline waters have $10,000\text{--}100,000 \text{ mg l}^{-1}$ TDS, whereas brines have even higher salinities

of the analytical precision (i.e. repeatability). Blanks of deionized water should be included in order to check for unclean sample processing or inaccurate chemical analysis. The low pH of AMD waters will aid in preservation of dissolved metals; otherwise, neutral or alkaline waters need to be acidified to keep metals in solution. Degassing of CO_2 -rich samples is possible after sampling, so containers should be completely filled and tightly closed.

The longer the period of time between collection and analysis, the more likely it is that unreliable analytical results will be measured. Exposure to light and elevated

temperatures will cause precipitation of salts, or dissolution of transitional and solid species. Consequently, it is of paramount importance to preserve water samples on ice in a closed container and to submit collected samples as soon as possible to the laboratory. Upon receipt of the analytical results, analytical values of duplicates/triplicates and blanks should be evaluated, and the charge balance of anions and cations should be confirmed (Appelo and Postma 1999).

The concentrations of dissolved substances in water samples are presented in different units. The most commonly used units are mg l^{-1} and ppm or ppb. The units mg l^{-1} and ppm are numerically equal, assuming that 1 l of water weighs 1 kg. Such a conversion is only valid for dilute freshwaters, yet many mine waters are saline. Thus, any conversion has to consider the increased density (Appelo and Postma 1999). The density of waters needs to be determined if it is desired to convert analytical values from mg l^{-1} to ppm.

With the advent of modern field equipment, many mine water parameters (i.e. pH, dissolved oxygen, temperature, electrical conductivity, turbidity) should be determined in the field since these values can quickly change during sample storage (Ficklin and Mosier 1999). If possible, an elemental analysis should be accompanied by the measurement of the reduction-oxidation (redox) potential (i.e. Eh), or of a redox pair such as $\text{Fe}^{2+}/\text{Fe}^{3+}$. Such an analysis is sufficient to define the redox state of the AMD water and allows the simulation of redox conditions during geochemical modeling.

3.4 Classification

There is no typical composition of mine waters and as a result, the classification of mine waters based on their constituents is difficult to achieve. A number of classification schemes of mine waters have been proposed using one or several water parameters:

- *Major cations and anions.* This is a standard technique to characterize ground and surface waters (e.g. Appelo and Postma 1999; Brownlow 1996; Drever 1997). It involves plotting the major cation (Ca^{2+} , Mg^{2+} , Na^+ , K^+) and anion (Cl^- , SO_4^{2-} , CO_3^{2-} , HCO_3^-) chemistry on a so-called *Piper* or trilinear diagram. The plotted waters are then classified according to their cation and anion abundances.
- *pH.* A basic scheme labels mine waters according to their pH as acidic, alkaline, near-neutral, and others (Morin and Hutt 1997).
- *pH and Fe^{2+} and Fe^{3+} concentration.* This classification technique requires a knowledge of the pH and of the amount of Fe^{2+} and Fe^{3+} present (Glover 1975; cited by Younger 1995).
- *pH vs. combined metals.* Mine waters can also be classified according to pH and the content of total dissolved metals (Ficklin et al. 1992; Plumlee et al. 1999) (Fig. 3.6).

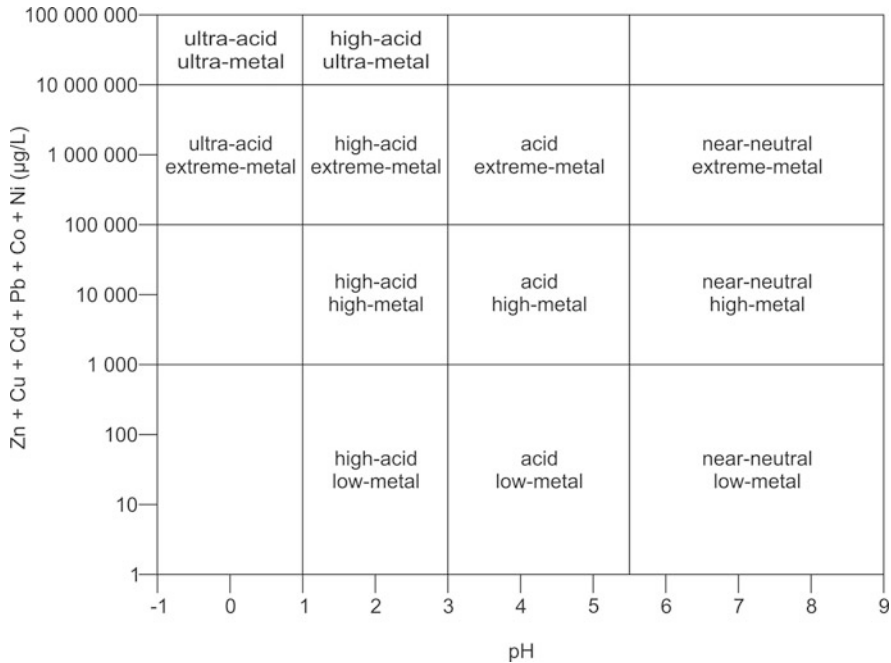


Fig. 3.6 Geochemical classification plot (Ficklin diagram) for waters based on the sum of dissolved metals (Zn, Cu, Cd, Pb, Co, Ni) and pH (after Ficklin et al. 1992; Plumlee et al. 1999)

- Alkalinity vs. acidity.** This scheme has been devised to allow classification of mine waters according to their treatability using passive treatment methods (Hedin et al. 1994a). It requires a knowledge of the alkalinity and acidity of the waters as determined by titration (Kirby and Cravotta 2005a, b). Estimates of the total acidity can also be made from water quality data using a formula (Hedin 2006). The literature offers various definitions for the terms *acidity* and *alkalinity* (cf. Table 3.2). Also, alkalinity can be defined as the total concentration (meq l⁻¹) of basic species in an aqueous solution, whereas acidity is the total concentration (meq l⁻¹) of acidic species in an aqueous solution (McAllan et al. 2009). The net or total acidity of mine waters consists of proton acidity (i.e. H⁺) and latent acidity caused by the presence of other acidic components. For example in coal mine waters, the acidic components are primarily accounted for by free protons (H⁺) and dissolved Fe²⁺, Fe³⁺, Al³⁺ and Mn²⁺ that may undergo hydrolysis (Hedin 2006). The alkalinity versus acidity categorization is useful for the selection of aerobic or anaerobic treatment methods as net acid waters require anaerobic treatment and net alkaline waters require aerobic remediation.
- Alkalinity vs. acidity and sulfate concentration.** This classification considers both the alkalinity and acidity as well as the sulfate content of mine waters (Younger 1995).

Table 3.3 Classification of mine waters based on pH (after Morin and Hutt 1997)

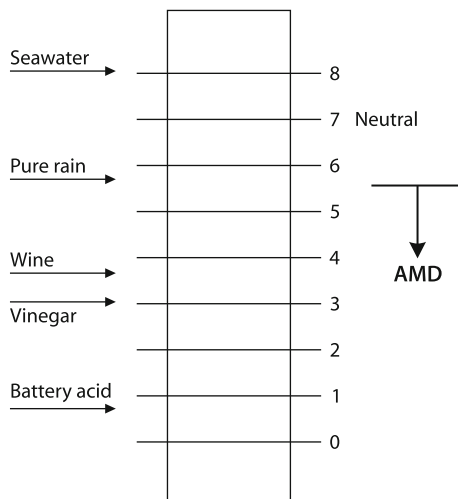
Class	Characteristics
Extremely acid	pH < 1. Extreme examples of acidities generated through sulfide oxidation and hydrolysis reactions. The rocks are distinctly enriched in pyrite and depleted in acid buffering materials
Acid	pH < 5.5. Acidity generated through oxidation of Fe-rich sulfides. Commonly found at base metal, gold and coal mines
Neutral to alkaline	pH 6–10. Acid producing and acid buffering reactions keep a pH balance, or abundant Fe-rich sulfides are absent. The drainage may become acid or alkaline with time upon exhaustion of acid producing or acid buffering minerals. High levels of alkalinity generated through dissolution of carbonates, alkali oxides, hydroxides, and silicates. Commonly found at diamond, base metal, gold, uranium, iron, coal and mineral sand mines
Saline	pH highly variable which influences the concentrations of aqueous ions. Associated with the mining of coal and industrial minerals, including evaporites such as potash, halite and borate

The above classifications have one or several short-comings: (a) the classifications do not include waters with neutral pH values and extraordinary salinities; (b) the schemes do not consider mine waters with elevated concentrations of arsenic, antimony, mercury, cyanide compounds, and other process chemicals; (c) the categorizations do not consider iron, manganese and aluminium which are present in major concentrations in AMD waters; and (d) routine water analyses do not include determinations of the Fe^{2+} and Fe^{3+} concentrations. Therefore, the categorizations are not inclusive of all mine water types. In this work, the simple classification scheme of Morin and Hutt (1997) has been modified (Table 3.3), and the following presentation of mine waters is given according to their pH.

3.4.1 Acid Waters

Oxidation of pyrite and other sulfides is the major contributor of hydrogen ions in mine waters, but a low pH is only one of the characteristics of AMD waters (Fig. 3.7). The oxidation of sulfide minerals does not only create acid, but it also liberates metals and sulfate into waters and accelerates the leaching of other elements from gangue minerals. As a consequence, AMD is associated with the release of sulfate, heavy metals (Fe, Cu, Pb, Zn, Cd, Co, Cr, Ni, Hg), metalloids (As, Sb), and other elements (Al, Mn, Si, Ca, Na, K, Mg, Ba, F). In general, AMD waters from coal mines typically contain much lower concentrations of heavy metals and metalloids than waters from base metal or gold deposits (Geldenhuis and Bell 1998).

Fig. 3.7 pH scale and comparison of AMD water with other familiar fluids (after Jambor et al. 2000b)



AMD waters are particularly characterized by exceptionally high sulfate ($>1000 \text{ mg l}^{-1}$), high iron and aluminium ($>100 \text{ mg l}^{-1}$), and elevated copper, chromium, nickel, lead and zinc ($>10 \text{ mg l}^{-1}$) concentrations. Dissolved iron and aluminium typically occur in significantly higher concentrations than the other elements. Elements such as calcium, magnesium, sodium, and potassium may also occur in strongly elevated concentrations. These latter elements are not of environmental concern themselves. However, they may limit the use of these waters because of their sodium content or their hardness. High sodium levels prevent the use of these waters for irrigation of soils, and the hardness influences the toxicity of heavy metals such as zinc.

Sulfide oxidation and the AMD process also form the basis for modern heap leach operations used to recover copper and uranium from geological ores. In these hydrometallurgical processes, copper and uranium ores are piled into heaps and sprinkled with acid leach solutions. Sulfuric acid is applied to dissolve the ore minerals (e.g. malachite, azurite, uraninite). Once the recovery of metals is complete, the heap leach piles are rinsed to reduce any contaminant loads (Ford 2000; Li et al. 1996; Shum and Lavkulich 1999). Despite rinsing, drainage waters emanating from spent heap leach piles can have high acidity, sulfate, metal, metalloid, and aluminium concentrations. In addition, sulfuric acid is used for the extraction of nickel from nickel laterite deposits and the production of synthetic rutile from placer deposits. Both processes result in the formation of acidic tailings. Finally, the presence of acid conditions in surface waters should not always be attributed to anthropogenic processes. Acidity of streams may also be caused by naturally occurring organic acids that are flushed from soils into surface waters. Therefore, acidic drainage waters are not exclusive to sulfidic wastes. In most cases, the acidity of mine waters is the result of sulfide oxidation.

3.4.2 *Extremely Acid Waters*

The pH of most drainages is buffered by acid neutralizing minerals. The buffering reactions ensure that AMD waters have pH values of greater than 1. There are, however, rare examples with drainage acidities of below pH 1, in extreme cases even with negative pH values (Nordstrom and Alpers 1999b; Nordstrom et al. 2000; Williams and Smith 2000). These waters not only contain exceptionally low pH values – in rare cases as low as -3 – they also exhibit extraordinarily high concentrations of iron, aluminium, sulfate, metals, and metalloids. The concentrations are so high that the waters are significantly over-saturated with mineral salts. Theoretically, precipitation of secondary minerals should occur. Precipitation of mineral salts from these waters is very slow, and the total ionic strengths of the waters exceed their theoretical maximum. Such conditions are referred to as *super-saturation*. Super-saturated AMD waters are generated from rocks distinctly enriched in pyrite and depleted in acid buffering carbonates. The acid buffering capacity of such rocks is minimal, and the formation of extremely acid mine waters is favoured by unhindered sulfide oxidation and hydrolysis reactions.

3.4.3 *Neutral to Alkaline Waters*

A low pH is not a universal characteristic of waters influenced by mining. The pH of mine waters extends to alkaline conditions, and the aqueous concentrations of anions and cations range from less than 1 mg l^{-1} to several $100,000 \text{ mg l}^{-1}$. In acid waters, sulfate is the principal anion, and iron, manganese and aluminium are major cations. In alkaline waters, sulfate and bicarbonate are the principal anions, and concentrations of calcium, magnesium, potassium and sodium are generally elevated relative to iron and aluminium (Rose and Cravotta 1998). Substantial concentrations of sulfate, metals (Cu, Cd, Fe, Hg, Mn, Mo, Ni, Pb, Tl, U, Zn), and metalloids (As, Sb, Se) have been documented in oxidized, neutral to alkaline mine waters (Ashley et al. 2003b; Carroll et al. 1998; Carvalho et al. 2009a; Cidu et al. 2007; Craw et al. 2004; Desbarats and Dirom 2007; Lindsay et al. 2009a; Lottermoser et al. 1997b, 1999; Pettit et al. 1999; Plumlee 1999; Plumlee et al. 1999; Scharer et al. 2000; Schmiermund 2000; Rollo and Jamieson 2006; Wilson et al. 2004; Younger 2000). Such waters are of environmental concern as they may adversely impact on the quality of receiving water bodies. Neutral to alkaline mine waters with high metal, metalloid, and sulfate contents can be caused by:

- Drainage from tailings repositories containing residues of alkaline leach processes or neutralized acidic tailings;
- Drainage from non-sulfidic ores and wastes;
- Drainage from sulfidic ores or wastes that have been completely oxidized during pre-mining weathering;
- Drainage from pyrite- or pyrrhotite-rich ores and wastes with abundant acid neutralizing minerals such as carbonate; and

- Drainage from sulfide ores or wastes depleted in acid producing sulfides (e.g. pyrite, pyrrhotite) and enriched in non-acid producing sulfides (e.g. galena, sphalerite, arsenopyrite, chalcocite, covellite, stibnite).

3.4.4 Coal Mine Waters

AMD waters of coal mines are characterized by low pH as well as high electrical conductivity, total dissolved solids, sulfate, nitrate, iron, aluminium, sodium, calcium and magnesium values (e.g. Zielinski et al. 2001; Vermeulen and Usher 2006; Cravotta 2008a, b). In addition, individual mine sites may have waters with elevated manganese and trace element values (Cravotta and Bilger 2001; Larsen and Mann 2005). Coal contains a range of trace elements and leaching of trace metals (e.g. Cd, Co, Cr, Cu, Li, Ni, Pb, Sr, Zn) and metalloids (e.g. As, B, Se) may impact on the receiving environment (e.g. Lussier et al. 2003; Søndergaard et al. 2007; Wu et al. 2009).

Mine waters of coal mines are not necessarily acid. Many mine waters of coal mines have near neutral pH values. However, such waters typically contain elevated total dissolved solids and exhibit high electrical conductivities (Foos 1997; Szczepanska and Twardowska 1999). Substantial concentrations of manganese have been documented for some near-neutral coal mine waters (Kruse and Younger 2009). Salt levels, particularly chloride concentrations, can be extreme. These saline waters originate from saline aquifers as dewatering of the mine may intersect deep saline formation waters. Also, atmospheric exposure of saline coals and marine sediments within the stratigraphic sequence, containing abundant salt crystals, will lead to the generation of saline mine waters. Such waters need to be contained on site. Discharge off-site should occur when suitable flow conditions in the receiving streams are achieved, and dilution of saline waters is possible.

In rare cases, coals have significant concentrations of uranium, thorium, and radioactive daughter products of the uranium and thorium decay series. Mine waters of such coals possess elevated radium-226 (Ra-226) levels. The dissolution of Ra-226 is possible if the waters contain low sulfate concentrations. This allows the dissolution of barium and radium (Ra-226) ions and causes elevated radiation levels (Pluta 2001; Schmid and Wiegand 2003).

3.5 Processes

There are several geochemical and biogeochemical processes which are important to mine waters, particularly to AMD waters. These processes, directly or indirectly, influence the chemistry of AMD waters. The processes are not exclusive to surface AMD environments and also operate below the surface in acid ground waters (e.g. Paschke et al. 2001).

3.5.1 Microbiological Activity

Conditions within AMD waters are toxic to *normal* aquatic biota. Thus, AMD waters are generally thought to be biologically sterile; however, they are hardly lifeless (Fig. 3.8). While AMD and AMD impacted waters are characterized by a limited diversity of plants, they display a great diversity of microorganisms. Microorganisms composed of all three domains of life (Archaea, Bacteria, Eukarya) are common and abundant in AMD waters (Fang et al. 2007; Johnson 1998a, b; Kim et al. 2009). The conditions in AMD waters are ideal for the proliferation of microorganisms (so-called *extremophiles*) that can thrive in these environments. For example, there are over 1300 different forms of microorganisms identified in the infamous acid waters of the Rio Tinto, Spain (Ariza 1998) (Case Study 3.1). The hostile environment also provides a niche for species that produce novel metabolites of potential significance and use to mankind. For example, the Berkeley acid pit lake contains microorganisms that generate metabolic compounds with selective anticancer activities (Stierle et al. 2004, 2006, 2007).

Bacteria isolated from AMD environments are numerous and include *Acidithiobacillus thiooxidans*, *Acidithiobacillus ferrooxidans*, *Leptospirillum ferrooxidans*, and *Thiobacillus thioparus* (Blowes et al. 1998; Gould and Kapoor 2003; Gould et al. 1994; Ledin and Pedersen 1996; Johnson 1998a, b; Nordstrom and Alpers 1999a). These bacteria function best in an acid, aerobic environment



Fig. 3.8 Acid-tolerant sedge (*Eleocharis equisetina*) growing in AMD waters (pH 2.7, EC 3.41 mS cm⁻¹) of an inactive tailings pond (Jumna tin mill, Australia)

(pH < 4). The bacteria need minor nitrogen and phosphorus for their metabolism, and they depend on the oxidation of Fe^{2+} , hydrogen sulfide, thiosulfate, sulfur, and metal sulfides for energy. They also transform inorganic carbon into cell building material (Ledin and Pedersen 1996). The inorganic carbon may originate from the atmosphere or from the dissolution of carbonates. The bacterial activity produces metabolic waste (i.e. sulfuric acid, Fe^{3+}) that accelerates the oxidation of sulfides (Sect. 2.3.1).

Algae are common organisms in AMD waters (Fig. 3.9). Such algae are not only capable of thriving in hostile AMD waters, they also remove metals and metalloids from solution. In addition, algae such as the protozoa *Euglena mutabilis* photosynthesize oxygen and contribute to dissolved oxygen in mine waters. This facilitates inorganic precipitation of iron and hence, the algae indirectly remove iron from AMD waters (Brake et al. 2001a, b). There are other life forms apart from bacteria and algae identified in AMD environments. For instance, a species of Archaea, *Ferroplasma acidarmanus*, has been found to thrive in exceptionally acid (pH 0), metal-rich waters (Edwards et al. 2000).

Certain microorganisms survive or even thrive in AMD environments because: (a) they tolerate elevated concentrations of dissolved metals and metalloids; and (b) they use the energy from the chemical oxidation reactions for their own growth. Furthermore, the microbes are capable of removing elements from AMD waters through adsorption and precipitation processes. The microbes thereby participate, actively or passively, in the removal of metals and metalloids from mine waters (Ferris et al. 1989; Johnson 1998a, b; Leblanc et al. 1996). For example, the bacterium *Acidithiobacillus ferrooxidans* oxidizes Fe^{2+} and promotes precipitation of iron as iron oxides and hydroxides (Ferris et al. 1989). Other microbes produce



Fig. 3.9 Streamers of filamentous algae (*Klebsormidium* sp.) growing in AMD waters (pH 4.2, 7.4 mg l^{-1} Cu in solution), Gulf Creek, Australia (Lottermoser et al. 1999). The algae contain up to 0.25 wt.% copper. Largest cobble is 20 cm long

oxygen, reduce sulfate to sulfide, actively precipitate metals outside their cells, or incorporate metals into their cell structure. Moreover, some microorganisms are capable of inducing the formation of *microbial* minerals such as ferrihyrite, schwertmannite and hydrozincite in AMD affected waters (Kim et al. 2002; Zuddas and Podda 2005). In extreme cases, the metals and metalloids accumulated by living microorganisms, or the dead biomass, may amount to up to several weight percent of the cell dry weight. In addition, organic matter and dead cells indirectly participate in the immobilization of metals. If any dead biomass accumulates at the bottom of an AMD stream or pond, its degradation will lead to anaerobic and reducing conditions. Under such conditions, most metals may precipitate as sulfides and become both insoluble and unavailable for mobilization processes.

In summary, all three major life groups (Archaea, Eukarya, Bacteria) on Earth are present as microorganisms in AMD environments. Some of these microorganisms accelerate the oxidation of sulfides whereas others adsorb and precipitate metals and metalloids from mine waters. Hence, microbes play an important role in the solubilization as well as immobilization of metals and metalloids in AMD waters.

3.5.2 *Precipitation and Dissolution of Secondary Minerals*

The precipitation of secondary minerals and of poorly crystalline and amorphous substances is common to AMD environments (Fig. 3.10) (Cortecci et al. 2008; Frau et al. 2009; Gammons 2006; Genovese and Mellini 2007; Kim and Kim 2003; McCarty et al. 1998; Romero et al. 2006a; Valente and Gomes 2009)

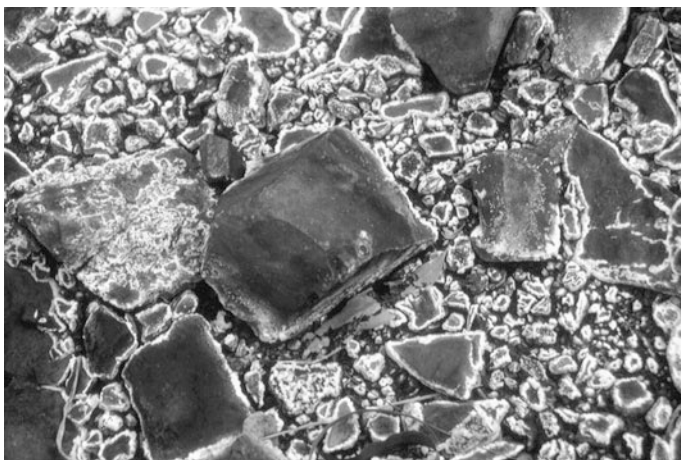
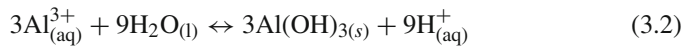
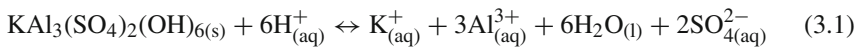


Fig. 3.10 Secondary minerals (iron oxyhydroxides, aluminium hydroxides, gypsum, jarosite) encrusting stream sediments of the acid Dee River (pH 3), downstream of the historic Mt. Morgan copper mine, Australia. Field of view 70 cm

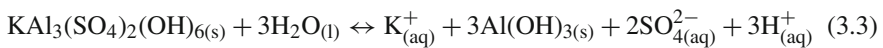
(Sect. 2.6). Common minerals include soluble metal salts (mainly sulfates), iron-hydroxysulfates (e.g. jarosite, schwertmannite), and iron-oxyhydroxides (e.g. ferrihydrite, goethite). The precipitation of solids is accompanied by a decrease of individual elements and compounds, resulting in lower total dissolved solids (TDS) in the mine waters.

The precipitated metal salts can also be redissolved. In particular, the exposure of soluble mineral salts to water, through ground water flow changes or rainfall events, will cause their dissolution. The secondary salts can be classified as *readily soluble*, *less soluble*, and *insoluble*. Examples of readily soluble secondary salts are listed in Table 3.4. Soluble salts can be further classified as *acid producing*, *non-acid producing*, and *acid buffering* phases. Above all, the formation of soluble Fe^{3+} and Al^{3+} salts as well as of Fe^{2+} , Fe^{3+} and Mn^{2+} sulfate salts influences the solution pH since their formation can consume or generate hydrogen ions (Sect. 2.6.3). However, such a classification scheme is too simplistic and does not consider the physical, chemical and biological environments in which the minerals dissolve. The solubility of secondary minerals is highly variable and primarily pH, Eh and solution chemistry dependent.

