Chapter One

Introduction

1.1 Fundamentals of AMD

Sulphide minerals are a common minor component of most rocks in the Earth's crust. In some geological environments, particularly metallic ore deposits and organic sediments, sulphides may comprise a significant proportion of the rock. Exposure of these sulphides, particularly pyrite and pyrrhotite, to an oxygenated environment by mining may lead to the development of acid mine drainage (AMD). AMD is defined as the formation of "a low pH leachate formed by the oxidation of sulphide minerals contained in a waste usually produced by a mining or mineral processing operation" (Nyavor and Egiebor, 1995, p225).

The acidic waters of AMD have the ability to dissolve other minerals present in the waste, releasing cations and anions into solution. Certain metal ions will have a detrimental effect on the environment if the leachate pollutes local ground and surface waters. The most common metals and metalloids associated with AMD are Al, As, Cd, Co, Cu, Fe, Hg, Mn, Mo, Ni, Pb, Sb and Zn (Parker and Robertson, 1999).

Sulphidic mine wastes have the potential to produce AMD for hundreds of years after mine closure, creating major financial and environmental liabilities for the mining company or government agency responsible. The scale of the problem has been outlined in a survey by Mine Environment Neutral Drainage (MEND) Program in 1995 (Harries, 1997) showing that Canada had approximately 2.65 billion tonnes of potentially acid generating mine waste with an estimated total liability of between C$1.92 to C$5.25 billion; the cost being dependent on the treatment/control option chosen. In the USA up to 10,000 km of watercourses may be affected by AMD (Harries, 1997). Using data from a mining industry survey conducted by Harries (1997), the author calculated that the costs of managing AMD in Australia were A$40,000 ha^{-1} at currently operating mine sites. This figure rose to A$100,000 ha^{-1} for the remediation of historic mine sites. These figures support the view that AMD is the greatest environmental technical challenge facing the mining industry today (Mitchell, 1999).

AMD will typically occur when mine waste meets the following conditions, (Hutchison and Ellison, 1992):

1) Chemical: enough sulphide is present to form acid leachate more rapidly than it can be neutralised by reactions of alkaline compounds.
2) Physical: permeability is high enough to allow infiltration of sufficient oxygen and water to support the acid producing reactions.
3) Climatical: local climate is humid enough to provide sufficient water for the reactions to occur.

The two major strategies for the management of AMD problems are treatment and control. Treatment involves various methods designed to capture the leachate produced by mine waste, raise pH and remove the contained metal before the waters are released into the off-mine environment. Control methods of AMD management are designed to prevent the production of AMD.

Control methods typically involve the modification of conditions 1 and/or 2. Condition 1 is altered by the addition of alkaline material to neutralise any acidity produced. Condition 2 is changed by various methods to reduce permeability and therefore access of oxygen and/or water to the sulphides, inhibiting oxidation. All control methods currently in use at mining operations have limitations involving long-term stability, initial and ongoing expense or geographical and climatological suitability.

A new method currently under development involves stabilisation of sulphide minerals with phosphate or silicate coatings (Evangelou, 2001). Ongoing research into this control method may lead to the development of an inexpensive, efficient, long-term technique to prevent the oxidation of sulphides and therefore AMD generation in mine wastes.

This introduction contains an overview of the current state of research into AMD processes, secondary mineralogical influences on AMD and phosphate stabilisation techniques for AMD prevention. Definitions critical to the understanding of the subject are also included. The primary objective and specific aims of the research project are outlined in context with the current research. Finally an outline of the thesis is presented.

1.2 Sulphide oxidation and generation of AMD waters

1.2.1 Acid generation

The oxidation of sulphide minerals is the most important acid-generating reaction occurring in weathering mine wastes. Oxidation occurs with the exposure of the sulphide minerals to oxygen and water, described by the following reaction:

$$2MeS_{(S)} + 7/2O_{2(g)} + H_2O_{(l)} \Rightarrow 2Me^{+}_{(aq)} + 2SO_4{}^{2-}{}_{(aq)} + 2H^{+}_{(aq)} \qquad (1.1)$$

where Me represents a metal (e.g. Fe, Cu or Zn) (St-Arnaud, 1994). The exact reaction stoichiometry is dependent on the mineral species; the most important acid-generating minerals are pyrite, pyrrhotite, chalcopyrite, arsenopyrite and sphalerite (Table 1.1) (Jennings et al., 2000). Various chemical, physical and biological factors control the path, rate and products of the oxidation reactions.