Jarosite-type phases can be viewed as less soluble phases as their dissolution is strongly influenced by the solution's pH (Smith et al. 2006). Their dissolution can be a two-step process. For example, alunite ($\text{KAl}_3(\text{SO}_4)_2(\text{OH})_6$) and jarosite ($\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$) dissolution initially consumes acid (Reaction 3.1). This may be followed by the precipitation of gibbsite ($\text{Al}(\text{OH})_3$), which generates acid (Reaction 3.2). The overall combined Reaction 3.3 illustrates that the dissolution of alunite and jarosite produces acid:



(Reaction 3.1 + Reaction 3.2 = Reaction 3.3)



Sulfate salts are particularly common in AMD environments and soluble under oxidizing conditions, especially the Ca, Mg, Fe^{2+} , Fe^{3+} and Mn^{2+} sulfate salts (Cravotta 1994; Jambor et al. 2000a, b). A decrease in pH is principally caused by the dissolution of Fe^{2+} sulfate salts, which are capable of producing acidity due to the hydrolysis of Fe^{3+} . For instance, melanterite ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) can control the acidity of mine waters (Frau 2000). Melanterite dissolution releases hydrogen ions as shown by the following equations (White et al. 1999):

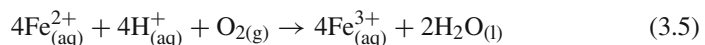
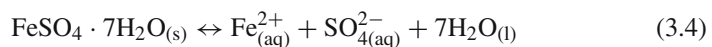
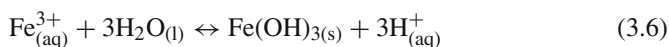
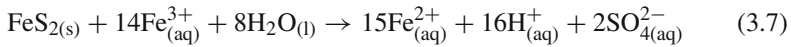


Table 3.4 Examples of soluble secondary minerals classified according to their ability to generate or buffer any acid upon dissolution (after Alpers et al. 1994; Keith et al. 1999)

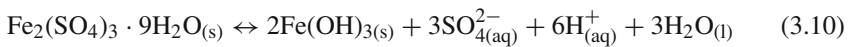
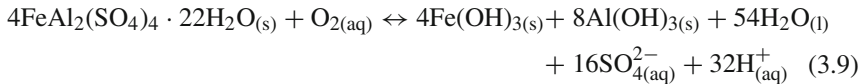
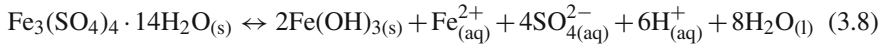
Acid producing soluble mineral		Formula
Fe ²⁺ and Mn ²⁺ sulfates	Melanterite	FeSO ₄ · 7H ₂ O
	Ferrohexahydrate	FeSO ₄ · 6H ₂ O
	Siderotil	FeSO ₄ · 5H ₂ O
	Rozenite	FeSO ₄ · 4H ₂ O
	Szomolnokite	FeSO ₄ · H ₂ O
	Apjohnite	MnAl ₂ (SO ₄) ₄ · 22H ₂ O
Mixed Fe ²⁺ –Fe ³⁺ sulfates and hydroxysulfates	Halotrichite	FeAl ₂ (SO ₄) ₄ · 22H ₂ O
	Copiapite	Fe ₅ (SO ₄) ₆ (OH) ₂ · 20H ₂ O
	Ferricopiapite	Fe ₅ (SO ₄) ₆ O(OH) ₂ · 20H ₂ O
	Bilinite	Fe ₃ (SO ₄) ₄ · 22H ₂ O
	Römerite	Fe ₃ (SO ₄) ₄ · 14H ₂ O
	Voltaite	K ₂ Fe ₈ Al(SO ₄) ₁₂ · 18H ₂ O
Fe ³⁺ sulfates	Rhomboclase	HFe(SO ₄) ₂ · 4H ₂ O
	Kornelite	Fe ₂ (SO ₄) ₃ · 7H ₂ O
	Coquimbite	Fe ₂ (SO ₄) ₃ · 9H ₂ O
Al ³⁺ hydroxysulfate Al sulfates	Jurbanite	Al(SO ₄)(OH) · 5H ₂ O
	Kalinite	K ₂ Al ₂ (SO ₄) ₄ · 22H ₂ O
	Pickeringite	MgAl ₂ (SO ₄) ₄ · 22H ₂ O
	Alunogen	Al ₂ (SO ₄) ₃ · 17H ₂ O
Non acid producing soluble mineral		Formula
Mg sulfates	Epsomite	MgSO ₄ · 7H ₂ O
	Hexahydrate	MgSO ₄ · 6H ₂ O
Zn sulfates	Goslarite	ZnSO ₄ · 7H ₂ O
	Bianchite	ZnSO ₄ · 6H ₂ O
	Gunningite	ZnSO ₄ · H ₂ O
Ca sulfates	Gypsum	CaSO ₄ · 2H ₂ O
	Bassanite	CaSO ₄ · 0.5H ₂ O
	Anhydrite	CaSO ₄
Cu sulfates	Chalcanthite	CuSO ₄ · 5H ₂ O
As minerals	Arsenolite	As ₂ O ₃
Acid buffering soluble mineral		Formula
Metal carbonates	Smithsonite	ZnCO ₃
	Otavite	CdCO ₃
	Malachite	Cu ₂ (CO ₃)(OH) ₂
	Azurite	Cu ₃ (CO ₃) ₂ (OH) ₂
	Hydrozincite	Zn ₅ (CO ₃) ₂ (OH) ₆



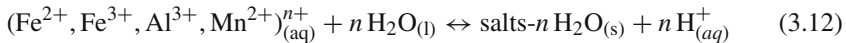
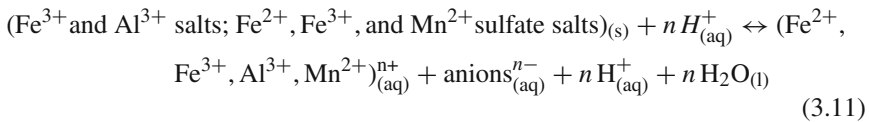
The release of Fe²⁺ into water does not necessarily result in only the precipitation of iron hydroxides but can also trigger more sulfide oxidation (Alpers and Nordstrom 1999; Keith et al. 1999; Plumlee 1999). The dissolution of melanterite releases Fe²⁺ which can be oxidized to Fe³⁺. Any pyrite may subsequently be oxidized by Fe³⁺ as shown by the following equation:



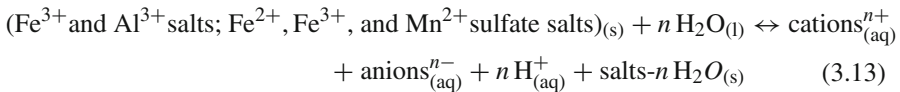
Similarly, the dissolution of r merite ($\text{Fe}_3(\text{SO}_4)_4 \cdot 14\text{H}_2\text{O}$), halotrichite ($\text{FeAl}_2(\text{SO}_4)_4 \cdot 22\text{H}_2\text{O}$), and coquimbite ($\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$) generates acid (Cravotta 1994; Rose and Cravotta 1998):



Generalized reactions for the dissolution of Fe^{3+} and Al^{3+} salts and of Fe^{2+} , Fe^{3+} , and Mn^{2+} sulfate salts can be written as follows:



(Reaction 3.11 + Reaction 3.12 = Reaction 3.13)



Iron sulfate minerals can be significant sources of acidity and sulfate when later dissolved. Release of Fe^{2+} from these salts can also trigger more sulfide oxidation. Furthermore, other forms of sulfur such as native sulfur (S^0) and thiosulfate ($\text{S}_2\text{O}_3^{2-}$) can be intermediate products that tend to be oxidized to sulfate under oxidizing conditions. Moreover, many of the secondary minerals allow substitution of iron and aluminium by numerous other metals (e.g. substitution of Fe by Cu and Zn in melanterite). As a result, dissolution of secondary minerals will lead to the release of major and minor metals, and metalloids (Lin 1997). For example, soluble Fe^{2+} sulfate salts (e.g. coquimbite, copiapite, bilinite, kornelite, r merite) can contain minor amounts of Fe^{3+} (Hurowitz et al. 2009). This Fe^{3+} is released upon dissolution of the mineral, and rapid hydrolysis of Fe^{3+} may then cause acidification (Hurowitz et al. 2009). By contrast, the dissolution of soluble aluminium (e.g. alunogen: $\text{Al}_2(\text{SO}_4)_3 \cdot 17\text{H}_2\text{O}$), magnesium (e.g. epsomite: $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$), or calcium sulfate minerals (e.g. gypsum: $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) does not generate any acid. Their dissolution does not influence mine water pH (Keith et al. 1999). Other soluble

secondary minerals are acid buffering, and a variety of metal carbonates such as smithsonite (ZnCO_3), malachite ($\text{Cu}_2(\text{CO}_3)(\text{OH})_2$), and azurite ($\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$) are effective acid consumers (Table 3.4).

The presence of soluble salts in unsaturated ground water zones of waste rock dumps, tailings dams, and other waste repositories is important because their dissolution will lead to a change in the chemistry of drainage waters. Evaporation, especially in arid and seasonally dry regions, causes the precipitation of secondary minerals which can store metal, metalloids, sulfate, and hydrogen ions. The formation of soluble secondary, sulfate-, metal- and metalloid-bearing minerals slows down sulfate, metal and metalloid mobility but only temporarily until the next rainfall (Bayless and Olyphant 1993; Keith et al. 1999).

Rapid dissolution of soluble salts and hydrolysis of dissolved Fe^{3+} may occur during the onset of the wet season or the beginning of spring. This in turn can result in exceptionally high sulfate, metal and metalloid concentrations as well as

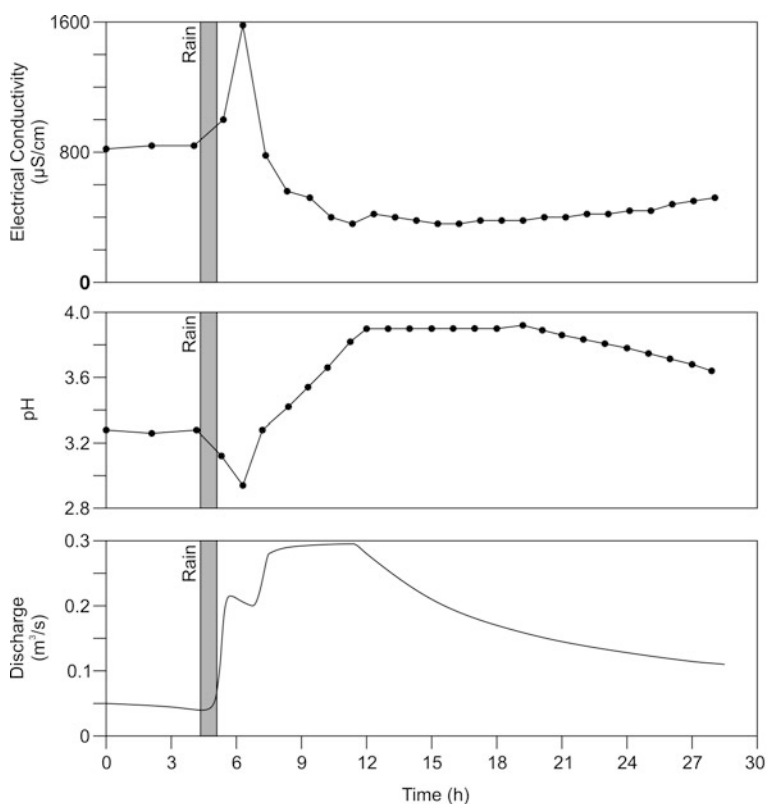


Fig. 3.11 Temporal variation of the discharge rate, pH and electrical conductivity (EC) of creek waters associated with the dissolution of mineral efflorescences during a storm event (after Seal and Hammarstrom 2003). The sudden decrease in pH and increase in discharge rate and EC after the rainfall event relate to the rapid dissolution of soluble acid-generating waste minerals. At AMD sites, the rise in EC generally reflects higher sulfate and metal values

strong acidity of waters during the initial flushing event (Kwong et al. 1997; Keith et al. 2001; Smuda et al. 2007; Søndergaard et al. 2007; Valente and Gomes 2009) (Fig. 3.11). Such rapid increases in dissolved element concentrations are referred to as *first flush* phenomena (e.g. Gzyl and Banks 2007; Nordstrom 2009). The concentrations of metals in these first flush waters are controlled by the solubilities of secondary phases and by the desorption of metals from mineral surfaces and particles. In particular, the dissolution of iron sulfate efflorescences releases incorporated sulfate, metals, metalloids, and acidity to ground and surface waters. The pH of drainage waters may eventually change to more neutral conditions due to increased dilution. Such neutral pH values will limit heavy metal mobility. Upon changes to drier conditions, evaporation will again cause the precipitation of secondary minerals.

This type of wetting and drying cycle can result in dramatic seasonal variations in acidity, and metal and metalloid concentrations of seepages and local streams (Bayless and Olyphant 1993; Cánovas et al. 2007; Desbarats and Dirom 2007; Ferreira da Silva et al. 2009; Keith et al. 1999; Pérez-López et al. 2008; Smuda et al. 2007; Søndergaard et al. 2007; Sarmiento et al. 2009a). Thus, the production of contaminant pulses at the onset of rainfall is common to mine sites in seasonally wet-dry climates. In these environments, seasonal variations in the chemistry of drainage waters from sulfidic mine wastes and mine workings are generally caused by the dissolution and precipitation of efflorescent salts and the adsorption and desorption of metals.

3.5.3 Coprecipitation

Coprecipitation refers to the removal of a trace constituent from solution which occurs at the same time as the precipitation of a major salt. This eventuates even when the solubility product of the trace constituent is not exceeded. The precipitating solid incorporates the minor constituent as an impurity into the crystal lattice. Various minerals can thereby host a wide variety of cations as *impurities*. The cations can be incorporated into the crystal lattice of the minerals via single or coupled substitution. For example, a large number of ions have been reported to substitute for iron in the goethite crystal lattice (e.g. Al, Cr, Ga, V, Mn, Co, Pb, Ni, Zn, Cd) (Cornell and Schwertmann 1996). Also, jarosite has been found to incorporate various elements into its mineral structure (e.g. Cu, Zn, Pb, K, Na, Ca) (Levy et al. 1997).

3.5.4 Adsorption and Desorption

Trace elements move between dissolved and particulate phases. Adsorption is the term which refers to the removal of ions from solution and their adherence to the surfaces of solids (Langmuir 1997). The attachment of the solutes onto the solid phases

does not represent a permanent bond, and the adsorption is based on ionic attraction of the solutes and the solid phases (Smith 1999). The solid phases can be of organic or inorganic composition and of negative or positive charge attracting dissolved cations and anions, respectively. Adsorption reactions are an important control on the transport, concentration and fate of many elements in waters, including AMD waters.

Adsorption may occur in various AMD environments (Bowell and Bruce 1995; Fuge et al. 1994; Jönsson et al. 2006a; Lee and Faure 2007; Stillings et al. 2008; Swedlund and Webster 2001). It may occur on iron- and aluminium-rich particulates and clay particles suspended in mine waters, on precipitates at seepage points, or on clayey sediments of stream beds and ponds. Different ions thereby exhibit different adsorption characteristics. Generally, solid compounds adsorb more anions at low pH and more cations at near neutral pH (Fig. 3.12). In addition, the kind of metal adsorbed and the extent of metal adsorption is a function of: (a) the solution pH; (b) the presence of complexing ligands; and (c) the metal concentration of the AMD. Arsenic and lead are the most effectively adsorbed metals at acid pH values, whereas zinc, cadmium, and nickel are adsorbed at near-neutral pH values (Plumlee et al. 1999). Therefore, when AMD waters are gradually neutralized, various secondary minerals precipitate and adsorb metals. Adsorption is selective, and the chemical composition of the water changes as the pH increases. Ions are removed from solution by this process, and metal-rich sediment accumulates.

While sediment may remove ions from solution, it may also release adsorbed metals if the water is later acidified. In contrast, other elements such as arsenic and molybdenum may desorb at near-neutral or higher pH values to form oxy-anions in the water (e.g. AsO_4^{3-}) (Jönsson and Lövgren 2000). Similarly, uranium, copper, and lead may desorb at near-neutral or higher pH values to form aqueous

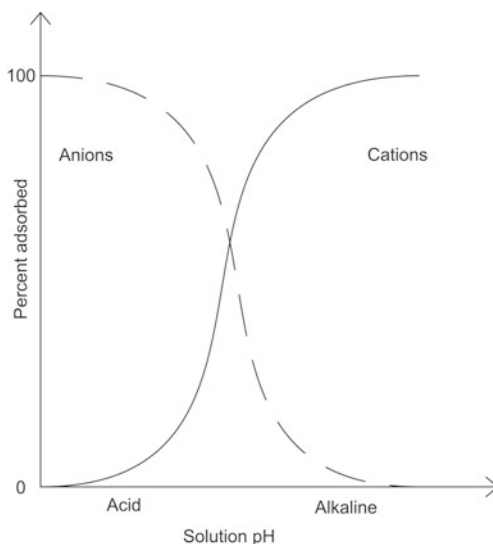


Fig. 3.12 Simplified diagram showing the adsorption for cations and anions on a metal-oxide mineral (after Smith 1999)

carbonate complexes. Sulfate may also be released from ferric precipitates if pH values raise to neutral or even alkaline values (Plumlee et al. 1999; Rose and Elliott 2000). As a result, sulfate, metal, and metalloid ions desorb and regain their mobility at near-neutral or alkaline pH values, and dissolved sulfate, metal, and metalloid concentrations of mine waters may in fact increase with increasing pH.

Sorption sites of particulates represent only temporary storage facilities for dissolved metals, metalloids and sulfate. In a worst case scenario, if excessive neutralization is used to treat AMD effected streams, sulfate, metals, and metalloids previously fixed in stream sediments may then be redissolved by the treated water. Thus, remediation of AMD waters should raise the pH only to values necessary to precipitate and adsorb metals.

3.5.5 Eh-pH Conditions

The solubility of many dissolved heavy metals is influenced by the pH of the solution. The generation of low pH waters due to sulfide oxidation, or the presence of process chemicals such as sulfuric acid, enhances the dissolution of many elements. This acidity significantly increases the mobility and bioavailability of elements, and the concentration of total dissolved solids in mine waters. Most of the metals have increasing ionic solubilities under acid, oxidizing conditions, and the metals are not adsorbed onto solids at low pH. In many cases, the highest aqueous concentrations of heavy metals are associated with oxidizing, acid conditions.

Precipitation of many of the dissolved metals occurs during neutralization of low pH drainage waters, for example, due to mixing with tributary streams or due to the movement of the seepage water over alkaline materials such as carbonate bedrocks. The metals are adsorbed onto solid phases, particularly precipitating iron-rich solids. Alternatively, the metals are incorporated into secondary minerals coating the seepage area or stream bed. Generally, as pH increases, aqueous metal species are inclined to precipitate as hydroxide, oxyhydroxide or hydroxysulfate phases (Berger et al. 2000; Munk et al. 2002). The resultant drainage water contains the remaining dissolved metals and products of the buffering reactions. Therefore, with increasing pH the dissolved metal content of mining influenced waters decreases.

The ability of water to transport metals and metalloids is not only controlled by pH but also by the Eh of the solution. The reduction-oxidation potential as measured by Eh affects the mobility of those metals and metalloids which can exist in several oxidation states (Table 3.5). Metals such as chromium, molybdenum, selenium, vanadium, and uranium are much more soluble in their oxidized states (e.g. U^{6+} , Cr^{6+}) as oxy-anions rather than in their reduced states (e.g. U^{4+} , Cr^{3+}). Oxygenated water may oxidize metals present in their reduced, immobile state and allow their mobility as oxy-anions. These salient aspects of aqueous element chemistry are commonly described by Eh-pH diagrams. The diagrams illustrate the stability and instability of minerals under particular Eh-pH conditions and show the ionic element species present in solution (Brookins 1988).

Table 3.5 Simplified dissolution characteristics of selected elements in surface waters (after Smith and Huyck 1999)

Element	Forming oxy-anions in water	Forming cations in water	Sensitive to oxidation/reduction
Aluminium (Al)		X	
Antimony (Sb)	X		X
Arsenic (As)	X		X
Barium (Ba)		X	
Beryllium (Be)		X	
Boron (B)	X		
Cadmium (Cd)		X	
Chromium (Cr)	X	X	X
Cobalt (Co)		X	
Copper (Cu)		X	X
Iron (Fe)		X	X
Lead (Pb)		X	X
Manganese (Mn)		X	X
Mercury (Hg)		X	X
Molybdenum (Mo)	X		X
Nickel (Ni)		X	
Selenium (Se)	X		X
Silver (Ag)		X	
Thorium (Th)		X	X
Uranium (U)	X		X
Vanadium (V)	X		X
Zinc (Zn)		X	

While neutralization of AMD causes the removal of most metals, oxidized neutral to alkaline mine waters are known to contain elevated metal and metalloid concentrations. In fact, oxidized neutral to alkaline mine waters can have very high metal (Cd, Cu, Hg, Mn, Mo, Ni, U, Zn) and metalloid (As, Sb, Se) values (Carroll et al. 1998; Lottermoser et al. 1997b, 1999; Pettit et al. 1999; Plumlee 1999; Plumlee et al. 1999; Scharer et al. 2000; Schmiermund 2000; Younger 2000). Such waters are of environmental concern because the elements tend to remain in solution, despite pH changes. In particular, elements that form oxy-anions in water (e.g. As, Se, Sb, Mo, V, W) are rather mobile under neutral pH conditions (Table 3.5). The elements can be carried for long distances downstream of their source, and they may adversely impact on the quality of receiving water bodies.

3.5.6 Heavy Metals

The oxidation of various sulfide minerals will release their major and trace elements, including numerous heavy metals (Table 2.1). In some cases, the degradation of organic matter particularly in carbonaceous rocks (i.e. black shales)

may release metals such as nickel to pore and drainage waters (e.g. Falk et al. 2006; Wengel et al. 2006). As a result, elevated concentrations of one or more heavy metals are characteristic of waters in contact with oxidizing sulfidic and carbonaceous rocks. The controls on heavy metal concentrations in mine waters are numerous, highly metal specific, and controlled by environmental conditions such as pH.

Heavy metals can occur in various forms in AMD waters (Fig. 3.13). A metal is either dissolved in solution as ion and molecule, or it exists as a solid mass. Dissolved metal species include cations (e.g. Cu^{2+}), simple radicals (e.g. UO_2^{2+}), and inorganic (e.g. CuCO_3) and organic complexes (e.g. $\text{Hg}(\text{CH}_3)_2$). Metals may also be present in a solid form as substitutions in precipitates (e.g. Cu in eugsterite $\text{Na}_4\text{Ca}(\text{SO}_4)_3 \cdot 2\text{H}_2\text{O}$), as mineral particles (e.g. cerussite PbCO_3), and in living biota (e.g. Cu in algae) (Brownlow 1996; Smith and Huyck 1999). There is also a transitional state whereby very small particles, so-called *colloids*, are suspended in water (Stumm and Morgan 1995). A colloid can be defined as a stable electrostatic suspension of very small particles ($<10 \mu\text{m}$) in a liquid (Stumm and Morgan 1995). The mineralogical composition of colloids can be exceptionally diverse and includes parent rock as well as organic and inorganic substances. Metals can be

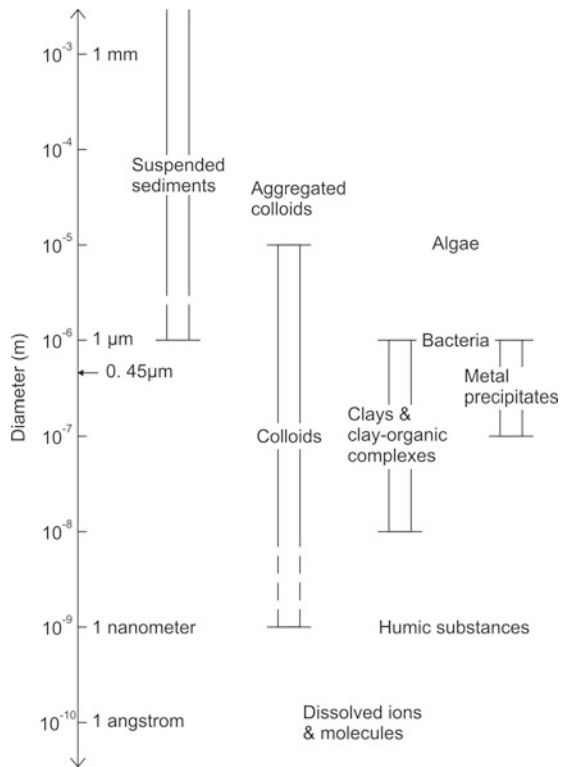


Fig. 3.13 Size spectrum of solutes, colloids and particles in waters (after Stumm and Morgan 1995)

incorporated into organic (e.g. Pb fulvic acid polymers) or inorganic colloids (e.g. FeOOH), or are adsorbed onto parent rock particles (e.g. Ni on clays). The stability of these colloids is influenced by a range of physical, chemical and biological changes of the solution (Brownlow 1996; Ranville and Schmiermund 1999). Upon such changes, colloids will aggregate into larger particles; that is, they undergo *floc-culation* and occur as *suspended particles* in the water. Iron- and aluminium-rich colloids and suspended particles are especially common in AMD waters (Filella et al. 2009; Schemel et al. 2000; Suteerapataranon et al. 2006; Zänker et al. 2002).

Metals may be transported in mine waters in various speciations (Lachmar et al. 2006). In AMD waters, most metals occur as simple metal ions or as sulfate complexes. In neutral and alkaline mine waters, elevated metal and metalloid concentrations are promoted by the formation of oxy-anions (e.g. AsO_4^{3-}) and aqueous metal complexes (e.g. U carbonate complexes, Zn sulfate and hydroxide complexes) as well as the lack of adsorption onto and coprecipitation with secondary iron hydroxides (Plumlee et al. 1999).

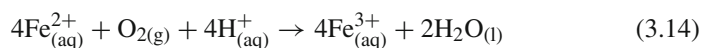
The size of the metal species progressively increases from cation to metal particle in living biota. The different size of the metal species and the common procedure to filter water prior to chemical analysis have a distinct implication on the analytical result. A common filter pore size used is 0.45 μm . Such filters will allow significant amounts of colloidal material to pass through, and analyses of these samples will reflect dissolved and colloidal constituents (Brownlow 1996; Ranville and Schmiermund 1999). For this reason, the collection of both unfiltered and filtered water samples has been suggested (Butler et al. 2008; Ranville and Schmiermund 1999). If significant differences are found in the metal concentrations, it is possible that the metals are transported via colloids and suspended particles. If detailed information on the speciation and bioavailability of metals is needed, other analytical methods need to be performed, including ultrafiltration and the use of exchange resins or Diffusive Gradients in Thin Films (DGTs) (Balistrieri et al. 2007; Casiot et al. 2009; Jung et al. 2006; Søndergaard 2007).

3.5.7 The Iron System

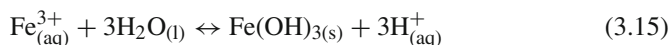
Elevated iron concentrations in mine waters are an obvious by-product of the oxidation of pyrite, pyrrhotite or any other iron-bearing sulfide. Dissolved iron is found in two oxidation states, ferrous (Fe^{2+}) and ferric (Fe^{3+}). Iron may also combine with organic and inorganic ions, so iron can be present in mine waters in several forms (e.g. Fe^{2+} , Fe^{3+} , $\text{Fe}(\text{OH})^{2+}$, $\text{Fe}(\text{OH})_2^+$, $\text{Fe}(\text{SO}_4)^+$, $\text{Fe}(\text{SO}_4)_2^-$).

Upon weathering of iron-bearing sulfides, iron enters the solutions as Fe^{2+} . Pore and drainage waters of sulfidic materials are commonly oxygen deficient, and reducing conditions are often prevalent. The rate of iron oxidation from Fe^{2+} to Fe^{3+} is now controlled by the pH of the mine water, the amount of dissolved oxygen, and the presence of iron oxidizing bacteria. Under reducing abiotic conditions and as long as the pH of the water remains less than approximately 4–4.5, the dissolved iron will

remain in the ferrous state. Abiotic oxidation of Fe^{2+} to Fe^{3+} is relatively slow and strongly inhibited at a pH less than approximately 4.5 (Ficklin and Mosier 1999). However, in the presence of iron oxidizing bacteria, the oxidation rate of Fe^{2+} to Fe^{3+} is increased by five to six orders of magnitude over the abiotic rate (Singer and Stumm 1970). Therefore, AMD waters with bacteria, low dissolved oxygen concentrations, and acid to near neutral pH values can have elevated iron concentrations, with iron present as a mixture of Fe^{2+} and Fe^{3+} . Significant dissolved concentrations of Fe^{3+} only occur at a low pH; the exact pH value depends on the iron and sulfate contents of the mine water. The Fe^{2+} and Fe^{3+} ions participate in the oxidation of sulfides (Sect. 2.3.1). Alternatively, in the presence of abundant molecular oxygen and above pH values of approximately 3, the Fe^{2+} is oxidized to Fe^{3+} as illustrated in the following oxidation reaction:



This Fe^{3+} will become insoluble and precipitates as ferric hydroxide, oxyhydroxide, and oxyhydroxysulfate colloids and particulates. The precipitation occurs as a result of the following hydrolysis reaction:



This reaction also generates hydrogen acidity. If appreciable amounts of Fe^{2+} are present in neutral mine drainage waters, oxidation of the Fe^{2+} to Fe^{3+} will result in precipitation of large amounts of Fe^{3+} hydroxides, and the neutral solution will become acid due to abundant hydrolysis reactions (Reaction 3.15). Oxidation of Fe^{2+} (Reaction 3.14) and hydrolysis of Fe^{3+} (Reaction 3.15) do not take place until the water is aerated. Nevertheless, further Fe^{2+} may be oxidized without the help of oxygen by oxidation at the surface of previously formed Fe^{3+} hydroxides. Such an iron removal process is referred to as *autocatalytic iron oxidation*.

The dissolved iron concentration and speciation (i.e. Fe^{2+} or Fe^{3+}) are strongly Eh and pH dependent. In addition, the dissolved iron concentration of AMD waters is influenced by factors other than the presence of iron oxidizing bacteria. For example, solar radiation and associated photolytic processes increase the dissolved Fe^{2+} and reduce the dissolved Fe^{3+} . Iron photoreduction involves the absorption of UV radiation by Fe^{3+} species, resulting in Fe^{2+} and OH^{-} ions. As a consequence, the colloidal Fe^{3+} hydroxide concentrations in oxygenated surface waters can be reduced during daytime or summer (Nordstrom and Alpers 1999a). While seasonal variations in the composition of AMD waters are typically controlled by climatic factors (e.g. evaporation, precipitation, runoff events and volumes) (Herbert 2006), other factors such as the water temperature can also impact indirectly on the chemistry of mine waters. Higher water temperatures favour the optimum rate of bacterially mediated iron oxidation (Butler and Seitz 2006).

AMD waters typically precipitate iron hydroxides, oxyhydroxides or oxyhydroxysulfates (Reaction 3.17) which are collectively termed *ochres*, *boulder coats*, or with the rather affectionate term *yellow boy*. The iron solids commonly occur as

colourful bright reddish-yellow to yellowish-brown stains, coatings, suspended particles, colloids, gelatinous flocculants, and precipitates in AMD affected waters, streams and seepage areas (e.g. Cravotta 2008a; Genovese and Mellini 2007; Kim and Kim 2004; Kumpulainen et al. 2007; Jönsson et al. 2006b; Lee and Chon 2006; Sánchez España et al. 2005; Peretyazhko et al. 2009; Zänker et al. 2002). The poor crystallinity of ochre precipitates has led some authors to the conclusion that these substances should be referred to as *amorphous ferric hydroxides* or *hydrous ferric oxides* (i.e. HFO). The iron precipitates, in fact, consist of a variety of amorphous, poorly crystalline and/or crystalline Fe^{3+} hydroxides, oxyhydroxides and oxyhydroxysulfate minerals. Mixed valent Fe^{2+} - Fe^{3+} oxyhydroxides (so-called *green rusts*) may also occur (Ahmed et al. 2008; Mazeina et al. 2008; Zegeye et al. 2007). Moreover, the ochres may contain other crystalline solids including sulfates, oxides, hydroxides, arsenates, and silicates (Table 2.5).

Iron minerals such as jarosite ($\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$), ferrihydrite ($\text{Fe}_5\text{HO}_8 \cdot 4\text{H}_2\text{O}$), schwertmannite ($\text{Fe}_8\text{O}_8(\text{SO}_4)(\text{OH})_6$), and the FeOOH polymorphs goethite, feroxyhyte, akaganéite, and lepidocrocite are very common (Fig. 3.14). Different iron minerals appear to occur in different AMD environments (Bigham 1994; Bigham et al. 1996; Carlson and Kumpulainen 2000; Jönsson et al. 2006b) (Fig. 3.15). Low pH (<3), high sulfate concentrations (>3000 mg l^{-1}) and sustained bacterial activity cause the formation of jarosite. Schwertmannite is most commonly associated with mine effluents with pH from 2 to 4 and medium dissolved sulfate concentrations (1000–3000 mg l^{-1}), whereas ferrihydrite is associated with mine drainage with a pH of about 6 and higher (Bigham 1994; Bigham et al. 1996; Bigham and Nordstrom 2000; Carlson and Kumpulainen 2000; Lee et al. 2002; Murad and Rojik 2003; Sánchez España et al. 2005). Goethite (α - FeOOH) may be formed at near neutral conditions, or when low pH ($\text{pH} < 4$), low sulfate (<1000 mg l^{-1}) solutions are neutralized by carbonate-rich waters. Whether such a simplified iron mineral occurrence is valid remains to be confirmed with further field and laboratory studies. The mineralogy of secondary iron precipitates is complex

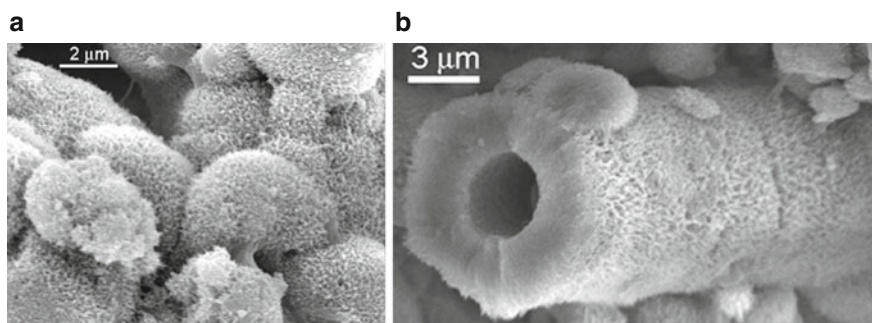


Fig. 3.14 Scanning electron microscopy photographs of fine-grained schwertmannite ($\text{Fe}_8\text{O}_8(\text{SO}_4)(\text{OH})_6$) showing: (a) the characteristic pin-cushion texture and (b) a hollow tubular texture (Oakey Creek impacted by AMD, Australia) (Photos courtesy of D. Harris)

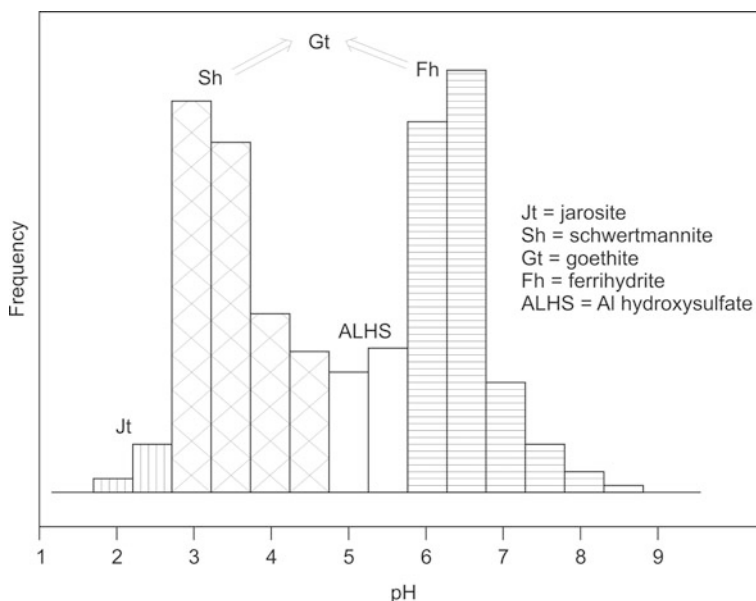


Fig. 3.15 Simplified distribution of Fe and Al phases in coal mine drainage waters (after Bigham and Nordstrom 2000)

and depends on solution composition, pH, temperature, redox conditions, and the rate of Fe^{2+} oxidation (Alpers et al. 1994; Blodau and Gatzek 2006; Knorr and Blodau 2007; Jönsson et al. 2005, 2006a).

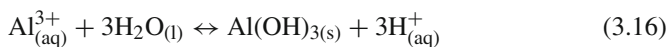
Various soluble Fe^{2+} sulfates such as melanterite precipitate from AMD waters. These secondary salts can be regarded as intermediate phases. Melanterite may dehydrate to less hydraous Fe^{2+} sulfates. The Fe^{2+} of these reduced minerals will eventually be oxidized and hydrolyzed to form one or more of the FeOOH polymorphs. Also, when iron is precipitated from solutions enriched in sulfate, these anions often combine with hydroxyl (OH^-) to form metastable schwertmannite. Schwertmannite may convert to goethite as it is metastable with respect to goethite (Acero et al. 2006; Davidson et al. 2008; Schroth and Parnell 2005). Similarly, ferrihydrite and the goethite polymorphs feroxyhyte, akaganéite, and lepidocrocite are thought to be metastable. Over time, they may ultimately convert and recrystallize forming goethite and hematite, respectively (Bigham et al. 1996; Murad et al. 1994; Rose and Cravotta 1998; Yee et al. 2006). Therefore, a distinct paragenetic sequence of secondary iron minerals may occur (Jerz and Rimstidt 2003).

The formation of secondary iron minerals also impacts on the behaviour of other elements. Freshly precipitated iron minerals have a fine particle size and a large surface area which favours the adsorption of metals. In addition, coprecipitation of metals occurs with the formation of the secondary solids. As a result, the iron ochre minerals can contain significant concentrations of metals through coprecipitation

and adsorption. The precipitates may contain apart from iron and sulfur a number of other elements (e.g. Al, Cr, Co, Cu, Pb, Mn, Ni, REE, Sc, U, Y, Zn) due to coprecipitation and adsorption processes (Dinelli et al. 2001; Lee and Chon 2006; Lee et al. 2002; Schroth and Parnell 2005; Sidenko and Sherriff 2005; Swedlund et al. 2003; Regenspurg and Pfeiffer 2005; Rose and Ghazi 1998). In particular, arsenic readily adsorbs to and is incorporated into precipitated iron minerals (Foster et al. 1998). These metal-rich suspended particles and colloidal materials may be deposited in stream sediments or transported further in ground and surface waters. Colloidal iron precipitates are exceptionally small. Therefore, such materials with adsorbed and incorporated trace elements can represent important transport modes for metals and metalloids in mine environments and streams well beyond the mine site (Schmiermund 1997; Smith 1999).

3.5.8 The Aluminium System

High aluminium and silicon concentrations in acid waters derive from the weathering of aluminosilicate minerals such as clays, or from the dissolution of secondary minerals such as alunite ($\text{KAl}_3(\text{SO}_4)_2(\text{OH})_6$). Aluminium is least soluble at a pH between 5.7 and 6.2; above and below this range aluminium may be solubilized. Dissolved aluminium is found in only one oxidation state as Al^{3+} . Aluminium may combine with organic and inorganic ions; hence, it can be present in mine waters in several forms (e.g. Al^{3+} , $\text{Al}(\text{OH})^{2+}$, $\text{Al}_2(\text{OH})_2^+$, $\text{Al}_2(\text{OH})_2^{4+}$, $\text{Al}(\text{SO}_4)^+$, $\text{Al}(\text{SO}_4)_2^-$) (Nordstrom and Alpers 1999a). Aluminium is similar to iron in its tendency to precipitate as hydroxides, oxyhydroxides, and oxyhydroxysulfates in waters which have increased their pH from acid to near neutral conditions. These precipitated phases are predominantly amorphous, colloidal substances. The poor crystallinity of these precipitates has led some authors to the conclusion that these substances should be referred to as *hydrous aluminium oxides* (i.e. HAO). Aggregation of these phases may eventually form microcrystalline gibbsite ($\text{Al}(\text{OH})_3$) and other solids (Munk et al. 2002; Schemel et al. 2000, 2007). Dissolved aluminium concentrations are strongly pH dependent, and the formation of secondary aluminium minerals, colloids, and amorphous substances controls the aqueous aluminium concentrations (Nordstrom and Alpers 1999a). While a change to more neutral pH conditions results in the precipitation of aluminium hydroxides, the formation of aluminium hydroxides such as gibbsite also generates acid. The dissolved trivalent aluminium thereby hydrolyses in a manner similar to ferric iron:

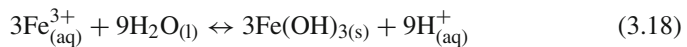
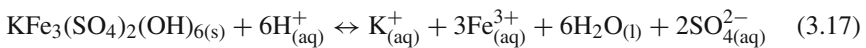


The solid phase resulting from Reaction (3.16) typically forms a white precipitate, which is commonly amorphous and converts to gibbsite upon ageing. In aqueous environments with turbulence, the phase may occur as white foam floating on the water surface (Fig. 3.16). As in the case of dissolved iron, flocculation and precipitation of dissolved aluminium will add colloidal and suspended matter to

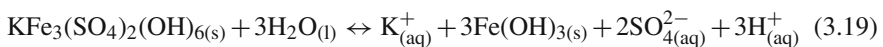


Fig. 3.16 Aluminium hydroxide phases floating as freshly formed white froth on AMD waters (Herberton tin tailings dam, Australia)

the water column, causing increased turbidity. In some mine waters, the aluminium concentrations are limited by the precipitation of aluminium-bearing sulfate minerals such as jarosite. Jarosite ($\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$) forms a solid solution with alunite ($\text{KAl}_3(\text{SO}_4)_2(\text{OH})_6$), and alunite-jarosite minerals commonly form because of evaporation of AMD seepage and pore waters (Alpers et al. 1994). Jarosite is a diagnostic yellow precipitate and occurs in mine drainage waters at pH values of less than 2.5 (Bigham 1994). The most prevalent type of jarosite is a potassium-type formed with available dissolved K^+ in the system. Other jarosite-type phases include the sodium-rich natrojarosite and the lead-rich plumbojarosite. The Al^{3+} , K^+ and Na^+ derive from dissolved ions in solution or from the decomposition of alkali feldspars, plagioclase, biotite, and muscovite. Jarosite-type phases are a temporary storage for acidity, sulfate, iron, aluminium, alkalis, and metals. The minerals release these stored components upon redissolution in a strongly acid environment and form solid Fe^{3+} hydroxides, according to the following equilibrium reactions (Hutchison and Ellison 1992; Levy et al. 1997):



(Reaction 3.17 + Reaction 3.18 = Reaction 3.19)



3.5.9 The Arsenic System

Elevated arsenic concentrations are commonly found in tailings and sulfidic mine wastes of gold, copper-gold, tin, lead-zinc, and some uranium ores. The common occurrence of arsenic in gold deposits is explained by the similar solubility of arsenic and gold in the ore forming fluids. Consequently, mine waters of many gold mining operations are enriched in arsenic (Craw and Pacheco 2002; Lazareva et al. 2002; Gieré et al. 2003; Marszalek and Wasik 2000; Serfor-Armah et al. 2006; Pfeifer et al. 2007). Arsenic in mine waters generally originates from the oxidation of arsenopyrite (FeAsS), orpiment (As_2S_3), realgar (AsS), enargite (Cu_3AsS_4), tennantite ($(\text{Cu,Fe})_{12}\text{As}_4\text{S}_{13}$), arsenical pyrite and marcasite (FeS_2) (Corkhill and Vaughan 2009; Corkhill et al. 2008; Foster et al. 1998; Lengke et al. 2009; McKibben et al. 2008; Morin and Calas 2006; O'Day 2006; Roddick-Lanzilotta et al. 2002). Oxidation of these primary sulfides results in the release of arsenic, sulfate and metals. Consequently, weathering of arsenic-bearing mine wastes leads to the formation of secondary arsenic minerals (e.g. scorodite, $\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$; arsenolite, As_2O_3 ; pharmacolite, $\text{Ca}(\text{AsO}_3\text{OH}) \cdot 2\text{H}_2\text{O}$), minerals containing minor amounts of arsenic (e.g. Fe^{3+} hydroxides and oxyhydroxides, jarosite), and amorphous phases (Courtin-Nomade et al. 2003; Petrunic et al. 2006). The variable solubility of these arsenic minerals and phases influences the chemical mobility and the bioaccessibility of arsenic in mine wastes and waste-contaminated soils and sediments (Groisbois et al. 2007; Slowey et al. 2007; Haffert and Craw 2008a, b; Walker et al. 2009). This in turn impacts on the abundance of arsenic in mine waters and impacted streams.

The aqueous chemistry of arsenic differs significantly from that of heavy metals. Mobilization of heavy metals is controlled by pH and Eh conditions and occurs primarily in low pH, oxidizing environments. In contrast, arsenic is mobile over a wide pH range (i.e. extremely acid to alkaline), and mine waters of an oxidized, neutral to alkaline pH nature can contain several mg l^{-1} of arsenic (Marszalek and Wasik 2000; Roddick-Lanzilotta et al. 2002; Williams 2001). Thus, contamination of mine waters by arsenic is not exclusive to AMD waters.

Arsenic exists in natural waters in two principal oxidation states, as As^{3+} in arsenite (AsO_3^{3-}) and as As^{5+} in arsenate (AsO_4^{3-}) (O'Day 2006; Yamauchi and Fowler 1994). In oxygenated environments, As^{5+} is the stable species. In more reduced environments, As^{3+} is the dominant form. The more reduced species As^{3+} is more soluble, mobile and toxic than As^{5+} (Yamauchi and Fowler 1994). The oxidation of As^{3+} to As^{5+} is relatively fast and increases with pH and salinity and in the presence of particular bacteria and protozoa (Casiot et al. 2003, 2004; Morin and Calas 2006). Thus, the relative proportions of As^{3+} and As^{5+} in mine waters are governed by Eh, pH and the presence/absence of microorganisms.

Iron exerts an important control on the mobility of arsenic in water (Bednar et al. 2005; Egal et al. 2009; Paktunc et al. 2008; Slowey et al. 2007). In an oxidizing environment with a pH greater than 3, hydrous ferric oxides (HFO) are abundantly precipitated. Dissolved arsenic species are adsorbed by and coprecipitated with these ferric hydroxides, and As^{5+} is thereby more strongly sorbed than As^{3+}

(Manceau 1995; O'Day 2006; Roddick-Lanzilotta et al. 2002). Adsorption onto and coprecipitation with Fe^{3+} hydroxides and oxyhydroxides are very efficient removal mechanisms of arsenic from mine waters. The formation of jarosite, schwertmannite and ferrihydrite may also remove arsenic from solution (Courtin-Nomade et al. 2005; Fukushi et al. 2003; Gault et al. 2005; Majzlan et al. 2007; Slowey et al. 2007). In general, precipitation of Fe^{3+} from mine waters is accompanied by a reduction in the concentration of dissolved arsenic.

The solubility of arsenic is not only influenced by its strong sorption affinity for iron hydroxide and oxyhydroxide minerals, it is also limited by: (a) the adsorption of arsenic onto minerals such as calcite or clays; (b) the formation of amorphous arsenic phases and secondary arsenic minerals such as scorodite ($\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$), arsenolite (As_2O_3), or iron-calcium arsenates such as pharmacolite ($\text{Ca}(\text{AsO}_3\text{OH}) \cdot 2\text{H}_2\text{O}$); and (c) the substitution of arsenic for sulfate in jarosite and gypsum, and for carbonate in calcite (Foster et al. 1998; Gieré et al. 2003; Haffert and Craw 2008a; Lee et al. 2005; Morin and Calas 2006; Román-Ross et al. 2006; Savage et al. 2000). In turn, the dissolution of arsenic salts will lead to arsenic release and mobilization. For instance, arsenolite (As_2O_3) is a high solubility phase that readily liberates arsenic into waters (Williams 2001). Also, scorodite is a common arsenic mineral which is formed during the oxidation of arsenopyrite-rich wastes. Scorodite solubility is strongly controlled by pH (Bluteau and Demopoulos 2007; Krause and Ettl 1988). It is soluble at very low pH; its solubility is at its minimum at approximately pH 4; and the solubility increases above pH 4 again. Hence, scorodite leads to the fixation of arsenic at approximately pH 4 whereas waters of low pH (<pH 3) and high pH (>pH 5) can contain significant amounts of arsenic.

While precipitation of secondary arsenic minerals and adsorption can limit the mobility of arsenic, the mobilization of arsenic from minerals back into mine waters may be triggered through various processes. Important processes include: (a) dissolution of arsenic minerals (i.e. arsenates, scorodite); (b) ageing of arsenic-rich amorphous material to more crystalline phases; (c) desorption at alkaline, oxidizing conditions; (d) desorption from Fe^{3+} hydroxides at acid or reducing conditions; and (e) acid or reductive dissolution of Fe^{3+} hydroxides (Frau et al. 2008; Majzlan et al. 2007; Paktunc et al. 2003; Salzsauler et al. 2005; Slowey et al. 2007; Smedley and Kinniburgh 2002). In particular, very low pH or reducing conditions can lead to the desorption of arsenic from Fe^{3+} hydroxides and oxyhydroxides and to the dissolution of such Fe^{3+} phases, also leading to an arsenic release (Bayard et al. 2006; Drahota et al. 2009; Pedersen et al. 2006). Therefore, the reduction of Fe^{3+} to Fe^{2+} increases the mobility of arsenic. However, strongly reducing conditions do not favour arsenic mobility because both iron and hydrogen sulfide would be present, leading to the coprecipitation of arsenic sulfide with iron sulfide. By contrast, mildly reducing environments that lack hydrogen sulfide can allow the dissolution of arsenic. In such environments, iron is in the soluble Fe^{2+} state, and arsenic is present as As^{3+} in the arsenite form (AsO_3^{3-}). In mildly reducing environments such as saturated tailings, precipitated Fe^{3+} oxyhydroxides, hydroxides and oxides can be reduced with the help of microorganisms to form dissolved Fe^{2+} and As^{3+} (Babechuk et al. 2009; Macur et al. 2001; McCreadie et al. 2000). Consequently,

pore and seepage waters of such tailings repositories may contain strongly elevated iron and arsenic concentrations. When these seepage waters reach the surface, oxidation of the waters will result in the precipitation of iron and coprecipitation of arsenic, forming arsenic-rich yellow boys.

3.5.10 The Mercury System

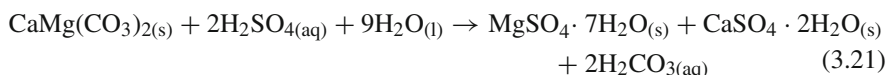
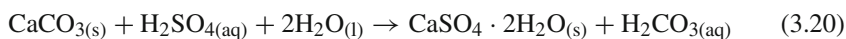
The determination of mercury speciation in mine waste requires the application of appropriate methods (Kim et al. 2004; Sladek and Gustin 2003; Sladek et al. 2002). Mercury in mine waters is sourced from the weathering of cinnabar (HgS), metacinnabar (HgS), calomel (HgCl), quicksilver ($\text{Hg}_{(l)}$), livingstonite (HgSb_4S_7), and native mercury (Hg) (Navarro et al. 2006, 2009). It may also be released from mercury amalgams present in wastes as well as stream and floodplain sediments downstream of historic and artisanal gold mines (Al et al. 2006; Dominique et al. 2007; Feng et al. 2006; Lecce et al. 2008). While cinnabar weathers slowly under aerobic conditions (Barnett et al. 2001), the slow oxidation of mercury-bearing sulfides can still provide elevated mercury levels to mine waters. Mercury exists in natural waters as elemental mercury (Hg^0) and ionic mercury (Hg^+ and Hg^{2+}), and it is prone to be adsorbed onto organic matter, iron oxyhydroxides, and clay minerals (Covelli et al. 2001; Domagalski 1998, 2001). The presence of organic acids in vegetated mine wastes promotes the release and colloidal transport of mercury from such wastes. As a result, mercury can be transported in natural waters as dissolved species and adsorbed onto suspended particles and colloids (Slowey et al. 2005a, b). Furthermore, mercury is transformed by bacteria into organic forms, notably monomethyl mercury (CH_3Hg^+) and dimethyl mercury ($(\text{CH}_3)_2\text{Hg}$) (Bailey et al. 2002; Gray et al. 2002b, 2004, 2006; Li et al. 2008a). These organic forms are highly toxic, fat-soluble compounds and tend to bioaccumulate in the foodchain (Ganguli et al. 2000; Hinton and Veiga 2002; Johnson et al. 2009; Li et al. 2008b; Qiu et al. 2009). Factors encouraging mercury methylation include high concentrations of dissolved carbon and organic matter, abundant bacteria and acidic water. Consequently, AMD waters are especially susceptible to mercury methylation.

3.5.11 The Sulfate System

Upon oxidation of sulfides, the sulfur S^{2-} (S: 2-) in the sulfides will be oxidized to elemental sulfur (S: 0), and more commonly to sulfate SO_4^{2-} (S: 6+). The sulfate may remain in solution or precipitate to form secondary minerals (e.g. melanterite $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$). However, sulfides may not be completely oxidized to form dissolved sulfate ions or sulfate minerals. The sulfur may be oxidized to metastable, intermediate sulfur oxy-anions. These include sulfite SO_3^{2-} (S: 4+), thiosulfate $\text{S}_2\text{O}_3^{2-}$ (S: 2+), and polythionates ($\text{S}_n\text{O}_6^{2-}$), which are then subsequently oxidized to sulfate (Descostes et al. 2004; Moses et al. 1987). The occurrence of these intermediate sulfur species in mine waters is controversial, yet such reactions are supported

by the occurrence of sulfite and thiosulfate minerals as natural weathering products (Braithwaite et al. 1993).

AMD waters carry significant concentrations of sulfate which exceed those of iron and heavy metals. Strongly elevated sulfate concentrations are prevalent because relatively few natural processes remove sulfate from ground and surface waters. Only the precipitation of secondary sulfate minerals influences the concentration of sulfate in solution. The formation of secondary sulfates generally occurs in response to evaporation or neutralization reactions. Gypsum and other sulfates such as epsomite ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$) and jarosite ($\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$) are such precipitates in AMD affected seepages, streams, and ponds. Gypsum is the most common sulfate salt in AMD environments. The Ca^{2+} for gypsum formation is released by the acid weathering of carbonate and silicate minerals such as dolomite, calcite, and plagioclase. The concentration of calcium sulfate in mine waters may rise to a level at which gypsum precipitates. This level is not influenced by pH and is dependent on the detailed chemical conditions of the water such as the amount of magnesium in solution. Gypsum formation may also be due to neutralization of AMD waters. Neutralization reactions between AMD waters and calcite or dolomite result in gypsum (Reaction 3.20) and epsomite precipitation (Reaction 3.21). The reactions can be written as follows:

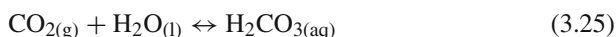
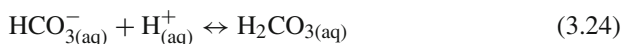
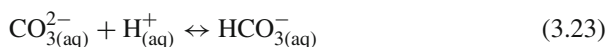
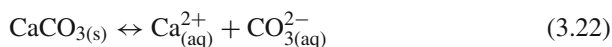


While the formation of gypsum and other sulfates reduces the dissolved sulfate concentration, the minerals' solubility in water is also high. The major chemical mechanism that removes sulfate from solution also causes elevated sulfate concentrations in water. In addition, many oxidized ores may contain gypsum as a pre-mining mineral. Thus, not all high sulfate concentrations of mine waters are caused by sulfide oxidation; they can also be the result of the dissolution of gypsum and other sulfates.

AMD processes lead to high concentrations of dissolved sulfate at the AMD source. Once released into solution, the sulfate ion has the tendency to remain in solution. Sulfate concentrations in AMD waters are exceptionally high when compared to those of uncontaminated streams. Therefore, the sulfate ion can be used to trace the behaviour of contaminant plumes impacting on streams and aquifers. For example, sulfate-rich mine waters discharge into a surface stream with little organic activity, and there is a decrease in sulfate concentration downstream from the discharge point. This can only be ascribed to dilution by non-contaminated streams (Ghomshei and Allen 2000; Schmiermund 1997). If other mine derived constituents such as metals decrease to a greater extent in the same reach of the stream, then they must have been removed from the water by geochemical processes such as adsorption or coprecipitation. The behaviour of sulfate helps to trace and assess the fate of other mine water constituents.

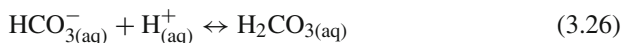
3.5.12 The Carbonate System

The so-called *carbonic acid system* or *carbonate system* greatly affects the buffer intensity and neutralizing capacity of waters (Langmuir 1997; Brownlow 1996). The system comprises a series of reactions involving carbon dioxide (CO_2), bicarbonate (HCO_3^-), carbonate (CO_3^{2-}), and carbonic acid (H_2CO_3). The reactions affecting these different species are very important in ground and surface waters and involve the transfer of carbon among the solid, liquid and gas phase. This transfer of carbon also results in the production of carbonic acid. Carbonic acid in water can be derived from several sources, the most important of which are the weathering of carbonate rocks (Reactions 3.22, 3.23 and 3.24) and the uptake of carbon dioxide from the atmosphere (Reaction 3.25):



Contribution of carbonic acid from weathering processes of carbonate rocks is far more important than the uptake of carbon dioxide from the atmosphere. Which carbonate species will be present in the water is determined by the pH of the water, which in turn is controlled by the concentration and ionic charge of the other chemical compounds in solution. Bicarbonate is the dominant species found in natural waters with a pH greater than 6.3 and less than 10.3; carbonate is dominant at pH greater than 10.3; carbonic acid is the dominant species below pH 6.3 (Brownlow 1996; Langmuir 1997; Sherlock et al. 1995).

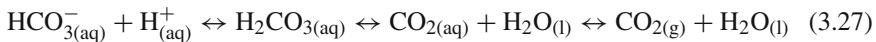
The distinction between bicarbonate and carbonic acid is important for the evaluation of AMD chemistry. Firstly, bicarbonate is a charged species whereas carbonic acid does not contribute any electrical charge or electrical conductivity to the water. In other words, in a low pH AMD water, the carbonic acid does not contribute a significant amount of anionic charge or conductivity to the water. With increasing pH value of the AMD water, the proportions of carbonic acid and bicarbonate will change. This alters the amount of negative charge and conductivity because bicarbonate ions will contribute to the negative charge. Secondly, dissolved bicarbonate ions consume hydrogen ions; hence, bicarbonate ions provide neutralizing capacity to the water as illustrated by the following reaction:



Bicarbonate removes free hydrogen from the solution, lowering the solution's acidity. Thus, the greater the total concentration of the bicarbonate species, the greater the buffering capacity and alkalinity of the AMD water. The alkalinity of

a water is a measure of the bicarbonate and carbonate concentration, indicating the buffering capacity of the water (Table 3.2). The greater the alkalinity, the greater the hydrogen concentration that can be balanced by the carbonate system.

The reaction of free hydrogen with bicarbonate is easily reversible (Reaction 3.26). Consequently, carbonic acid formation does not cause a permanent reduction in acidity of AMD waters. The consumed hydrogen may be released back into the mine water. In fact, Reaction 3.26 is part of a series of equilibrium reactions (Reaction 3.27): bicarbonate reacts with hydrogen ions to form carbonic acid; carbonic acid then reacts to dissolved carbon dioxide and water; and finally to gaseous carbon dioxide and water:

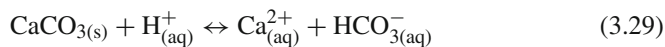
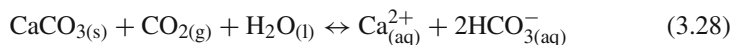


These equilibrium reactions can be forced to react towards the production of gaseous carbon dioxide. For example, if AMD water is neutralized with limestone and stirred at the same time, the carbon dioxide exsolves as a gas phase; the dissolved carbon dioxide content is lowered. As a result, the degassing of carbon dioxide does not allow the equilibrium reactions to proceed back to the production of hydrogen ions. Carbon dioxide degassing supports the permanent consumption of hydrogen by bicarbonate ions, and the acidity of AMD waters can be permanently lowered (Carroll et al. 1998).

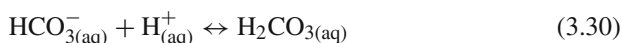
3.5.13 pH Buffering

At mine sites, water reacts with minerals of rocks, soils, sediments, wastes, and aquifers. Different minerals possess different abilities to buffer the solution pH (Blowes and Ptacek 1994). Figure 3.2 shows a schematic diagram of AMD production for a hypothetical sulfidic waste dump. The initial drainage stage involves the exposure of sulfide to water and oxygen. The small amount of acid generated will be neutralized by any acid buffering minerals such as calcite in the waste. This maintains the solution pH at about neutral conditions. As acid generation continues and the calcite has been consumed, the pH of the water will decrease abruptly. As shown in Fig. 2.3, the pH will proceed in a step-like manner. Each plateau of relatively steady pH represents the weathering of specific buffering materials at that pH range. In general, minerals responsible for various buffering plateaus are the calcite, siderite, aluminosilicate, clay, aluminium hydroxysulfate, aluminium/iron hydroxide, and ferrihydrite buffers (Gunsinger et al. 2006a; Jurjovec et al. 2002; Sherlock et al. 1995). Theoretically, steep transitions followed by pH plateaus should be the result of buffering by different minerals. Such distinct pH buffering plateaus may be observed in pore and seepage waters of sulfidic tailings, waste rock piles, spoil heaps or in ground waters underlying sulfidic materials. However, in reality, such distinct transitions and sharp plateaus are rarely observed as many different minerals within the waste undergo kinetic weathering simultaneously and buffer the mine water pH.

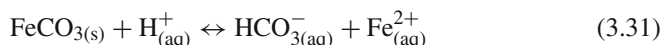
The buffering reactions of the various minerals operate in different pH ranges. Nonetheless, there are great discrepancies in the literature about the exact pH values of these zones (Blowes and Ptacek 1994; Ritchie 1994b; Sherlock et al. 1995). Broad pH buffering of calcite occurs around neutral pH (pH 6.5–7.5) in an open or closed system (Sect. 2.4.2):



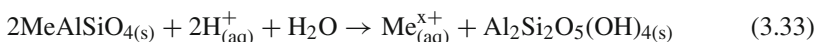
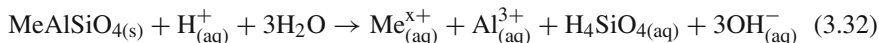
The presence of bicarbonate is influenced by the pH of the solution. Below pH 6.3, the dominant carbonate species in solution is carbonic acid. Hence, bicarbonate may form carbonic acid as follows:



If all of the calcite has been dissolved by acid, or the mineral is absent, then siderite provides buffering between pH values of approximately 5 and 6 (Blowes and Ptacek 1994; Sherlock et al. 1995):

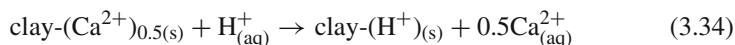


The silicate minerals provide neutralizing capacity between pH 5 and 6. Their chemical weathering can be congruent (Reaction 3.32) or incongruent (Reaction 3.33) (Sect. 2.4.1). Either reaction pathway results in the consumption of hydrogen ions:

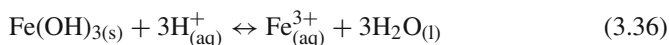
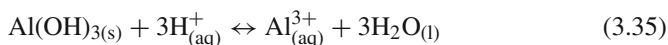


(Me = Ca, Na, K, Mg, Mn or Fe)

Exchange buffering of clay minerals is dominant between pH 4 and 5 and causes alkali and alkali earth cation release:



Aluminium and iron hydroxide buffering of minerals (e.g. ferrihydrite, goethite, gibbsite, hydroxysulfates, and amorphous iron and aluminium hydroxides) occurs at a lower pH than all other minerals; that is, between pH values of approximately 3 and 5. Their buffering results in the release of aluminium and iron cations:



3.5.14 Turbidity

Turbidity is the ability of a water to disperse and adsorb light. It is caused by suspended particles floating in the water column. The suspended particles of AMD affected streams and seepages are diverse in composition. Firstly, they may include flocculated colloids due to hydrolysis and particulate formation. Such flocculants are typically composed of poorly crystalline iron hydroxides, oxyhydroxides, and oxyhydroxysulfates (e.g. schwertmannite), and less commonly of aluminium hydroxides (Mascaro et al. 2001; Sullivan and Drever 2001). Secondly, suspended particles may also originate from the overflow of tailings dams and from the erosion of roads, soils, and fine-grained wastes during periods of heavy rainfall. These particulate may consist of clays and other inorganic and organic compounds.

Regardless of their origin, suspended solids can be important in transporting iron, aluminium, heavy metals, metalloids, and other elements in solid forms far beyond the mine site (Schemel et al. 2000). The poorly crystalline nature of suspended particulates also allows the release of the incorporated or adsorbed elements back into the water column. The release may be initiated due to bacterial activity, reduction or photolytic degradation (McKnight et al. 1988).

3.6 Prediction of Mine Water Composition

The prediction of mine water quality is an important aspect of mining and mineral processing activities. Static and kinetic test data on sulfidic wastes provide information on the potential of wastes to generate acid (Sect. 2.7.4). However, the prediction of mine water composition is a very complex task and remains a major challenge for scientists and operators (Younger et al. 2002). Nevertheless, the mine operator would like to know in advance: (a) the composition of the mine water at the site; (b) whether or not mine water can be discharged without treatment; (c) whether or not mine water will meet effluent limits; and (d) whether or not the drainage water will turn acid, and if so, when.

3.6.1 Geological Modeling

The geological approach is an initial step in assessing the mine water quality of a particular ore deposit. Similar to the geological modeling of sulfidic wastes (Sect. 2.7.1), geological modeling of mine waters involves the classification of the deposit and the deduction of water quality problems (Plumlee et al. 1999). The reasoning behind this method is that the same types of ore deposits have the same ore and gangue minerals, meaning the same acid producing and acid buffering materials.

Consequently, the mine waters should be similar in terms of pH and combined metal contents. This empirical classification constrains the potential ranges in pH and ranges in metal concentrations of mine waters that may develop. However, the technique cannot be applied to predict the exact compositions of mine waters (Plumlee et al. 1999).

3.6.2 Mathematical and Computational Modeling

There are simple mathematical models and computational tools which help to predict the chemistry of water at a mine site. All presently available mathematical and computational models have limitations and rely on good field and laboratory data obtained from solid mine wastes and mine waters. In other words, any modeling will only be as good as the data used to generate the model.

A simple mathematical model for predicting the chemistry of water seeping from waste rock piles has been presented by Morin and Hutt (1994). This empirical model provides rough estimates of future water chemistries emanating from waste rock piles. It considers several factors including:

1. The production rates of metals, non-metals, acidity, and alkalinity under acid and pH neutral conditions from a unit weight of rock;
2. The volume of water flow through the waste pile based on the infiltration of precipitation;
3. The elapsed time between infiltration events;
4. The residence time of the water within the rock pile; and
5. The percentage of mine rock in the pile flushed by the flowing water.

In Morin and Hutt's (1994) example, a hypothetical waste rock pile is 600 m long, 300 m wide, and 20 m high, and contains 6.5 Mt of rock. The long-term production rate of zinc has been obtained from kinetic test data at 5 mg kg^{-1} per week (factor 1). Rainfall occurs every second day and generates 1 mm of infiltration. Such infiltration converts to 180,000 l of water over the surface of the waste pile (factor 2). The elapsed time between rainfall and infiltration events is assumed to be equal to the infiltration events of every two days (factor 3). As a result, the waste pile accumulates 1.4 mg kg^{-1} zinc between events ($5 \text{ mg kg}^{-1} \text{ Zn per } 7 \text{ days} \times 2 \text{ days} = 1.4 \text{ mg kg}^{-1} \text{ Zn}$). The residence time of the water within the waste is also assumed to be 2 days (factor 4), and the percentage of the total waste flushed by the pore water is assumed to be 10% (factor 5). Accordingly, the predicted zinc concentration in the waste rock seepage amounts to 506 mg l^{-1} ($1.4 \text{ mg kg}^{-1} \text{ Zn} \times 6.5 \text{ Mt} \times 10\%/180,000 \text{ l} = 506 \text{ mg l}^{-1} \text{ Zn}$).

Thus, simple mathematical models provide some insights into seepage chemistry. Simple mass balance models also allow the computation of contaminant loads

(mg s^{-1}) or fluxes (t a^{-1}) in mine waters and the calculation of discharging element loads from different sources at a mine site (e.g. discharge from a mine shaft versus seepage of a waste pile) (Adams et al. 2007). This in turn allows an assessment of the potential lifetime of discharge from a mine site and the determination of remediation priorities of particular mine site domains.

Complex geochemical processes, occurring in ground and surface waters of a mine site and waste repository, need to be modelled using computational models. There are simulation programs which model mass balances, water balances, sulfide oxidation rates, oxygen diffusion, secondary mineral saturations, speciations of metals and metalloids, kinetic geochemical reactions, reactions paths, and water flows (Accornero et al. 2005; Acero et al. 2009; Brookfield et al. 2006; Fala et al. 2005; Gerke et al. 2001; Kohfahl et al. 2008; Malmström et al. 2008; Perkins et al. 1997). Each computational tool has been developed for slightly different purposes. Each model relies on accurate and complete data sets. Input parameters may include water composition, mineralogy and geochemistry of wastes, bacterial activity, reactive surface area, temperature, oxygen availability, water balance, waste rock pile structure and composition, humidity cell and leach column test data, and thermodynamic data (Perkins et al. 1997). Modeling may also be used to evaluate the optimal design of covers for preventing sulfide oxidation and the production of AMD waters (Molson et al. 2008; Ouangrawa et al. 2009; Schwartz et al. 2006).

The predicted concentrations of individual metals, metalloids, and anions in mine waters obtained from computational geochemical models should be compared with actual mine water chemistries measured in the field or obtained through kinetic test work. Geochemical modeling programs of waters are also able to calculate the mineral saturation indices and to identify minerals that might be forming and limiting solution concentrations of these constituents. In low pH environments, many metals are mobilized and present at concentrations which cause precipitation of secondary minerals. Adsorption is also an important geochemical process operating in these waters. Precipitation and adsorption capabilities of an acidic system need to be evaluated using computational software (Smith 1999). The computational programs are used to predict the precipitation of secondary minerals from mine waters. These predicted mineral precipitates have to be verified by comparing them with those secondary minerals actually identified in the AMD environment.

Modeling is not an exact science; its application has numerous pitfalls, uncertainties, and limitations, and the calculations are at best well-educated guesses (Alpers and Nordstrom 1999; Nordstrom and Alpers 1999a). Discrepancies between field observations and simulation results are common (Brookfield et al. 2006). Hence, none of the simulations and modelling efforts should be used to predict the exact water composition even though they can be used to improve the understanding of geochemical processes and to perform comparisons between possible scenarios (Perkins et al. 1997).

3.7 Field Indicators of AMD

Any seepage water flowing from a mine, mine waste pile, tailings dam or pond may be acid. The most common indicators in the field for the presence of AMD waters are:

- *pH values less than 5.5.* Many natural surface waters are slightly acidic (pH ~5.6) due to the dissolution of atmospheric carbon dioxide in the water column and the production of carbonic acid. Waters with a pH of less than 5.5 may have obtained their acidity through the oxidation of sulfide minerals.
- *Disturbed or absent aquatic and riparian fauna and flora.* AMD waters have low pH values and can carry high levels of heavy metals, metalloids, sulfate, and total dissolved solids. This results in the degradation or even death of aquatic and terrestrial ecosystems.
- *Precipitated iron-rich solids covering stream beds and banks.* The observation of colourful yellow-red-brown precipitates, which discolour seepage points and stream beds, is typical for the AMD process. The sight of such secondary iron-rich precipitates (i.e. yellow boy) is a signal that AMD generation is well underway.
- *Discoloured, turbid or exceptionally clear waters.* AMD water can have a distinct yellow-red-brown colouration, caused by an abundance of suspended iron hydroxides particles. The turbidity of the AMD water generally decreases downstream as the iron and aluminium flocculate, and salts precipitate with increasing pH. As a result, acid waters can also be exceptionally clear and may give the wrong impression of being of good quality.
- *Abundant algae and bacterial slimes.* Elevated sulfate levels in AMD waters favour the growth of algae, and acid waters may contain abundant slimy streamers of green or brown algae.

3.8 Monitoring AMD

Mine water monitoring is largely based on the analysis and measurement of ground, pore and surface waters over a significant time period because their chemistry commonly changes over time (Scientific Issue 3.1). The monitoring of waters in and around mine sites is designed: (a) to define natural baseline conditions; (b) to identify the early presence of or the changes to dissolved or suspended constituents; (c) to ensure that discharged water meets a specified water quality standard; (d) to protect the quality of the region's water resources; and (e) to provide confirmation that AMD control measures on sulfide oxidation are operating as intended. The acquisition of baseline data prior to mining is particularly important as some sulfide orebodies may have undergone natural oxidation prior to mining. Ground and surface waters in these environments can be naturally enriched in sulfate, metals and metalloids. It is of critical importance to know the water, soil and sediment chemistry in a region prior to the development of a mining operation. Otherwise,

pre-existing natural geochemical enrichments might be mistaken by the statutory authorities as being a result of mining and processing and could be thus subject to subsequent unnecessary (and unfair) remediation processes.

Scientific Issue 3.1. Seasonal and Diel Factors Controlling Water Composition.

Seasonal Factors

The chemistry of rivers, streams and lakes as well as mine waters and natural waters draining mined lands may change over time (Herbert 2006; Kim and Kim 2004; Kimball et al. 2007). Such changes are largely a function of local climatic, hydrological and geochemical factors. For example, seasonal variations in the composition of AMD waters are typically controlled by evaporation, precipitation as well as runoff events and volumes. Increased evaporation will lead to concentration of solutes and hence higher concentrations, whereas high rainfall, associated runoff events and greater stream flow volumes cause dilution of chemical constituents. Significant increases in solute concentrations (i.e. first flush events) have been reported during the melting of ice and snow covers and during flushing events in semi-arid regions, when sulfide oxidation products are washed from waste repositories (Elberling et al. 2007; Harris et al. 2003; Herbert 2006). Other factors such as the water temperature can impact indirectly on the chemistry of mine waters. Higher water temperatures favour the proliferation of bacteria. This in turn leads to an optimum rate of bacterially mediated iron oxidation, increased sulfide oxidation and greater trace metal release to waters. In addition, the dissolved iron concentration of AMD waters is influenced by solar radiation and associated photolytic processes, which increase the dissolved Fe^{2+} and reduce the dissolved Fe^{3+} . Iron photoreduction involves the absorption of UV radiation by Fe^{3+} species, converting Fe^{3+} present in either dissolved or suspended particle form into soluble Fe^{2+} (Butler and Seitz 2006; McKnight et al. 1988). As a consequence, the colloidal Fe^{3+} hydroxide concentrations in oxygenated surface waters can be reduced during daytime or summer, and such waters contain higher Fe^{2+} and total Fe concentrations. Also, Fe precipitates such as schwertmannite, ferrihydrite and goethite may exhibit seasonal variations and the phase transformations may be accompanied by changes in pH values and element concentrations of waters (Kumpulainen et al. 2007).

Diel Factors

Rivers and lakes are not only known to possess seasonal but also daily cycles in pH, dissolved oxygen and water temperature. These cycles occur in response to the daily cycles of photosynthesis and respiration and to weather

changes. For example, the pH of natural waters varies with the amount of amount of carbon dioxide present because carbon dioxide combines with water to form carbonic acid. During the day, plants consume carbon dioxide and the pH generally increases. At night, photosynthesis ceases and the increase in carbon dioxide due to respiration and decay of organic matter is most evident, causing pH to decrease. As a result, stream waters possess a photosynthesis-induced diel (24-hour) cycle in pH. In addition, the concentrations of several elements in acid stream waters draining mined land have been reported to change substantially during a 24-hour period, irrespective of stream flow. Diel fluctuations in the concentration of total iron and the $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio have been related to: (a) daytime photoreduction of Fe^{3+} to Fe^{2+} , and (b) subsequent re-oxidation of Fe^{2+} to Fe^{3+} and temperature-dependent hydrolysis and precipitation of hydrous ferric oxides at night (Butler and Seitz 2006; McKnight et al. 1988).

Diel fluctuations have also been reported for dissolved arsenic, cadmium, copper, iron, manganese, nickel and zinc (e.g. Butler 2006; Gammons et al. 2007, 2008; Morris and Meyer 2007). At some sites, the reported concentrations of zinc increased as much as 500 % during the night (Nimick et al. 2003; Shope et al. 2006). The cyclic changes of arsenic, cadmium, copper, manganese, nickel and zinc contents have been related to adsorption/desorption equilibria onto secondary ferric iron and manganese oxide precipitates in the streambed. Sorption behaviour is thereby influenced by the pH and temperature of the stream water, and the characteristics and abundance of the precipitate (Gammons et al. 2005; Parker et al. 2007; Shope et al. 2006). Thus, the diel cycles in iron, pH and water temperature may induce a diel cycle in dissolved trace element concentrations, with large fluctuations possible during a 24-hour period. Consequently, a properly collected water sample does not necessarily provide an accurate assessment of trace metal and arsenic concentrations on a given day at a particular sampling location (Nimick et al. 2003).

Effective monitoring of a mine site for its water composition requires the following.

- *Setup of monitoring system.* An effective monitoring system is site specific and fulfills the above mentioned monitoring aims. Most importantly, surface water sampling localities and ground water monitoring bores need to be established within and outside the mining area. Sites outside and upstream the mining area provide information on natural background conditions of waters whereas other sites serve as sampling points for mine waters as well as observation points for flow rates (Harries and Ritchie 1988). Monitoring of mine waters relies exclusively on chemical analyses obtained from surface and ground waters.

- *Monitoring climate.* Climate (i.e. precipitation, evapotranspiration, temperature) is an important factor that determines: (a) the quality and quantity of mine waters; and (b) the volume of surface water run-off vs. ground water recharge (Plumlee and Logsdon 1999; Younger et al. 2002). Meteorological data, measured on a regular basis, are needed to understand site surface and ground water hydrology. Calculation of seasonal evapotranspiration rates and a net water balance at the site are crucial as they affect ground water recharge rates and water accumulation rates in mine water storage ponds.
- *Monitoring pore waters of sulfidic waste rock dumps.* Samples of water from the unsaturated zone of sulfidic waste rock dumps are taken using so-called *lysimeters*. Lysimeters are small or large drums buried in waste piles, in some cases under dry covers, and connected with tubes to the surface enabling the collection of the leachate. Meteoric data and analyses of these leachates provide information on water infiltration rate into the dump and contaminant production rates (Bews et al. 1999; Ritchie 1998). The analysis of lysimeter leachates also allows an evaluation as to what depth water infiltrates into waste rock piles, and whether water infiltrates into sulfidic material. Consequently, lysimeters allow a performance evaluation of dry covers.
- *Monitoring ground waters.* Major fractures are commonly present within sulfidic ore deposits, and the hydrology of many metal mines is structurally controlled. These fractures represent permeability zones for ground water, and the interaction between water and the sulfide-bearing rocks along such fractures can lead to AMD. Highly metalliferous and strongly acidic solution may develop and flow along permeable fractures. Some of the waters may surface in open pits as distinct seepages. Therefore, it is important to ensure that ground water monitoring bores are sunk into fracture zones.

AMD impacts more frequently on ground water quality than on the surface drainage from a mine. In particular, in low rainfall arid areas, most of the drainage is likely to move into the aquifer. Ground water samples from the saturated zone immediately beneath sulfidic waste dumps or tailings can be obtained using piezometers. Chemical analyses of such waters will indicate the contaminant transport into the local aquifer.

Electrical and electromagnetic techniques can be used to map ground water contamination and pore waters in waste dumps, watersheds and mined areas (Ackman 2003; Benson 1995; Campbell and Fitterman 2000; Hammack et al. 2003a, b; Rucker et al. 2009). The geophysical surveys measure the electrical conductivity, which increases with increasing TDS concentrations that are particularly found in acidic, metal-rich ground waters. However, geophysical techniques only provide indirect information about the ground water composition, and the data can be difficult to interpret as changing rock types cause pronounced resistivity or conductivity variations. The detection and mapping of contaminant plumes in areas of diverse lithologies are only possible in highly contaminated areas where other factors have a relatively small effect on the data variations.

- *Monitoring open pit lakes.* Acid waters may accumulate within final mining voids, and these acid pit lakes require detailed monitoring and hydrological studies (Scientific Issue 3.2).
- *Monitoring the ecosystem health.* The ecosystem health of waterways surrounding a mine site can be measured using indicator species (e.g. mussels; Angelo et al. 2007; Martin et al. 1998). Such indicator species are sensitive to contaminants which may be released from a mining operation. The chemistry, behaviour, breeding cycle, population size, and health of indicator species in ecosystems immediately downstream of the mine site may then be compared with those upstream. This direct biological monitoring can reveal any significant impacts on the health of ecosystems surrounding the mine.
- *Monitoring surface waters.* The monitoring of surface waters is based on the analysis and measurement of surface waters over a significant time period. Changes to pH, conductivity, and sulfate and metal content over time are good indicators of AMD generation. In particular, the SO_4/Cl ratio is a good indicator of an input of sulfate from the oxidation of sulfides. Nonetheless, high sulfate concentrations, elevated conductivities up to 100 times higher than the local ground and surface water, and extreme salinities in pore and seepage waters do not necessarily indicate sulfide oxidation. They may also be the result of dissolution of soluble secondary sulfates within the wastes. Furthermore, changes in pH, conductivity and sulfate, metal and major cation concentrations may be the result of changes in hydrological conditions such as evaporation or dilution. These latter processes lead to increases or decreases in the contaminant's concentration and do not reflect changing chemical processes at the contamination source. Therefore, sites should measure or estimate flow rates or periodic flow volumes as they are additional important parameters of mine waters. The measurement of the solute concentration (mg l^{-1}) and of the flow rate or flow volume (l s^{-1}) will allow the calculation of the contaminant load (mg s^{-1}) in the mine water. The load of a chemical species is defined as the rate of output of the species over time (mg s^{-1}). Monitoring solute concentration and flow rate over time will allow the calculation of the output rate of the species over time. As a result, chemical processes within the contaminant source can be recognized. For example, seepage water appears at the toe of a sulfidic waste pile. The changing water flow rate ($\text{l}^3 \text{s}^{-1}$) is measured using a calibrated flow gauging structure instrumented with a water sampler (Younger et al. 2002). In addition, contaminant concentrations (mg l^{-1}) are determined in the water samples over time. The knowledge of flow rates and contaminant concentrations over time allows the calculation of loads (mg s^{-1}) of individual chemical species released from the waste pile. Increases in metal and sulfate loads (mg s^{-1}) over time indicate the onset of AMD. A knowledge of annual contaminant fluxes (t a^{-1}) from mine workings, waste repositories and streams in a single catchment also provides the necessary information to prioritise any monitoring and remediation efforts. Such efforts can then focus on individual domains of a mine site or on particular mines in the catchment that release the largest proportions of contaminants and seriously impair the environmental quality of aquatic systems (Mighanetara et al. 2009).

Scientific Issue 3.2. Acid Pit Lakes

Formation of Pit Lakes

The mining industry extracts a number of mineral commodities and coal from open pits. The large increase in open pit mining of metal ores since the 1970s has resulted in the ever increasing creation of mining voids worldwide. If open pit mines extend below the water table, ground water must be removed to permit mining operations. This is achieved through water pumping and extraction and temporarily lowering of the water table. The effect is generally limited to the immediate vicinity of the mining operation. The mining method leaves an open pit (i.e. final mining void) at the end of the operations.

Final mining voids may be used as water storage ponds, wetland/wildlife habitats, recreational lakes, engineered solar ponds, or waste disposal sites. However, the range of realistic end-use options is limited for a specific mine void, particularly in remote areas, and many open pits are left to fill with water. If a pit remains unfilled, the water table usually returns to its pre-mining level after pumping is discontinued, and the large void will flood. Open pit water can percolate into ground water or ground water can flow into the void, coming in contact with the atmosphere. As a result, changes in the water quality and quantity of the final mining void occur, and pit lake properties change over time. Thus, water balance and water quality of a final void are highly site specific and may evolve for many years before approaching a steady state. The final use of the pit lake will be determined largely by long-term trends in the quantity and quality of water within the void.

General Characteristics of Pit Lakes

The key processes which control the quantity of water in a final void are direct rainfall into the pit, evaporation from the standing water, and surface and ground water inflows and outflows (Doyle and Runnels 1997; Warren et al. 1997). Generally, pit lakes represent – similar to natural lakes – ground water discharge lakes, recharge lakes, or flow-through lakes. Evaporation of water and resulting concentration of solutes in pit lakes is less significant at most pit lakes than at natural lakes. This is because pit lakes are much smaller and deeper than natural lakes; therefore, the surface area to depth ratio of pit lakes is several magnitudes smaller than that of natural lakes.

The key processes which determine the water chemistry of final voids include: (a) weathering reactions in pit walls and wastes draining into the pit; (b) concentration as a result of evaporation; (c) stratification of the water column due to temperature or chemical gradients; (d) adsorption of dissolved

elements on and coprecipitation with particulates; (e) precipitation of secondary salts from the pit water; and (f) biochemical and redox reactions in the water (Balistrieri et al. 2006; Bowell 2002; Castendyk et al. 2005; Davis and Ashenberg 1989; Delgado et al. 2008; Denimal et al. 2005; Eary 1998, 1999; Meyer et al. 1997; Miller et al. 1996; Ramstedt et al. 2003; Shevenell 2000; Shevenell et al. 1999; Tempel et al. 2000) (Fig. 3.17).

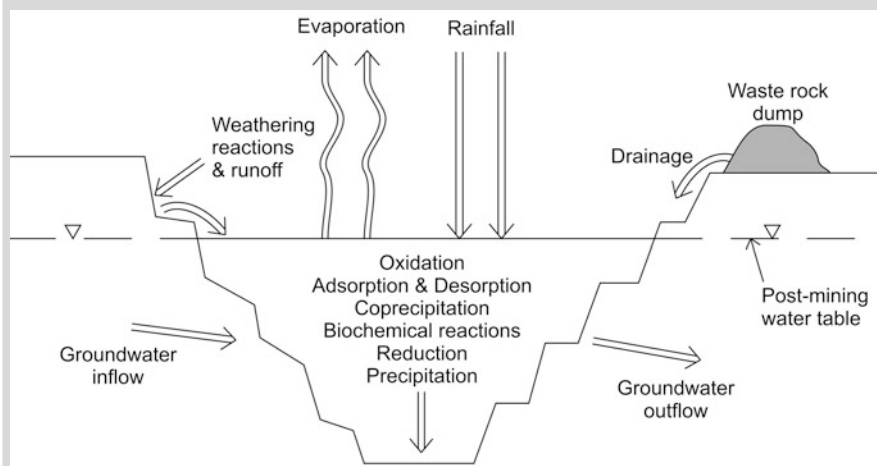


Fig. 3.17 Schematic cross-section of a flow-through pit lake and the geochemical processes that influence its water quality (after Bowell 2002)

Acid Pit Lakes

Open pit lakes may be acidic because they receive drainage from adjacent mine workings or sulfidic wastes, soluble salts are leached from the weathered pit walls, or subaqueous oxidation of sulfides occurs via dissolved Fe^{3+} on the submerged pit walls (Gammons and Duaine 2006; Migaszewski et al. 2008, 2009; Pellicori et al. 2005; Sánchez España et al. 2008b, 2009). If any sulfidic pit walls are exposed to atmospheric conditions, the remaining sulfides will undergo oxidation to a particular depth (Fennemore et al. 1998). A vuggy texture and intense fracturing of the wall rocks will greatly aid sulfide oxidation. The oxidation of sulfide minerals and the dissolution of secondary minerals contribute to the generation of acid solutes into pit waters, and surface run-off waters draining into the pit can be saline, acid and metal-rich. Concentrations of dissolved metals may reach saturation levels. Consequently, secondary minerals may precipitate out of the water column, forming unconsolidated sediments at the bottom of acid pit lakes (Triantafyllidis and Skarpelis 2006;

Twidwell et al. 2006). Natural attenuation of any acid formed may occur in pit lakes located in limestone or marble units. Such voids have alkaline ground water inflows which can react with acid mine waters, forming precipitates and resulting in metal-rich sludges accumulating at the bottom of the voids. In regions with distinct wet and dry seasons, exposed, reactive pit walls can become invariably coated with oxidation products, including soluble and insoluble secondary mineral salts. The alternate wetting and drying of the walls will favour the oxidation of pyrite, the dissolution of secondary phases, and the periodic generation of acid, saline surface run-off waters into the pit. In arid environments, the oxidation rate of pyrite is retarded due to the lack of moisture, and the thickness of oxidized pyritic wall rocks is reduced. This in turn reduces the solute loads entering the incipient acid pit lake (Fennemore et al. 1998).

Remediation practices of acid pit lakes include the addition of organic waste such as wood sawdust, hay, straw, manure, mushroom compost, raw sewage waste water and sewage sludge, and of neutralizing materials such as lime, caustic soda, and limestone (Bozau et al. 2007; Castro and Moore 2000; Geller et al. 2009; McCullough 2008; McCullough et al. 2008). Organic matter accelerates the reduction of dissolved metals and sulfate and leads to their precipitation as metal sulfides (Costa and Duarte 2005; Levy et al. 1996). Also, rapid filling of a pit with water can suppress sulfide oxidation and result in good water quality (Castro and Moore 2000; Parker et al. 1996). By contrast, controlled eutrophication of pit water through the addition of phosphorus does not promote the production of significant alkalinity by algae and diatoms and does not lead to a substantial removal of acidity in acid pit lakes (Fyson et al. 2006; Totsche et al. 2006).

3.9 AMD from Sulfidic Waste Rock Dumps

Sulfidic waste rock dumps and spoil heaps are, because of their sheer volume, the major sources of AMD. The chemistry and volume of AMD seepage waters emanating from sulfidic piles are largely influenced by the properties of the waste materials. AMD development in waste heaps occurs via complex weathering reactions (Sect. 2.2). The different rates of the various weathering reactions within the waste may cause temporal changes to the drainage chemistry. Thus, the composition of drainage waters from waste rock piles depends on three factors:

- The hydrology of the waste pile;
- The presence of different weathering zones within the pile; and
- The rate of weathering reactions (i.e. weathering kinetics), causing temporal changes to the composition of the drainage waters.

3.9.1 Hydrology of Waste Rock Dumps

Waste rock piles have physical and hydrological properties unlike the unmined, in situ waste. Mining and blasting increase the volume and porosity of waste rocks and create large pores and channels through which atmospheric gases and water can be transported.

Waste rock dumps frequently contain *perched aquifers* located well above the underlying bedrock (Younger et al. 2002). The dumps generally contain an unsaturated and a saturated zone separated by a single continuous water table with a moderate hydraulic gradient (Blowes and Ptacek 1994; Hawkins 1998; Younger et al. 2002) (Fig. 3.18). The water table tends to reflect the waste dump surface topography. Within the unsaturated part, water typically fills small pores and occurs as films on particle surfaces. Flow rates of the water vary from relatively rapid movements through interconnected large pores, fractures and joints, to slow movements or nearly stagnant conditions in water films or small pores (Rose and Cravotta 1998). Within the saturated part, flow rates depend on the hydraulic properties of the waste material. Water movement is thought to be highly channellized, similar to karst environments, where water flows preferentially through randomly located channels, voids and conduits (Hawkins 1998; Younger et al. 2002). The flow of water is also influenced by the physical properties of the dump material. For instance, clay-bearing rocks tend to break to small fragments during mining and weather readily to release small mineral particles, decreasing the hydraulic conductivity

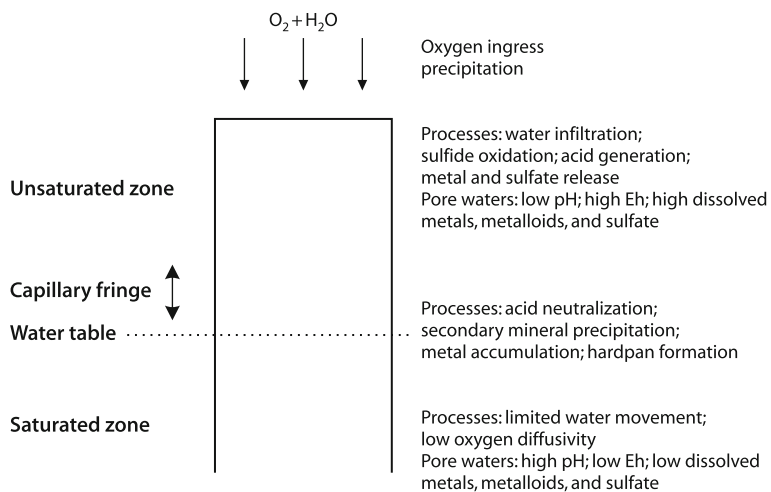


Fig. 3.18 Generalized profile of a sulfidic waste rock dump undergoing sulfide oxidation and AMD development. Hydrological subdivisions as well as hydrological, hydrochemical and geochemical processes are also shown (after Blowes and Ptacek 1994). The profile and processes of a sulfidic tailings pile are analogous

(Hawkins 1998). Also, many dumps are constructed by end-dumping. This leads to some segregation of dump material down the slope at the end of the dump and causes some layering in the dump. Where large rock fragments are present, a significant volume of interstitial pores is created. Consequently, the hydraulic properties of waste rock are influenced by the dump structure, particularly the propensity of coarse material to collect at the bottom of the dump end-slope, and the tendency of fine material to remain on the sides and top. Differential settling and piping of finer material will occur shortly after dumping of waste materials. The shifting and repositioning of dump fragments are further facilitated by infiltrating meteoric water or surface run-off. Fine-grained materials migrate towards the base of the dump, and the settling of dump fragments may cause decreasing hydraulic conductivities (Hawkins 1998). Alternatively, ground water flow and infiltration of meteoric water may result in the interconnection of voids and increasing hydraulic conductivity.

The shear strength of a waste dump and its stability are influenced by the pore water pressure. Increasing pore water pressures may develop due to the increasing weight and height of the waste dump, or due to increasing seepage through the dump. Excess pore water pressures are usually associated with fine-grained materials since they possess lower permeabilities and higher moisture contents than coarse-grained wastes. Fine-grained wastes may, therefore, become unstable and fail at lower pore water pressures than coarse-grained wastes.

The hydraulic properties of wastes (e.g. hydraulic conductivity, transmissivity, porosity, pore water velocity, recharge) vary greatly. As a result, the flow direction and paths of pore waters, as well as the location and elevation of saturated zones are often difficult to predict. Detailed hydrological models are required to understand water storage and transport in waste rock dumps (Moberly et al. 2001).

3.9.2 Weathering of Waste Rock Dumps

Perkins et al. (1997) have provided a simplified model for the generation of drainage waters from sulfidic waste rock piles. The production and flow of drainage from waste rock piles is controlled by wetting and drying cycles. The waste piles are intermittently wetted by meteoric water and seasonal run-off; they are dried by drainage and evaporation. The time it takes to complete the entire wetting-drying cycle is dependent upon porosity, permeability, and climatic factors. A complete wetting-drying cycle, for a waste rock pile located in a region of moderate to high rainfall with distinct seasons, consists of four sequential stages (Perkins et al. 1997):

1. Sulfide oxidation and formation of secondary minerals;
2. Infiltration of water into the dump;
3. Drainage of water from the dump; and
4. Evaporation of pore water.

The first stage represents the atmospheric oxidation of sulfides which results in the destruction of sulfides and the formation of secondary minerals. The second stage is the infiltration of meteoric water and seasonal run-off. Pores are wetted to the extent that weathering of minerals occurs. The third stage involves drainage of water from the pore spaces. Solutes dissolved in the pore water are transported to the water table or are channelled to surface seepages. Air replaces the pore water during drainage, and a thin pore water film is left behind, coating individual grains. The fourth stage is the evaporation of the water film during the drying cycle. During drying, the relative importance of drainage compared to evaporation is determined by the physical properties of the waste rock pile such as hydraulic conductivity. The drying results in the precipitation of secondary minerals that may coat the sulfide mineral surfaces. If drying continues, some of these minerals may dehydrate, crack, and spall from the sulfide surfaces, exposing fresh sulfides to atmospheric oxygen (Perkins et al. 1997). In an arid climate, there are no percolating waters present, and the flow of water through a waste rock pile is greatly reduced. In such locations, sulfide oxidation occurs, and the secondary salts generated from the limited available moisture reside within the waste. As a result, the first (i.e. sulfide oxidation and formation of secondary minerals) and fourth (i.e. evaporation of pore water) stages of the wetting-drying cycle may only be important (Perkins et al. 1997). In an arid environment, sulfide destruction does not necessarily lead to drainage from waste rock piles. However, during high rainfall events, excess moisture is present, and the secondary weathering products are dissolved and transported with the water moving through the material to the saturated zone or surface seepages. The waters may then emerge as a significant first flush that contains elevated contaminant concentrations.

The position of the water table in mine wastes has an important role in influencing the composition of drainage waters (Fig. 3.18). This is because the water table elevation fluctuates in response to seasonal conditions, forming a zone of cyclic wetting and drying. Such fluctuations provide optimal conditions for the oxidation of sulfides in the unsaturated zone and subsequent leaching of sulfides and associated secondary weathering products.

Ritchie (1994b) and Paktunc (1998) provide a model for the weathering of a hypothetical sulfidic waste rock dump. Weathering has proceeded for some time in the dump. Such a *mature* dump has three distinct domains (i.e. outer unsaturated zone, unsaturated inner zone, saturated lower zone), reflecting the different distribution of oxidation sites and chemical reactions. This model implies that the types and rates of reactions and resulting products are different in the individual zones (Paktunc 1998; Ritchie 1994b). The outer zone of a mature waste pile is expected to have low levels of sulfide minerals. It is rich in insoluble primary and secondary minerals and can be depleted in readily soluble components. In contrast, the unsaturated inner zone is enriched in soluble and insoluble secondary minerals. In this zone, oxidation of sulfides should occur along a front slowly moving down towards the water table of the dump.

On the other hand, some authors reject the model of a stratified waste rock profile. They have argued: (a) that sulfidic waste dumps are heterogeneous; and (b) that any infiltrating rainwater would follow preferential flow paths acting as

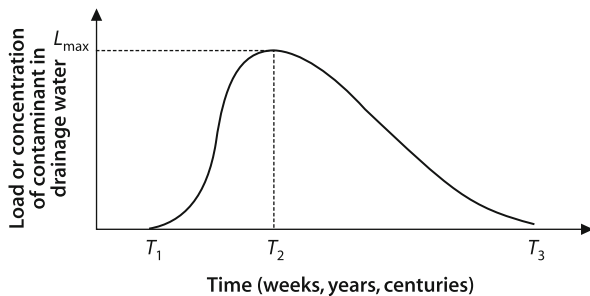
hydraulic conduits (Eriksson 1998; Hawkins 1998; Hutchison and Ellison 1992). Such discrete hydrogeological channels would limit water-rock interactions. In addition, local seeps from a single waste dump are known to have substantially different water qualities, which supports the hypothesis of preferential flow paths in waste piles. Also, the abundance and distribution of acid producing and acid buffering minerals vary from one particle to another. Waste parcels with abundant pyrite, free movement of air, and impeded movement of water are expected to develop higher acidities than equal volumes that contain less pyrite or that are completely saturated with water (Rose and Cravotta 1998). Chemical and physical conditions within waste dumps vary even on a microscopic scale. The resulting drainage water is a mixture of fluids from a variety of dynamic micro-environments within the dump. Consequently, the water quality in different parts of waste dumps exhibits spatial and temporal variations. One could conclude that prediction of drainage water chemistry from waste dumps is difficult and imprecise.

3.9.3 Temporal Changes to Dump Seepages

When mine wastes are exposed to weathering processes, some soluble minerals go readily into solution whereas other minerals take their time and weather at different rates (Morin and Hutt 1997). The drainage chemistry of readily soluble minerals remains constant over time as only a limited, constant amount of salt is able to dissolve in water. Such a *static* equilibrium behaviour is commonly found in secondary mineral salts such as sulfates and carbonates. Secondly, there are other minerals such as silicates and sulfides which weather and dissolve slowly over time. Their reactions are strongly time dependent (i.e. *kinetic*); hence, the drainage chemistry of these minerals changes through time.

Kinetic or equilibrium chemical weathering and dissolution of different minerals within mine wastes have an important influence on the chemistry of mine waters. The different weathering processes cause or contribute to the chemical load of waters draining them. In particular, kinetic weathering processes determine changes to mine water chemistries over time because acid producing and acid neutralizing minerals have different reaction rates. These different weathering and dissolution behaviours of minerals have an influence on the temporal evolution of mine water chemistries. The drainage water chemistry of a dump or tailings dam evolves with time as different parts of the material start to contribute to the overall chemical load. Generally, the chemical load reaches a peak, after which the load decreases slowly with time (Fig. 3.19).

When altered, weathered or oxidized wastes are subjected to rinsing and flushing, the pore water will be flushed first from the waste. Then easily soluble alteration minerals, weathering and oxidation products, and secondary efflorescences will dissolve and determine early rates of metal release and seepage chemistry. In particular, the soluble and reactive minerals will contribute to equilibrium dissolution at an early stage. Finally, weathering kinetics of sulfides and other acid neutralizing minerals will take over and determine the drainage chemistry.



- T_1 time to first appearance of AMD
(weeks to years)
- T_2 time when pollutant concentration/load reaches a maximum
(years to tens of years)
- T_3 time when drainage water is no longer contaminated
(tens to thousands of years)
- L_{\max} maximum contaminant load/concentration
(e.g. Cu, Zn or SO_4 in mg l^{-1})

Fig. 3.19 Schematic evolution of contaminants in AMD waters emanating from sulfidic mine wastes (after Ritchie 1995)

Mine drainage quality prediction cannot be based on the assumption that 100% of the waste material experiences uniform contact with water (Hawkins 1998). Water moving through the unsaturated portion of the waste contacts waste briefly whereas water of the saturated zone has a longer contact time with the waste. In addition, some material may have a very low permeability, allowing very little ground water to flow through it. These waste portions contribute little to the chemistry of drainage waters. In order to understand the chemistry of drainage waters emanating from waste rock dumps, it is important to determine what waste portions are contacted by water and what is the nature of this contact (Hawkins 1998).

3.10 Environmental Impacts

Drainage water from tailings dams, mine waste dumps, heap leach pads, and ore stockpiles may contain suspended solids and dissolved contaminants such as acid, salts, heavy metals, metalloids, and sulfate. Such waters should not be released from a mine site without prior treatment. The uncontrolled discharge of mine waters with elevated contaminant concentrations into the environment may impact on surface waters, aquatic life, soils, sediments, and ground waters. Investigations of the environmental impacts of mine waters require an assessment of the concentration of elements in waters of background and contaminated sample populations. This will allow the distinction of natural geogenic from induced anthropogenic factors.

3.10.1 Surface Water Contamination

In particular the release of AMD waters with their high metal and salt concentrations impacts on the use of the waterways downstream for fishing, irrigation, stock watering and drinking water supplies (Table 3.6). Metal and metalloid concentrations and acidity levels may exceed aquatic ecosystem toxicity limits, leading to diminished aquatic life (Seal et al. 2008). Irrigation of crops with stream water that is affected by AMD effluents may be inappropriate if the impacted stream has metal and metalloid concentrations well above threshold values that are considered to be phytotoxic to crops (Dolenec et al. 2007). Potable water supplies can be affected when national drinking water quality guidelines are not met (Cidu and Fanfani 2002; Gilchrist et al. 2009; Sarmiento et al. 2009b). Poor water quality also limits its reuse as process water at the mine site and may cause corrosion to and encrustation of the processing circuit.

In general, the severity of surface water contamination decreases downstream of the contamination source due to mixing with non-contaminated streams, which causes the dilution of elements and compounds and the neutralization of acidity. Mineral precipitation, adsorption and coprecipitation may also remove elements

Table 3.6 Main characteristics of AMD waters and their environmental impact (after Ritchie 1994a)

Property	Chemical species	Concentration range in solution	Environmental impact
Acidity	H ⁺	pH < 4.5	Loss of bicarbonate to photosynthetic organisms; degradation and death to animals and plants; reduction in drinking water quality; mobilization of metal ions; corrosion of man-made structures
Iron precipitates	Fe ³⁺ , Fe ²⁺ , Fe(OH) _{3(s)}	100 to 1000 mg l ⁻¹	Discoloration and turbidity in receiving water as pH increases and ferric salts precipitate; smothering of benthic organisms and clogging up of fish gills; reduction in light penetrating the water column; encrustation of man-made structures
Dissolved heavy metals and metalloids	Cu, Pb, Zn, Cd, Co, Ni, Hg, As, Sb	0.01 to 1000 mg l ⁻¹	Degradation and death to animals and plants; bioaccumulation; reduction in drinking water quality; soil and sediment contamination
TDS	Ca, Mg, K, Na, Fe, Al, Si, Mn, sulfate	100 to more than 10000 mg l ⁻¹	Reduction in drinking water quality; reduction in stockwater quality; encrustation of man-made structures as TDS precipitate as salts; soil and sediment contamination

from solution, leading to lower dissolved contaminant concentrations in impacted waterways (Delgado et al. 2009; Balistrieri et al. 2007).

High concentrations of acidity and metals and increased conductivity, total dissolved and suspended solids, and turbidity can be observed in mine seepage and runoff waters at the beginning of the wet season or spring (e.g. Gray 1998). The observed rise in analyte concentrations is a so-called *first flush* (Sect. 3.5.2). Such first flush phenomena are known to occur during the early part of storm events, especially after a prolonged dry spell, in terranes with a semi-arid climate as well as during thawing of mine wastes in arctic environments (Elberling et al. 2007). The sudden increase in metal and sulfate values relates to the wetting and rapid dissolution of soluble waste minerals (i.e. gypsum, etc). Specifically, the first flush can cause distinct impacts on downstream ecosystems with potentially severe effects on biota.

3.10.2 Impact on Aquatic Life

The high acidity of AMD waters can destroy the natural bicarbonate buffer system which keeps the pH of natural waters within a distinct pH range. The destruction of the bicarbonate system by excessive hydrogen ions will result in the conversion of bicarbonate to carbonic acid and then to water and carbon dioxide (Reaction 3.27). Photosynthetic aquatic organisms use bicarbonate as their inorganic carbon source; thus, the loss of bicarbonate will have an adverse impact on these organisms. They will not be able to survive in waters below a pH value of less than 4.3 (Brown et al. 2002). In addition, the bulk of the metal load in AMD waters is available to organisms and plants since the contaminants are present in ionic forms. The use of Diffusive Gradients in Thin Films (DGTs) allows an evaluation of what proportion of dissolved metals is available to aquatic organisms (Balistrieri et al. 2007; Casiot et al. 2009). Heavy metals and metalloids, at elevated bioavailable concentrations, can be lethal to aquatic life and of concern to human and animal health (Gerhardt et al. 2004). Moreover, the methylation of dissolved mercury and other metals and metalloids is favoured by a low pH which turns the elements into more toxic forms. The impact of contaminated waters and sediments, containing high concentrations of bioavailable metals and metalloids, on aquatic ecosystems and downstream plant and animal life can be severe. A reduction of biodiversity, changes in species, depletion of numbers of sensitive species, or even fish kills and death of other species are possible (Table 3.6) (Angelo et al. 2007; Askaer et al. 2008; Dsa et al. 2008; Gray 1998; Kauppila et al. 2006; Lufs et al. 2009; Peplow and Edmonds 2006).

3.10.3 Sediment Contamination

Improper disposal of contaminated water from mining, mineral processing, and metallurgical operations releases contaminants into the environment (Herr and



Fig. 3.20 Stream channel impacted by AMD, Rum Jungle uranium mine, Australia. The channel is devoid of plant life and encrusted with white sulfate efflorescences

Gray 1997; Gray 1997) (Table 3.6). If mine waters are released into local stream systems, the environmental impact will depend on the quality of the released effluent. Precipitation of dissolved constituents may result in abundant colourful mineral coatings in stream channels (Fig. 3.20) (Zheng et al. 2007). Originally dissolved elements may be removed from solution through mineral precipitation, adsorption and coprecipitation. This may cause soils as well as floodplain, stream and lake sediments to become contaminated with metals, metalloids, and salts (Juracek 2008; Mäkinen and Lerssi 2007; Roychoudhury and Starke 2006). Transport and deposition of waste particles will also add contaminants to soils and sediments in a solid form. Consequently, metals and metalloids may be contained in various sediment fractions. Sequential extraction techniques can be used to demonstrate that elements are 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 (Morais et al. 2008). However, metals and metalloids are not necessarily captured and stored in the deposited sediment. Contaminated sediment may be transported further and deposited in downstream environments. Also, changes in water chemistry may cause the contaminated sediment to become a source of metals and metalloids to the stream water (Butler 2009).

3.10.4 Ground Water Contamination

The release of mine waters impacts more frequently on the quality of ground waters than on that of surface waters. Mining-derived contaminants may enter waters of

the unsaturated or saturated zone or become attenuated at the ground water – surface water interface (Gandy et al. 2007). Ground water contamination may originate from mine workings, tailings dams, waste rock piles, heap leach pads, ore stockpiles, coal spoil heaps, ponds, and contaminated soils (Eary et al. 2003; Paschke et al. 2001). Contamination of ground water is not limited to mines exploiting metal sulfide ores, it also occurs at industrial mineral deposits (Gemici et al. 2008). Contaminated water may migrate from waste repositories into aquifers, especially if the waste repository is uncapped, unlined and permeable at its base, or if the lining of the waste repository has been breached. Also, the flooding of underground workings may impact on the chemistry of mine waters and local ground water (Cidu et al. 2007; Gammons et al. 2006). Water-rock reactions in open pits may also lead to the dissolution of contaminants. At such sites, water and dissolved contaminants may leak from the mine workings or the waste repository into the underlying aquifer.

Significant concentrations of sulfate, metals, metalloids, and other contaminants have been found in ground water plumes migrating from mine workings and waste repositories and impoundments at metal sulfide mines. If not rectified, a plume of contaminated water will migrate over time downgradient, spreading beyond the mine workings and waste repositories, possibly surfacing at seepage points, shafts and adits, and contaminating surface waters (Lachmar et al. 2006; Moncur et al. 2006). This can be of concern if only contaminated ground water feeds local streams. Then the impact of contaminated ground water on stream water quality can be severe (Cidu et al. 2009).

The migration rate of such a plume is highly variable and dependent on the physical and chemical characteristics of the aquifer or waste material. Generally, sulfate, metal, and metalloid concentrations in the ground water define a leachate plume extending downgradient of the AMD source (Johnson et al. 2000; Lind et al. 1998; Paschke et al. 2001). Contaminant levels depend on the interaction between the soil, sediment or rock through which the contaminated water flows and the contaminant in the water. Conservative contaminants (e.g. SO_4^{2-}) move at ground water velocities. However, reactive contaminants (e.g. heavy metals, metalloids) move more slowly than the ground water velocity, and a series of different pH zones may be present in the contaminant plume (Fig. 3.21). The occurrence of these zones is attributed to the successive weathering of different pH buffering phases in the aquifer. Such natural attenuation processes in the aquifer, including pH and Eh changes, can reduce the constituent concentrations to background levels in the pathway of the subsurface drainage. Neutralizing minerals – such as carbonates – may be contained in the aquifers, and these minerals buffer acidic ground waters. Depending on the neutralization property of the aquifer through which this water moves, it could be many years before significant impact on ground and surface water quality is detected. In the worst case scenario, the neutralizing minerals are completely consumed before the acid generation is halted at the source. Then the acidic ground water plume will migrate downgradient and can eventually discharge to the surface.

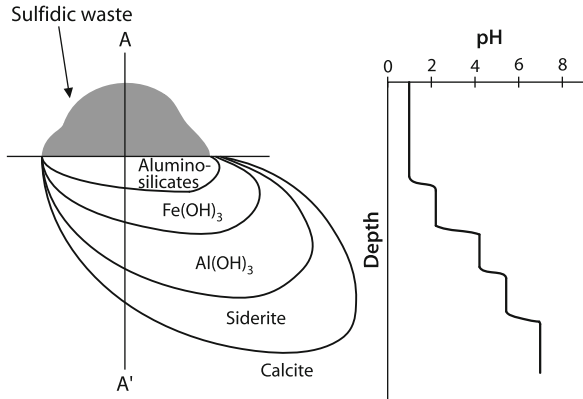


Fig. 3.21 Schematic cross-section of a sulfidic waste dump with a corresponding plume of acid water seeping into the ground. Various minerals buffer the acid ground water. The pH changes in the plume are shown for the cross-section AA' (Reprinted from Jurjovec et al. (2002) with permission from Elsevier Science)

3.10.5 Climate Change

Global-scale climate modelling suggest that there has been a significant rise in global temperature and that this temperature increase will continue, at least over the next few hundred years, leading to glacial melting, rising sea levels and ocean acidification and other far reaching environmental consequences beyond the 21st century. The predicted increase in global temperature is also expected to increase the rates of mine waste weathering about 1.3-fold higher than present by the year 2100 (Nordstrom 2009; Rayne et al. 2009). Moreover, longer dry spells and more intense rainstorms have been predicted for particular regions. Such changes in evaporation rates as well as rainfall patterns and events will impact on the chemistry of mine waters, in particular first flush events (Sect. 3.5.2). Prolonged weathering will lead to the formation of a greater abundance of soluble salts. Flushing of mine sites and waste repositories will lead to larger sudden increases in contaminant concentrations and higher average concentrations during longer low-flow periods (Nordstrom 2009). Thus, in future the remediation of AMD waters may require an increase in the capacity of treatment designs.

3.11 AMD Management Strategies

At mine sites, containment of all contaminated water is to be ensured using water management strategies. These strategies aim to protect aquatic environments and to reduce the water volume requiring treatment. Depending on waste and water characteristics and the location or climate of the mine site, different strategies are applied (Dold et al. 2009; Environment Australia 1999; O'Hara 2007; SMME 1998).

Various techniques can reduce mine water volumes: (a) interception and diversion of surface waters through construction of upstream dams; (b) diversion of run-off from undisturbed catchments; (c) maximization of recycling or reuse of water; (d) segregation of water types of different quality; (e) controlled release into nearby waters; (f) sprinkling of water over dedicated parts of the mine site area; (g) use of evaporative ponds; and (h) installation of dry covers over sulfidic wastes in order to prevent infiltration of meteoric water. These water management strategies will reduce the potential AMD water volume.

In coastal wet climates, the construction of pipelines and the discharge of AMD waters into the ocean may also be considered for the disposal of AMD waters (KoeHNken 1997). Seawater has a strong buffering capacity due to the abundance of bicarbonate whereas ground and surface waters in a carbonate terrain have similarly a significant natural buffering capacity. Releasing waste waters during periods of high rainfall or peak river flow may also achieve dilution and reaction of the effluent to pollutant concentrations below water quality standards (i.e. dilution is the solution to pollution). However, in most cases such a disposal technique is not possible or politically and environmentally acceptable, and treatment of AMD waters is required prior to their discharge.

In many cases, mining operations have to discharge mine water to streams outside their operating licence areas. The release of water from mine sites has to conform with statutory directives; that is, the quality of discharged water has to meet a specified standard comprising a list of authorized levels of substances. Water quality standards list values for parameters such as pH, total suspended matter, and concentrations of sulfate, iron, metals, metalloids, cyanide, and radionuclides. National water quality guidelines are commonly used as a basis for granting a mining licence and allowing discharge of mine water. They are designed to protect downstream aquatic ecosystems, drinking water, and water for agricultural use. Water quality guidelines for metals in aquatic ecosystems are commonly based on total concentrations. However, the bioavailability of metals (i.e. the ability to pass through a biological cell membrane) and the toxicity of metals to aquatic organisms are dependent on the chemical form, that is, the speciation of these metals. Metals present as free ions are more bioavailable than metals adsorbed to colloids or particulate matter. Consequently, guidelines which are based on total metal concentrations are overprotective since only a fraction of the total metal concentration in water will be bioavailable.

3.12 Treatment of AMD

Once started, AMD is a persistent and potentially severe source of pollution from mine sites that can continue long after mining has ceased (Fig. 3.22). Abandoned historic mine sites still releasing AMD waters are a large liability for governments. Liabilities for historic AMD have been estimated around the world to include US\$4000 million in Canada, US\$2000–3500 million in the United States, US\$6000 million for uranium mines in the former East Germany, US\$300 million in Sweden,

Fig. 3.22 Unvegetated waste rock dump at the Mt. Lyell copper mine, Queenstown, Australia. Waste rock dumps and mine workings are significant sources of AMD into the Queen River. It has been estimated that AMD will continue for another 600 years with the present copper load being 2000 kg per day (Koehnken 1997)



and US\$500 million in Australia (Brown et al. 2002; Harries 1997). The total worldwide liability related to AMD is likely to be in excess of 10,000 million US dollars. In the United States alone, the mining industry spends over US\$1 million every day to treat AMD water (Brown et al. 2002). The message is clear: it is always considerably more costly and more difficult to treat AMD problems after they have developed than to control the generation process through sulfide oxidation prevention technologies (Sect. 2.10). In other words, prevention or minimization of sulfide oxidation at the source is better than the treatment of AMD waters. Preventative measures applied to control sulfide oxidation will also help to control the volume of AMD waters (Sect. 2.10). A greater control of sulfide oxidation creates a smaller volume of AMD water requiring treatment.

Like the control techniques for sulfidic wastes, AMD treatment technologies are site specific, and multiple remediation strategies are commonly needed to achieve successful treatment of AMD waters (Brown et al. 2002; Environment Australia 1997; Evangelou 1998; Mitchell 2000; Skousen and Ziemkiewicz 1996; SMME 1998; Taylor et al. 1998; Younger et al. 2002). Collection and treatment of AMD can be achieved using established and sophisticated treatment systems.

Established treatment processes include evaporation, neutralization, wetlands, and controlled release and dilution by natural waters. More technologically advanced processes involve osmosis (i.e. metal removal through membranes), electrodialysis (i.e. selective metal removal through membranes), ion exchange (i.e. metal removal using various ion exchange media such as resins or polymers), electrolysis (i.e. metal recovery with electrodes), biosorption (i.e. metal removal using biological cell material), bioreactor tanks (i.e. vessels that contain colonies of metal immobilizing bacteria or contain *sulfate reducing bacteria* (SRB) causing the metal to precipitate as sulfides), aerated bioreactors and rock filters (i.e. removal of manganese from mine waters), limestone reactors (i.e. enhanced limestone dissolution in a carbon dioxide pressurized reactor), solvent extraction (i.e. removal of particular metals with solvents), vertical flow reactors (i.e. removal of iron using ochres), and removal of metals using silicate minerals (i.e. wollastonite or zeolites) (e.g. Brown

et al. 2002; Cui et al. 2006; Fernández-Caliani et al. 2008; Greben and Maree 2005; Johnson and Younger 2005; Li et al. 2007b; Sapsford and Williams 2009; Shelp et al. 1995; Sibrell et al. 2000; Watten et al. 2005; Wingenfelder et al. 2005).

Many of the innovative treatment techniques are not standard industry practices, are used only at some individual mine sites, or are still at the exploratory stage (Scientific Issue 3.3). Both established and innovative AMD treatment techniques are generally designed:

- To reduce volume;
- To raise pH;
- To lower dissolved metal and sulfate concentrations;
- To lower the bioavailability of metals in solution;
- To oxidize or reduce the solution; or
- To collect, dispose or isolate the mine water or any metal-rich sludge generated.

Scientific Issue 3.3. The Use of Red Mud from Bauxite Refineries to Treat AMD

Production of Bauxite Refinery Waste

More than 95% of bauxite is refined worldwide by using concentrated sodium hydroxide (NaOH) to dissolve the aluminium ore minerals. Materials that are insoluble in sodium hydroxide are filtered out of the alkaline aluminate solution and removed from the hydrometallurgical processing circuit. This waste product is known as *bauxite residue*. Alumina refineries generate significant volumes of extremely alkaline (pH 10–13), saline, sodic bauxite residues. For example, Australia alone produces up to 60 Mt of residue each year. The bauxite residue is frequently disposed of in large ponds or dry stacks. In the dry stacking disposal technique, the finer residue fraction (i.e. *red mud*) is separated from the coarser fraction (i.e. *red sand*). Washing of the coarser fraction produces a benign sand which can be safely disposed of. In contrast, red mud cannot be washed, is saturated with saline, alkaline, sodic pore waters, and requires secure disposal. The red mud is dewatered and dry stacked in lined waste repositories. Dry stacking involves discharging and spreading the red mud in layers, and allowing each layer to dry before adding another layer. Red mud waste repositories require careful capping, soil management and revegetation as long-term leaching of the waste may contaminate local ground waters. Untreated red mud has a pH value (10–13) which does not allow plant growth. Neutralizing the red mud with seawater lowers the pH value to approximately 8.5 and converts soluble, alkaline sodium salts into less soluble, weakly alkaline solids (Harrison 2002). As a result, seawater-neutralized red mud has a reduced pH and alkalinity as well as lower sodium

concentrations. These properties improve settling characteristics, simplify handling and allow plant growth.

Use of Bauxite Refinery Waste

Several alternatives to the disposal of bauxite residues have been proposed such as using the metallurgical waste as a raw material for making glass, ceramics or bricks. In addition, red mud can be used to treat dairy wastewaters, to remove dyes from wastewater, and to remove metals from solution (e.g. Soner Altundogan et al. 2000; Zouboulis and Kydros 1993). Seawater-neutralized red mud consists of a mixture of amorphous phases and finely crystalline minerals, including anhydrite/gypsum, quartz, hematite, goethite, anatase, rutile, calcite, aragonite (CaCO_3), boehmite ($\text{AlO}(\text{OH})$), brucite ($\text{Mg}(\text{OH})_2$), cancrinite ($(\text{Na,Ca})_8(\text{Si}_6\text{Al}_6)\text{O}_{24}(\text{CO}_3)_2$), gibbsite ($\text{Al}(\text{OH})_3$), hydrocalumite ($\text{Ca}_4\text{Al}_2(\text{OH})_{12}(\text{Cl},\text{CO}_3,\text{OH},\text{H}_2\text{O})_{2.5} \cdot 4\text{H}_2\text{O}$), hydrotalcite ($\text{Mg}_4\text{Al}_2(\text{OH})_{12}\text{CO}_3 \cdot 3\text{H}_2\text{O}$), portlandite ($\text{Ca}(\text{OH})_2$), sodalite ($\text{Na}_4(\text{Si}_3\text{Al}_3)\text{O}_{12}\text{Cl}$), and whewellite ($\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$) (Harrison 2002; McConchie et al. 1998, 2000). These amorphous and finely crystalline phases give the red mud very high acid neutralization and metal binding capacities. The injection of seawater-neutralized red mud into AMD waters does not only increase the pH but it also reduces the aqueous metal and metalloid concentrations. Thus, seawater-neutralized red mud has successfully been applied to neutralize AMD waters and to strip AMD waters of their dissolved metals and metalloids (Clark et al. 2009; Harrison 2002; Lapointe et al. 2006; McConchie et al. 1998, 2000; Munro et al. 2004; Paradis et al. 2007). By contrast, the use of BauxsolTM on pyritic waste rock to treat the acidity in drainage waters did not prove to be as successful as the application of powdered limestone and brucite (Barnes and Gold 2008). Regardless of whether red mud is used to neutralize AMD waters, to treat agricultural or industrial wastewaters, or to manufacture bricks, any recycling will reduce the amount of bauxite residues stacked in waste repositories.

AMD treatment techniques can also be classified as active or passive (Johnson and Hallberg 2005b; Walton-Day 2003):

- *Active treatment.* Active treatment systems such as lime neutralization require continued addition of chemical reagents, active maintenance and monitoring, and mechanical devices to mix the reagent with the water.
- *Passive treatment.* Passive methods like wetlands, bioreactors or anoxic limestone drains use the natural water flow and chemical and biological processes to reduce dissolved metal concentrations and to neutralize acidity (Table 3.7).

Table 3.7 Passive treatment of elements, compounds and properties in mine waters (after Gusek 2009; Neculita et al. 2007; Younger et al. 2002)

<i>Element</i>	Passive treatment method									
	Anoxic limestone drain (ALD)	Open limestone channel (OLC)	Successive alkalinity producing systems (SAPS)	Aerobic wetland	Anaerobic wetland	Bioreactor	Aeration pond	Algae-filled rock filter		
Aluminium (Al)	X	X	X		X	X				
Arsenic (As)				X		X				
Cadmium (Cd)				X		X				
Chromium (Cr)				X		X				
Cobalt (Co)				X		X				
Copper (Cu)						X				
Iron (Fe)		X	X	X		X	X			
Lead (Pb)						X				
Magnesium (Mg)						X				
Manganese (Mn)						X				
Mercury (Hg)						X		X		
Molybdenum (Mo)						X				
Nickel (Ni)						X				
Radium (Ra)						X				
Selenium (Se)						X				
Silver (Ag)						X				
Thallium (Tl)						X				
Uranium (U)						X				
Vanadium (V)						X				
Zinc (Zn)						X				

Table 3.7 (continued)

<i>Compound</i>	Passive treatment method							
	Anoxic limestone drain (ALD)	Open limestone channel (OLC)	Successive alkalinity producing systems (SAPS)	Aerobic wetland	Anaerobic wetland	Bioreactor	Aeration pond	Algae-filled rock filter
Ammonia (NH ₃)				X				
Cyanide (CN)				X		X		
Nitrate (NO ₃)						X		
Nitrite (NO ₂)						X		
Phosphate (PO ₄)				X				
Sulfate (SO ₄)						X		
Sulfide (S ²⁻)								X
<i>Parameter</i>								
pH	X	X	X			X		
Biochemical oxygen demand (BOD)				X			X	X
Dissolved oxygen (DO)				X			X	

Such methods require little or no reagents, active maintenance and monitoring, or mechanical devices.

Active treatment techniques such as neutralization and passive treatment methods such as abiotic ponds result in the precipitation of heavy metals from AMD waters and produce voluminous sludge (Dempsey and Jeon 2001). This sludge needs to be removed from the treatment system on a regular basis. The sludge is either disposed of in appropriate impoundments or treated further for metal recovery. In fact, the recovery of metals from sludge may partly pay for the costs of water treatment (Miedecke et al. 1997).

3.12.1 Active Neutralization

Treating the acidity of AMD waters can be pursued using passive or active treatment techniques (Fig. 3.23). Active neutralization is an approach that involves collecting the leachate, selecting an appropriate chemical, and mixing the chemical with the AMD water. In the process, acid is neutralized, and metals and sulfate are removed from solution and precipitated as sludge. Active neutralization treatment systems for AMD include:

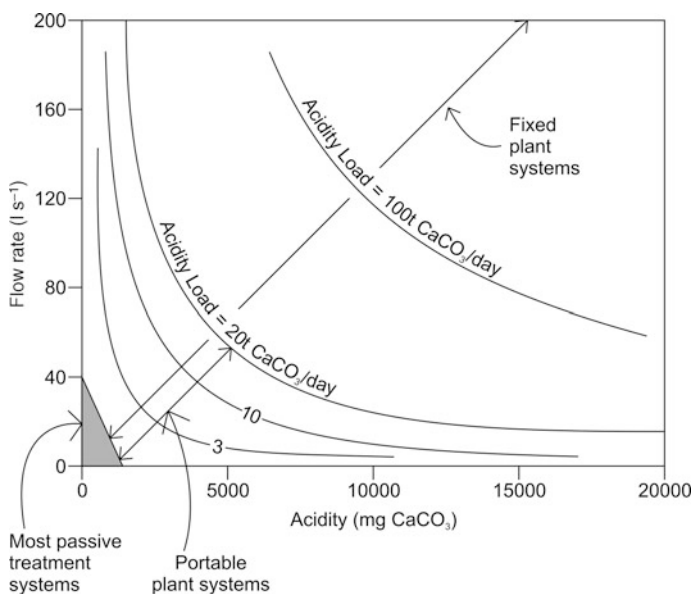
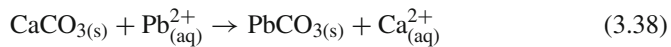
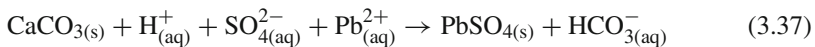


Fig. 3.23 Plot of flow rate versus acidity for AMD waters. Daily acidity loads (acidity load = (proton + latent acidity) × flow rate) are also shown. The selection of passive, portable plant or fixed plant treatment systems can be based on daily acidity loads (after Department of Industry, Tourism and Resources 2007)

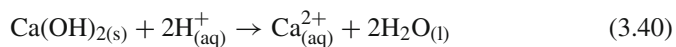
Table 3.8 Chemical compounds commonly used in AMD treatment (after Skousen and Ziemkiewicz 1996; Environment Australia 1997)

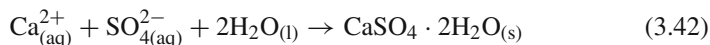
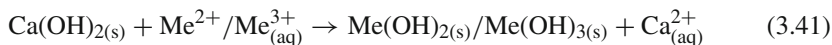
Common name	Chemical name	Chemical formula
Limestone	Mainly calcium carbonate	CaCO ₃
Quicklime or caustic lime	Calcium oxide	CaO
Hydrated lime	Calcium hydroxide	Ca(OH) ₂
Dolomite	Calcium-magnesium carbonate	CaMg(CO ₃) ₂
Caustic magnesia or brucite	Magnesium hydroxide	Mg(OH) ₂
Magnesite	Magnesium carbonate	MgCO ₃
Soda ash	Sodium carbonate	Na ₂ CO ₃
Caustic soda	Sodium hydroxide	NaOH
Ammonia	Anhydrous ammonia	NH ₃
Kiln dust		Largely CaO and Ca(OH) ₂
Coal fly ash		Largely CaCO ₃ and CaO

1. A *neutralizing agent*. A large variety of natural, by-product or manufactured chemicals are used for AMD treatment including local waste rock with high ANC (Table 3.8). Each of these neutralizing agents has different advantages and disadvantages. For example, the advantages of using limestone (largely CaCO₃) include low cost, ease of use, and formation of a dense, easily handled sludge. Disadvantages include slow reaction times and coating of the limestone particles with iron precipitates. In the reaction of limestone with AMD waters, hydrogen ions are consumed, bicarbonate ions generated, and dissolved metals are converted into sparingly soluble minerals such as sulfates, carbonates, and hydroxides:



Also, hydrated lime (Ca(OH)₂) is easy and safe to use, effective, and relatively inexpensive. The major disadvantages are the voluminous sludge produced and high initial costs for the establishment of the active treatment plant (Brown et al. 2002; Zinck and Griffith 2000). In this process, acid is neutralized (Reaction 3.40), metals (Me²⁺/Me³⁺) are precipitated in the form of metal hydroxides (Reaction 3.41), and gypsum is formed, if sufficient sulfate is in solution (Reaction 3.42):





Lime neutralization is efficient for removing metals such as cadmium, copper, iron, lead, nickel, and zinc from solution. Nonetheless, the solubility of metals varies with pH, and the lowest dissolved metal concentration is not achieved at the same pH (Brown et al. 2002; Kuyucak 2001). Not all metals can be precipitated at the same pH, and a combination of neutralizing agents (e.g. lime plus limestone) and other chemical additives may be needed to achieve acceptable water quality. Caustic soda (NaOH) is especially effective for treating AMD waters having a high manganese content. Manganese is difficult to remove from mine waters because the pH must be raised to above 9 before manganese will precipitate. Caustic soda raises the pH to above 10. Major disadvantages of caustic soda are its high costs, the dangers in handling the chemical, and poor sludge properties.

Other rock types (serpentinite; Bernier 2005) and unconventional industrial waste or byproducts such as fly ash from coal power stations or kiln dust from cement factories have been suggested for the treatment of AMD waters (Canty and Everett 2006; Pérez-López et al. 2007a, b). However, fly ash commonly contains elevated metal and metalloid concentrations, and its reaction rate is slow compared to lime (Kuyucak 2001).

The addition of neutralizing agents reduces the acidity and dissolved heavy metal concentrations of mine waters. Excessive neutralization can also lead to the enhanced dissolution of metals and metalloids and to waters with high metal and metalloid concentrations. Neutral to alkaline oxidizing conditions favour increased concentrations of some metals and metalloids (e.g. As, Sb, U) as ions or complexes in solution. Consequently, neutralization of AMD waters should raise the pH only to values necessary to precipitate and adsorb metals.

2. *Means for mixing AMD and the agents.* The chemicals are dispensed as a slurry by a range of neutralization plants or dosing systems. Active mixing of the chemicals is essential in order to prevent armouring of the reagent particles with reaction products such as metal hydroxides. These precipitates inhibit the neutralization reactions and cause excessive reagent consumption (Mitchell 2000).
3. *Procedures to delay iron oxidation.* Iron may need to remain in its reduced form (Fe^{2+}) until the precipitation of other metals has occurred and additional alkalinity has been dissolved in the AMD waters. Otherwise, the neutralizing solids may be coated with Fe^{3+} reaction products and rendered ineffective. Anoxic limestone drains are generally relied upon to keep iron in solution and to add alkalinity to the system.
4. *Settling ponds or vat reactors for removing precipitating metals.* The dissolved metals are forced to hydrolyze and precipitate during neutralization. The precipitates initially occur in suspension, and some of them may settle very slowly because of their small particle size (Kairies et al. 2005). Settling of precipitates

can be sped up by using flocculants and coagulants (Brown et al. 2002; Skousen and Ziemkiewicz 1996). Such reagents (e.g. inorganic Fe and Al salts, organic polymers) lead to the formation of larger solid aggregates. As a result, voluminous sludge, composed mainly of solid sulfates, hydroxides and carbonates as well as amorphous and poorly crystalline material, is produced which in most cases needs disposal (Dempsey and Jeon 2001; Ford et al. 1998; MEND 1997b; Widerlund et al. 2005; Younger et al. 2002; Zinck 1997). Depending on sludge characteristics, the sludge may have to be protected from oxidation, leaching, and potential metal mobilization. This is achieved by mixing it with more alkaline reagents prior to its disposal. Alternatively, depending on the mineralogical and chemical characteristics of the AMD sludge, metals can be recovered from the sludges using strong acids. Very pure Fe^{3+} hydroxide sludges may be used as pigments in the production of coloured bricks and concrete.

In many cases, the simple addition of neutralizing agents is not sufficient to reduce metal and metalloid concentrations in mine waters to acceptable levels. These waters need other chemical treatments to lower dissolved metal and metalloid loads. Ponds or wetlands may be required to further improve water quality prior to the discharge to a receiving stream.

3.12.2 Other Chemical Treatments

Waste waters with elevated antimony, arsenic, chromium, iron, manganese, mercury, molybdenum, and selenium contents may require chemical treatment methods other than neutralization. These methods do not employ the addition of traditional alkaline reagents like lime. They use unconventional industrial byproducts such as slags or rely on oxidation, reduction, precipitation, adsorption, or cation exchange processes (Ahn et al. 2003; Brant et al. 1999; Kuyucak 2001; Skousen and Ziemkiewicz 1996; Younger et al. 2002).

Mine waters may have elevated arsenic values at acid to alkaline pH values. A reduction in the dissolved arsenic content of AMD waters is achieved through aeration or the addition of ferric or ferrous salts (Dey et al. 2009; Seidel et al. 2005; Taschereau and Fytas 2000). This causes the coprecipitation and adsorption of arsenic with ferric hydroxides, or the precipitation of arsenic as an arsenate phase (AsO_4^{3-}). Some arsenates are considered to be stable (e.g. ferric arsenate) or unstable phases (e.g. calcium arsenate) under neutral pH conditions. Consequently, arsenate formation may result only in the temporary fixation of arsenic.

Other treatment techniques involve the addition of oxidants (e.g. Cl_2 , O_2 , NaOCl , CaCl_2 , FeCl_3 , H_2O_2 , KMnO_4) which will convert dissolved Fe^{2+} to insoluble Fe^{3+} precipitates, aqueous Mn^{2+} to insoluble Mn^{4+} precipitates, and As^{3+} to less toxic As^{5+} . Also, the addition of barium salts such as barium chloride (BaCl_2) or barium sulfide (BaS) forces the precipitation of barium sulfate (BaSO_4) and associated lowering of aqueous sulfate and metal concentrations (Hlabela et al. 2007; Maree et al.

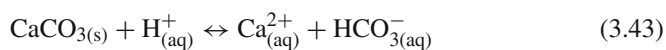
2004). Moreover, the addition of soluble sulfide reductants (e.g. FeS, BaS, $(\text{NH}_4)_2\text{S}$, NaS_2) causes the precipitation of mercury and other metals and metalloids as sulfides (Kuyucak 2001). Injection of gaseous sulfide compounds (e.g. H_2S) into AMD waters and the addition of zerovalent iron may also be a successful treatment technique (Herbert 2003; Lindsay et al. 2008).

The above treatment techniques commonly result in the formation of small suspended particles in the waste water. The addition of coagulants (e.g. FeSO_4 , FeCl_3 , MgCl_2 , CaCl_2) and flocculants (e.g. Na_4SiO_4 , starch derivatives, bentonite, polysaccharides) improves the settling of these small precipitates (Brown et al. 2002). These added chemicals are also useful in removing an array of metals from solution by adsorption. The addition of zeolites or synthetic polymeric resins to AMD waters can also be successful (Cui et al. 2006; Li et al. 2007b; Wingenfelder et al. 2005). The cation exchange capacity of these additives allows the substitution of harmless ions present in the additives for dissolved metals in the AMD waters.

3.12.3 Passive Neutralization

Passive neutralization based on the dissolution of calcite is widely used to remediate AMD waters (Cravotta and Ward 2008). AMD waters are thereby channeled through a bed of crushed limestone, placed into a cell or drain. The addition of crushed limestone to AMD impacted streams is also possible (Simmons et al. 2006).

Calcitic limestone is highly effective in treating AMD, while dolomitic limestone is less reactive and hence, less effective in treating AMD (Cravotta et al. 2008). The calcite dissolution consumes acidity and introduces buffering capacity in the form of bicarbonate ions into AMD waters:



Open limestone channels (OLC) are often implemented in the treatment of AMD. However, AMD waters contain high levels of dissolved iron that precipitates as Fe^{3+} hydroxides and oxyhydroxides on the surfaces of calcite grains. These mineral coatings prevent further reaction and dissolution of calcite grains. Consequently, the efficiency and lifetime of a limestone drain is dependent on the rate of Fe precipitation (Santomartino and Webb 2007). Conventional drains show early clogging of the porosity and coating of the calcite grains, particularly when high acidity and metal concentrations are treated. The formation of abundant mineral precipitates such Fe^{3+} hydroxides and oxyhydroxides as well as gypsum may render the limestone drain ineffective (Soler et al. 2008). The use of dolomite instead of calcite may prevent such secondary mineral formation (Huminicki and Rimstidt 2008). Also, the use of fine-grained calcitic limestone dispersed in a high porosity matrix of wood shavings could be more appropriate (Caraballo et al. 2009; Rötting et al. 2008a, b).

3.12.3.1 Anoxic Limestone Drains

In an oxidizing environment, limestone becomes coated with Fe^{3+} reaction products and rendered ineffective in the production of bicarbonate ions. This disadvantage is overcome by using so-called *anoxic limestone drains* (ALD) (Fig. 3.24) (Brown et al. 2002; Cravotta 2003; Cravotta and Trahan 1999; Hedin et al. 1994b; Kleinmann 1997; Kleinmann et al. 1998; Mukhopadhyay et al. 2007; Nuttall and Younger 2000; Skousen and Ziemkiewicz 1996; Younger et al. 2002). Anoxic limestone drains consist of shallow trenches backfilled with crushed limestone and covered with plastic and impermeable soil or sediment. These backfilled trenches are sealed from the atmosphere in order to maintain iron as dissolved Fe^{2+} species. This prevents oxidation of Fe^{2+} to Fe^{3+} and hydrolysis of Fe^{3+} which would otherwise form Fe^{3+} precipitates coating the carbonates. As a result, the pH can be raised to neutral or even alkaline levels, migration of Fe^{2+} -rich waters is possible, and there is no adsorption of metals onto the precipitating Fe^{3+} phases. The effluent pH of anoxic limestone drains is typically between 6 and 7. Once the pH has been adjusted and the drainage has exited from the channel, controlled aeration permits oxidation of dissolved metals, hydrolysis, and precipitation of metal hydroxides or carbonates.

While anoxic limestone drains provide alkalinity to AMD waters, certain AMD waters are not suitable for anoxic limestone drain treatment. If the mine water contains elevated dissolved Fe^{3+} and oxygen ($>1\text{--}2\text{ mg l}^{-1}$) concentrations, armoring of the limestone with iron phases will occur. Such waters require modified limestone beds (Hammarstrom et al. 2003) or anoxic ponds at the inflow to the limestone drain to induce reducing conditions and to convert any Fe^{3+} to Fe^{2+} . Appreciable Al^{3+} contents are also not suitable for anoxic limestone drain treatment. The aluminium will precipitate as hydroxide, causing the clogging of limestone pores, plugging of the drain, and armoring of the carbonates with aluminium precipitates (Demchak et al. 2001). Pre-treatment of the drainage water is needed in order to remove aluminium from the waters. This may also be achieved in anoxic abiotic ponds.

While anoxic limestone drains are commonly used in the treatment of AMD waters, their long-term performance remains to be determined. Their effectiveness is based on the dissolution of carbonate over time. The dissolution in a sealed trench

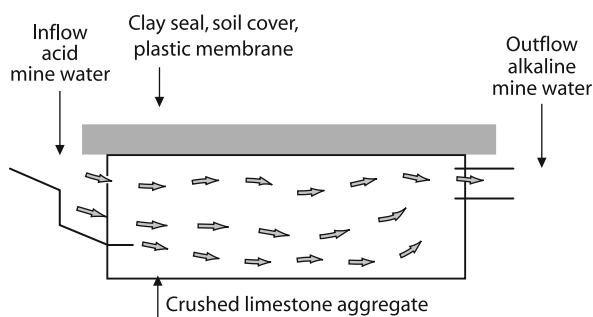


Fig. 3.24 Schematic cross-section of an anoxic limestone drain (after Environment Australia 1997; Younger et al. 2002)

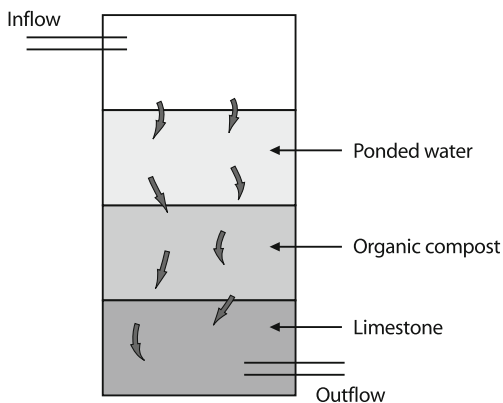
will undoubtedly lead to cavernous zones, to karst like features and, depending on its structural integrity, to the potential collapse of the subsurface drain.

3.12.3.2 Successive Alkalinity Producing Systems

Alkalinity may also be added in so-called *successive alkalinity producing systems* (SAPS) or more appropriately termed *reducing and alkalinity producing systems* (RAPS), whereby water passes vertically through successive layers of organic matter and limestone chippings (Brown et al. 2002; Demchak et al. 2001; Skousen and Ziemkiewicz 1996; Riefler et al. 2008) (Fig. 3.25). These vertical flow systems have a layer of organic substrate (e.g. mushroom compost) which reduces Fe^{3+} to Fe^{2+} and eliminates the oxygen dissolved in the water. The reduced water then enters an alkalinity generating layer of limestone before it is finally discharged.

The layer of organic matter is to support the activity of *sulfate reducing bacteria* (SRB). These bacteria reduce dissolved sulfate to hydrogen sulfide, which can then precipitate dissolved metals as solid sulfides, resulting in the removal of metals from solution (Reactions 3.49 and 3.50). Environmental conditions such as temperature influence the growth of SRB bacteria and control the treatment efficiency of SAPS (Bhattacharya et al. 2008; Ji et al. 2008).

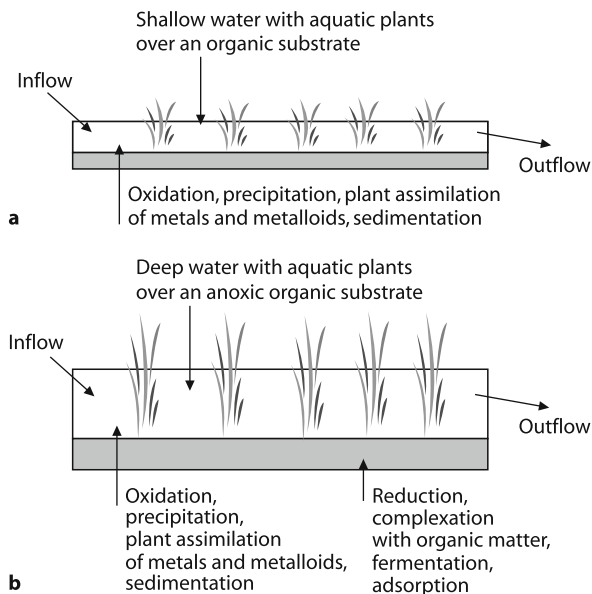
Fig. 3.25 Schematic cross-section of a successive alkalinity producing system (after Environment Australia 1997; Brown et al. 2002)



3.12.4 Wetlands

Wetlands are organic-rich, water-saturated shallow ponds. They are well established treatment options for sewage effluents and other wastewaters, including landfill leachates as well as agricultural and stormwater run-offs. Wetlands have also found their application in the treatment of AMD waters. The treatment is based on a number of physical, chemical and biochemical processes which ameliorate or *polish* AMD waters (Brown et al. 2002; Gazebo et al. 1996; Jones et al. 1998; Kalin 2004; Kalin et al. 2006; Mitsch and Wise 1998; Porter and Nairn 2008; Skousen

Fig. 3.26 Generalized profiles of (a) aerobic and (b) anaerobic wetlands (after Younger et al. 2002). Physical and chemical processes contributing to metal retention in wetlands are also shown (after Walton-Day 1999)



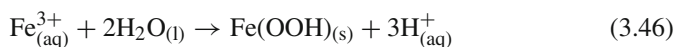
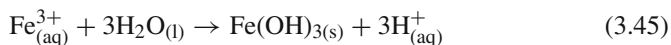
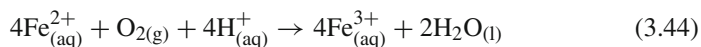
and Ziemkiewicz 1996; Tyrrell 1996; Walton-Day 1999; Whitehead and Prior 2005; Younger et al. 2002). These processes include sulfide precipitation, oxidation and reduction reactions, cation exchange and adsorption of metals onto the organic substrate, neutralization of proton acidity, adsorption of metals by precipitating Fe^{3+} hydroxides, and metal uptake by plants (Walton-Day 1999) (Fig. 3.26). Other wetland processes are filtering of suspended solids and colloidal matter from the mine water as well as sedimentation and retention of these precipitates by physical entrapment. Consequently, metal-rich sediments and sludges accumulate within wetlands, with the metal loadings increasing over time. Wetlands have been used to remediate AMD waters, and there is the potential for wetlands to treat highly alkaline ($\text{pH} > 12$) drainage waters as well (Mayes et al. 2009).

A basic design scheme for constructed wetlands includes an organic substrate and discrete, controlled in- and outflow locations (Skousen and Ziemkiewicz 1996; Walton-Day 1999). In addition, wetlands may grow plants (e.g. reeds, sphagnum moss, cattails) that replenish the organic substrate and support naturally occurring bacteria, vertebrates and invertebrates. Two types of wetlands, aerobic and anaerobic ones, are used for AMD water treatment.

3.12.4.1 Surface Flow or Aerobic Wetland

Aerobic wetlands are generally used for net alkaline waters [i.e. *net alkaline* according to the definition by Hedin et al. (1994a)] (Cravotta 2007; Hedin 2008). These wetlands are with or without vegetation and relatively shallow (~ 0.3 m). Water

flows above the surface of an organic substrate or soil (Fig. 3.26a). The wetlands are designed to encourage the oxidation and precipitation of metals. Most importantly, dissolved iron and manganese ions are oxidized and precipitated as iron and manganese hydroxides and oxyhydroxides. Such reactions are illustrated by the following reactions:

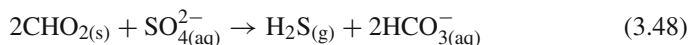
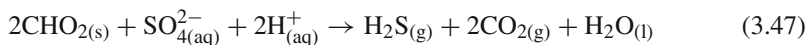


Aerobic wetlands use oxidation and hydrolysis reactions to treat mine waters (Iribar et al. 2000). The systems function well in precipitating iron and other metals from mine waters. If the mine waters are metal-bearing and alkaline, only the aerobic wetlands treatment is needed.

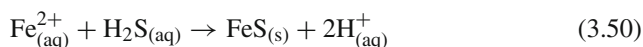
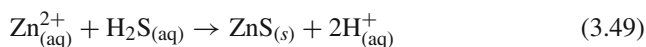
The hydrolysis of iron produces acidity (Reactions 3.45 and 3.46) and lowers the pH of the mine water in the wetland. The lowered pH causes stress to plants growing in the wetland. Surface flow wetlands do not produce enough alkalinity that is required to buffer the acidity produced from sulfide oxidation at the AMD source and hydrolysis reactions in the wetland. Alkalinity may have to be added to such waters. This can be achieved by growing certain plants in the wetland (e.g. reeds). Reeds are capable of passing oxygen through their root zone and the organic substrate. As a result, oxygen is converted to carbon dioxide. The carbon dioxide gas dissolves in the mine water, consumes hydrogen and adds alkalinity in the form of bicarbonate. Alternatively, anoxic limestone drains may have to be installed at the inflow location of the wetland. Such additional measures may lead to increased pH values at the wetland outflow and metal sedimentation and adsorption in the wetland. Despite these metal removal mechanisms, the treatment of high iron and low pH AMD waters by aerobic wetlands has not been adequate (Nyquist and Greger 2009).

3.12.4.2 Subsurface Flow or Anaerobic Wetland

Anaerobic wetlands are generally used for net acid waters [i.e. *net acid* according to the definition by Hedin et al. (1994a)]. Water flows through a relatively deep (~1 m), permeable, and anoxic organic substrate (Fig. 3.26b). Placement of organic waste (e.g. mushroom compost, saw dust, manure) into wetlands helps to establish the reducing conditions. Anoxic conditions favour the proliferation of *sulfate reducing bacteria* (SRB) (Gould and Kapoor 2003). Bacterial sulfate reduction, or reduction of oxidized acid waters by reactive organic matter (simplified as organic molecule CH_2O), results in a number of chemical reactions (Blowes et al. 1994; Deutsch 1997; Mills 1999; Mitchell 2000; Walton-Day 1999). The most important reaction is the reduction of dissolved sulfate to hydrogen sulfide gas:



The hydrogen sulfide gas formed during sulfate reduction may react with dissolved metals. Consequently, solid metal sulfides precipitate:



Precipitation of metal sulfides results in the production of hydrogen ions. However, the sulfate reducing reactions (Reactions 3.47 and 3.48) generate more alkalinity; thus, net alkaline conditions prevail. If bacterially mediated sulfate reduction is not achieved, a reduction in dissolved sulfate concentrations occurs through the precipitation of gypsum. Other chemical reactions will consume any dissolved oxygen, cause the precipitation of metal sulfides, convert iron and manganese hydroxides to sulfides, reduce metals, reduce sulfate to sulfur or sulfide, and generate bicarbonate (Tyrrell 1996; Walton-Day 1999). In addition, oxidation/hydrolysis reactions may occur at the wetland's surface.

Alkalinity is produced in the form of bicarbonate in the sulfate reduction reactions (Reactions 3.49 and 3.50). The bicarbonate acts a buffer to neutralize any hydrogen ions. However, the bicarbonate is not necessarily permanent. It will be permanent only if the hydrogen sulfide is removed by degassing. Alternatively, the sulfide ion reacts: (a) with an organic compound to form an organic sulfide; or (b) with a dissolved metal ion such as Zn^{2+} or Fe^{2+} to form a solid metal sulfide (Reactions 3.49 and 3.50) (Walton-Day 1999).

Overall, the chemical reactions result in sulfate reduction, the precipitation of metal sulfides into surface sediments, and an increase in pH and alkalinity (Morrison and Aplin 2009). Other wetland processes include sedimentation, physical entrapment of solid particulates and colloids, removal of metals through adsorption onto and coprecipitation with wetland particulates, complexation with organic materials, and plant assimilation (Ledin and Pedersen 1996; Walton-Day 1999).

A series of aquatic plants are known to grow in metalliferous surface sediments of wetlands and sequester metals and metalloids into their roots and above-ground biomass (Weis and Weis 2004). Selected aquatic plants (e.g. cattails *Typha*) are used to treat mine waters in constructed wetlands (Goulet and Pick 2001; Maine et al. 2006; Mishra et al. 2008; Sheoran 2006a, b; Upadhyay and Tripathi 2007). Some of these aquatic plants growing in wetlands or mine water ponds can take up large amounts of heavy metals and metalloids (Hozhina et al. 2001). Other plant species tolerate high metal concentrations and do not bioaccumulate metals to any significant degree, compared to the overall metal retention by the wetland substrate (Karathanasis and Johnson 2003).

The effectiveness of an anaerobic wetland to remediate AMD waters is largely controlled by the presence of a reduced organic substrate. Such a substrate promotes

the existence of a suitable microbial community including sulfate reducing bacteria (SRB). Replacement of the compost substrate or further addition of organic wastes may be required to promote the presence of microorganisms capable of remediating the waste waters (Dann et al. 2009).

3.12.4.3 Use of Wetlands

Wetland processes aim to decrease acidity and dissolved metal and sulfate concentrations. Effluents produced should be of such quality that they can be discharged to other surface water bodies. Nonetheless, in order to achieve adequate treatment of AMD waters, the aerobic or anaerobic wetlands may require additions. Alkalinity producing systems such as anoxic limestone drains may need to be installed where additional bicarbonate is needed (Barton and Karathanasis 1999). Also, manganese is persistent in mine waters unless the pH has been raised to above 9. Therefore, manganese can be carried for long distances downstream of a source of mine drainage. Aerobic and anaerobic wetlands are incapable of lowering dissolved manganese concentrations to a significant degree. Rock filters, bioreactors or limestone cobble ponds may need to be constructed in order to remove the elevated manganese concentrations (Brant et al. 1999; Bamforth et al. 2006; Johnson and Younger 2005; Mariner et al. 2008). Such rock filters operate as shallow wetlands and remove dissolved metals and hydrogen sulfide concentrations. Depending on the composition of the AMD waters, they may require a sequential sequence of water treatment stages (Lamb et al. 1998) (Fig. 3.27).

Typically, AMD waters pass through a settling pond to remove suspended solids and then through an anaerobic abiotic pond to reduce any Fe^{3+} to Fe^{2+} and to remove aluminium from the waters. The waters then flow through an anoxic limestone drain to induce alkalinity. The discharge passes through an anaerobic wetland to induce metal precipitation and sulfate reduction. The treatment is followed by an aerobic wetland – to achieve precipitation of iron – and possibly a rock filter or limestone cobble pond – to remove any dissolved metals such as manganese or hydrogen sulfide.

Generally, the establishment of wetlands is often a preferred option for the complete or partial treatment of AMD waters which have low TDS values. Wetlands are an aesthetically attractive, passive, low-cost, low-maintenance, and sustainable method (Brown et al. 2002; SMME 1998). However, a number of wetlands used to treat AMD waters have failed over time (Kalin et al. 2006; Woulds and Ngwenya 2004) (Fig. 3.28). Furthermore, wetlands are sensitive to pulses of high metal concentrations, and the accumulated metals may be mobilized by microbiological processes (Ledin and Pedersen 1996). Moreover, the accumulation of metals in wetlands creates a metal-rich aquatic environment which may experience changes in its hydrology or climate in the long or short term. A wetland needs a sufficient year-round supply of water that would ensure that the wetland remains in a permanently saturated condition (Jones and Chapman 1995). Drying out of a wetland will lead to the oxidation of biological materials and sulfides, and the formation of evaporative salts. If jarosite-type minerals and metal sulfate salts have formed in the

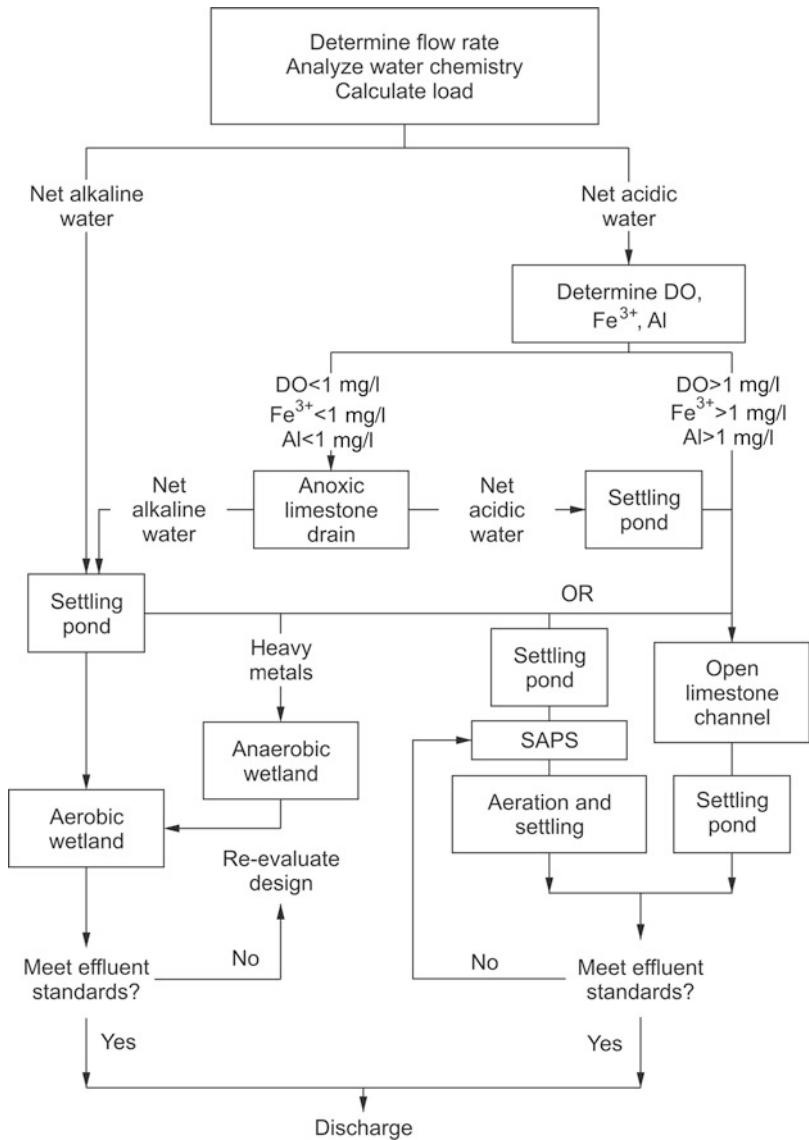


Fig. 3.27 Flow chart showing the chemical determinations necessary for the design of passive treatment systems (after Kleinmann et al. 1998; Gusek 2009). DO: dissolved oxygen; net alkaline: alkalinity > acidity; net acidic: acidity > alkalinity

wetland during drying, the minerals will become unstable upon water inundation (Zhu et al. 2008). At the beginning of the next rain period, sulfuric acid, metals, and salts are released. These contaminants are then flushed straight through the wetland and into receiving waters. Wetlands without sufficient water supply become



Fig. 3.28 Wetland at the Horn Island gold mine, Australia. The wetland has failed because an adjacent damwall was constructed using acid generating waste rocks (foreground), which resulted in significant AMD and caused plant death

chemical time bombs and net sources of metals, metalloids, and sulfate. Therefore, semi-arid areas, polar regions as well as areas with distinct seasonal rainfall and run-off are unsuitable for such a remediation measure.

3.12.5 Bioreactors

Sulfate reducing passive bioreactors are increasingly used for the treatment of AMD waters (Neculita et al. 2007). Bioreactors are generally specifically designed tanks; however, mine shafts can also be used as in situ bioreactors (Bless et al. 2008). The reactors employ organic and alkaline waste materials to increase pH and alkalinity and to accomplish metal and sulfate removal from AMD waters. The removal of metals and sulfate from solutions in bioreactors relies on an anaerobic environment that promotes the presence of a microflora including *sulfate reducing bacteria* (SRB). Such an environment is created by adding organic waste (e.g. compost, mussel shells, grass cuttings, biodiesel waste) to the reactor and in some cases bacterial biomass (e.g. rumen fluid), which is to inoculate the waste with sulfate reducing

bacteria (SRB) (Costa et al. 2008; Greben et al. 2009; McCauley et al. 2009; Touze et al. 2008; Zamzow et al. 2006). The precipitation process relies on the generation of sulfide activity and the microbiological reduction of dissolved sulfate to hydrogen sulfide by sulfate reducing bacteria (SRB). The sulfide then reacts with the dissolved metals, which precipitate as insoluble solid sulfides. Other metal removal mechanisms occur in the reactor, including adsorption of metals, precipitation of metal carbonate and hydroxide phases, and capture of metals by microorganisms. The presence of organic-rich materials does not only promote removal of dissolved metals from AMD solutions but also pH neutralization (Gibert et al. 2005; Johnson and Hallberg 2005a). Bioreactors have successfully treated AMD waters at several abandoned mine sites (Neculita et al. 2007, 2008).

3.12.6 Adit Plugging

Adits, shafts and tunnels are common point sources of AMD. Some of them were originally installed to drain the underground mine workings, and sealing such mine openings with plugs can reduce the volume of drainage waters (Plumlee and Logsdon 1999; SMME 1998). Adit plugs are concrete and grout hydraulic seals that exert hydraulic control on ground waters emanating from mine openings. The plugs minimize or even prevent ground waters from escaping from underground workings (Banks et al. 1997). The reasoning for this technique is that the plug removes an AMD point source. In addition, ground water will back up in the underground mine workings, precluding atmospheric oxygen from reaching and oxidizing sulfides (Plumlee and Logsdon 1999). Placement of organic material into flooded underground workings may help to induce anoxic conditions and prevent sulfide oxidation and AMD generation (SMME 1998). Adit plugs can prevent the infiltration of oxygen and water into, and the migration of AMD waters out of, underground workings.

A problem may arise if leakage of drainage water occurs around the plug or other hydrologic conduits, and pre-mining springs and water tables can be reactivated carrying now contaminated waters (Plumlee and Logsdon 1999). Moreover, flooding of historic mines with abundant soluble iron salts in the workings may trigger sulfide oxidation. As a consequence, the efficiency and long-term stability of seals are controversial, especially as there have been seal failures and associated massive releases of AMD effluents.

3.12.7 Ground Water Treatment

AMD contaminated ground water requires treatment. Unlike seepage and run-off, *acid ground water* cannot be easily intercepted. Current treatment techniques involve pumping of the water to the surface and treating it there (*ex situ*), or trying to contain and treat the contaminated ground water in the ground (*in situ*).

Pump-and-treat methods are well established ex situ techniques used to clean up contaminated waters. Such pump-and-treat systems flush contaminants from the aquifer and treat the pumped ground water at the surface using standard metal removal processes. The major shortcoming of the pump-and-treat approach is that massive amounts of ground water – commonly several times the volume of the contaminated plume – must be pumped to adequately dislodge the metal contaminants. Such aggressive pumping lowers the water table and leaves large pockets of metal-rich subsurface materials. The pump-and-treat technology often fails to achieve ground water clean-up standards in reasonable time frames, and the success rate of this conventional technology is rather poor. The pump-and-treat technology is recognized, therefore, as being quite inefficient.

In situ treatment techniques aim to take advantage of the natural hydrogeology of a site. They utilize the natural ground water flow. In some cases, a natural reduction in contaminant concentrations can be observed as contaminants migrate from the AMD source into the aquifer. This reduction is primarily due to neutralization reactions. The acid ground water may migrate through a carbonate aquifer, and the natural neutralization reactions can lead to decreased contaminant loads. Other *natural attenuation* mechanisms in aquifers involve dilution, adsorption, precipitation, dispersion and biodegradation processes. In addition, passive chemical or biological treatment systems can be employed for the remediation of contaminated ground waters. AMD contaminated ground waters can be remediated using a permeable, reactive zone of organic matter (e.g. sewage sludge, sawdust, wood chips, municipal leaf compost), calcite, zeolites, phosphates, ferric oxyhydroxides, zero valent iron or other materials submerged in the ground water flow path (Amos and Younger 2003; Amos et al. 2004; Benner et al. 2002; Blowes et al. 2003; Jarvis et al. 2006; Mayer et al. 2006; SMME 1998; Su and Puls 2008; Younger et al. 2002). These *permeable reactive barriers* are implemented by digging a trench in the flow path of a contaminant plume and backfilling the trench with the reagents mixed with permeable sand and gravel (Fig. 3.29). Neutralization, precipitation

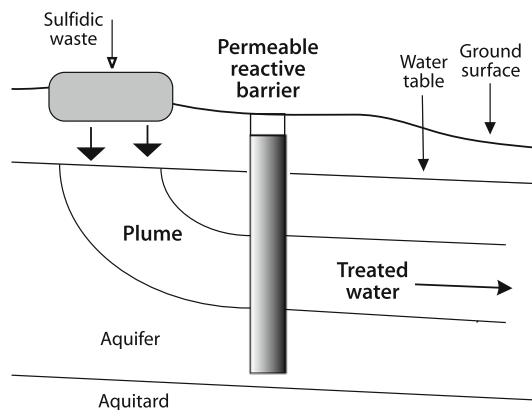


Fig. 3.29 Schematic cross-section showing in situ treatment of acid ground water with a permeable reactive barrier (after Jambor et al. 2000b)

and adsorption processes in these materials cause the metal and acidity concentrations in the ground water to decrease. The barriers remove the majority of the metals, metalloids and acidity from the polluted waters (Benner et al. 1999; Sasaki et al. 2008; Smyth et al. 2001). Also, the placement of permeable organic matter or liquid organic substances such as methanol in the ground water flow path can favour the abundance of sulfate reducing bacteria (Bilek 2006). The bacteria create a reducing zone and reduce sulfate to sulfide. Any dissolved metal are removed from solution as the metals precipitate as sulfides. Injection of sodium hydroxide into acid ground water may also be a successful treatment technique (Werner et al. 2008).

3.13 Summary

The constituents of mine waters are highly variable and include elements and compounds from mineral-rock reactions, process chemicals from mineral beneficiation and hydrometallurgical extraction, and nitrogen compounds from blasting operations. Aqueous solutions in contact with oxidizing sulfides will contain increased acidity, iron, sulfate, metal and metalloid concentrations. While AMD waters are well known for their elevated metal concentrations, neutral to alkaline conditions can also favour the release of metals and metalloids from waste materials. Elevated metal and metalloid concentrations in neutral to alkaline pH, oxidizing mine waters are promoted by: (a) the formation of ionic species (e.g. Zn^{2+}), oxy-anions (e.g. AsO_4^{3-}) and aqueous metal complexes (e.g. U carbonate complexes, Zn sulfate complexes); and (b) the lack of sorption onto and coprecipitation with secondary iron minerals.

Several processes influence the composition of AMD waters. These include biochemical processes, the precipitation and dissolution of secondary minerals, and the sorption and desorption of solutes with particulates. Changes to Eh and pH conditions influence the behaviour, concentrations and bioavailability of metals and metalloids.

The oxidation of Fe^{2+} and hydrolysis of iron in AMD waters produces hydrous ferric oxide (HFO) precipitates (i.e. ochres or yellow boys), which include non-crystalline iron phases as well as iron minerals such as schwertmannite and ferrihydrite. The occurrence of different iron minerals is largely pH dependent. The iron solids occur as colourful bright reddish-yellow to yellowish-brown stains, coatings, suspended particles, colloids, gelatinous flocculants, and precipitates in AMD affected waters. The high specific surface area of hydrous ferric oxide precipitates results in adsorption and coprecipitation of trace metals. Consequently, these solid phases control the mobility, fate and transport of trace metals in AMD waters.

The dissolution of soluble Fe^{2+} sulfate salts can be a significant source of acidity, Fe^{3+} and dissolved metals which were originally adsorbed onto or incorporated in solid phases. Also, the oxidation of Fe^{2+} to Fe^{3+} and subsequent hydrolysis of iron can add significant acidity to mine waters.

Metals are present in AMD waters as simple metal ions or metal complexes. However, significant metal concentrations can also be transported by colloidal materials in ground and surface waters. Colloidal iron precipitates with adsorbed metals can represent important transport modes for metals in mine environments and streams well beyond the mine site.

The monitoring of mine waters is designed: (a) to identify the early presence of, or the changes to, dissolved or suspended constituents; and (b) to ensure that discharged water meets a specified water quality standard. Sites should measure or estimate flow rates or periodic flow volumes in order to make calculations of contaminant loads possible. Possible tools for the prediction of water chemistry include geological, mathematical and computational modeling. These tools cannot be used, however, to predict the exact chemistry of mine waters.

Table 3.9 Web sites covering aspects of mine waters

Organization	Web address and description
International Mine Water Association (IMWA)	http://www.imwa.info/ Congresses, symposia, meetings
Acid Drainage Technology Initiative (ADTI), USA	http://ese.mines.edu/adti/ Information dissemination on AMD remediation technologies in the USA
US Environmental Protection Agency (EPA), National Pollutant Discharge Elimination System (NPDES)	http://cfpub.epa.gov/npdes/indpermitting/mining.cfm?program_id=14 Regulation of water discharge from mine sites
US Geological Survey (USGS) Mine Drainage Activities	http://mine-drainage.usgs.gov/ Information and reports on AMD monitoring and remediation
Department of Environmental Protection, Pennsylvania, USA	http://www.dep.state.pa.us/dep/deputate/minres/districts/cmdp/main.htm Technical reports on AMD and coal mine drainage
West Virginia Water Research Institute, USA	http://www.wri.nrcc.wvu.edu/index.cfm Technical reports on AMD prediction, remediation, and prevention
Mine Environment Neutral Drainage Program (MEND), Canada	http://www.nrcan-rncan.gc.ca/mms-smm/tect-tech/sat-set/med-ndd-eng.htm Extensive technical reports and manuals on AMD sampling, analyses, prediction, monitoring, prevention, and treatment
Minesite Drainage Assessment Group (MDAG), Canada	http://www.mdag.com Case studies, articles, resources and publications on mine waters
Remediation Technologies Development Forum (RTDF)	http://www.rtdf.org Information on reactive barrier technology
Partnership for Acid Drainage Remediation in Europe (PADRE)	http://www.padre.imwa.info Information on mine water management and treatment
InfoMine	http://technology.infomine.com/enviromine/ News and information on AMD for the mining industry

Sulfidic waste rock dumps are the major sources of AMD because of their sheer volume. The quality and volume of AMD seepages emanating from sulfidic piles are influenced by the properties of the waste materials. Despite their heterogeneity, waste dumps generally exhibit a single continuous water table with a moderate hydraulic gradient. The physical and chemical conditions, and mineralogical composition of waste materials vary on a microscopic scale. Therefore, drainage water from a sulfidic waste dump represents a mixture of fluids from a variety of dynamic micro-environments within the pile. The different rates of the various weathering reactions within the waste can cause temporal changes to the seepage chemistry.

At mine sites, water management strategies aim to protect aquatic environments and to reduce the water volume requiring treatment. Treatment techniques for AMD waters are designed: to reduce volume; to raise pH; to lower dissolved metal and sulfate concentrations; to lower the bioavailability of metals; to oxidize or reduce the solution; and to collect, dispose or isolate any waste waters or metal-rich precipitates. Established AMD treatment options include: neutralization using a range of possible neutralizing materials; construction of aerobic or anaerobic wetlands and bioreactors; installation of open limestone drainage channels, anoxic limestone drains, and successive alkalinity producing systems. Acid ground waters are treated using pump-and-treat, natural attenuation, and permeable reactive barrier technologies.

Further information on mine waters can be obtained from web sites shown in Table 3.9.