Pyrite (FeS_2) is the most common sulphide mineral in the Earth's crust (Wiersma and Rimstidt, 1984). Hence, the oxidation of pyrite is the most important and thoroughly investigated acid forming process that occurs in mine waste. Despite the voluminous research and literature dedicated to pyrite oxidation, uncertainties remain regarding the exact reaction mechanisms and reaction rates involved (Evangelou 1995b).

The two major oxidants of pyrite are oxygen and ferric iron. Both oxidation processes can operate by purely chemical means (abiotic oxidation) or be catalysed by chemoautotrophic bacteria (biotic oxidation) (Lundgren et al., 1972).

Table 1.1. Common sulphides known or inferred to generate acid when oxidised (from Plumlee, 1999).

Therefore, there are four different pathways for pyrite oxidation, which can be summarised as:

- Abiotic direct oxidation (oxidation by oxygen)

- Abiotic indirect oxidation (oxidation by ferric iron)
- Biotic direct oxidation (oxidation by oxygen catalysed by bacteria)
- Biotic indirect oxidation (oxidation by ferric iron catalysed by bacteria)

These pyrite oxidation pathways are represented by the following generally accepted chemical reactions (Nordstrom and Alpers, 1999a; Ritchie, 1994):

$FeS_{2(s)} + 7/2O_{2(g)} + H_2O_{(l)} \rightarrow FeSO_{4(aq)} + H_2SO_{4(aq)}$

or, (1.2)

$FeS_{2(s)} + 7/2O_{2(g)} + H_2O_{(l)} \rightarrow Fe^{2+}{}_{(aq)} + 2SO_4{}^{2-}{}_{(aq)} + 2H^+{}_{(aq)}$

(oxidation of pyrite by oxygen)

$2FeSO_{4(aq)} + H_2SO_{4(aq)} + 1/2O_{2(g)} \rightarrow Fe_2(SO_4)_{3(aq)} + H_2O_{(l)}$

or, (1.3)

$Fe^{2+}{}_{(aq)} + 1/4O_{2(g)} + H^+{}_{(aq)} \rightarrow Fe^{3+}{}_{(aq)} + 1/2H_2O_{(l)}$

(oxidation of Fe^{2+} to Fe^{3+})

$FeS_{2(s)} + Fe_2(SO_4)_{3(aq)} + 2H_2O_{(l)} + 3O_{2(g)} \rightarrow 3FeSO_{4(aq)} + 2H_2SO_{4(aq)}$

or (1.4)

$FeS_{2(s)} + 14Fe^{3+}{}_{(aq)} + 8H_2O_{(l)} \rightarrow 15Fe^{2+}{}_{(aq)} + 2SO_4{}^{2-}{}_{(aq)} + 16H^+{}_{(aq)}$

(oxidation of pyrite by Fe^{3+})

$Fe^{3+}{}_{(aq)} + 3H_2O_{(l)} \leftrightarrow Fe(OH)_{3(s)} + 3H^+{}_{(aq)}$ (1.5)

(hydrolysis of Fe^{3+}/precipitation of iron hydroxides)

These reactions operate in a sequence beginning with the initial reaction of pyrite with water and oxygen (Reaction 1.2), producing Fe^{2+}, sulphate and H^+ ions, thus lowering the solution pH. The released ferrous iron may then in turn be oxidised by molecular oxygen producing Fe^{3+} ions through Reaction 1.3. The ferric iron can then also oxidise pyrite (Reaction 1.4), producing more ferrous iron, sulphate and H^+ ions. This ferrous iron can then be oxidised by Reaction 1.3 to ferric iron which in turn may oxidise more pyrite. A continuous selfpropagating pyrite oxidation cycle is thus formed (Evangelou, 1995b). This cycle will continue until the pyrite or oxidant supply is exhausted.

The hydrolysis of Fe^{3+} (Reaction 1.5), controls the concentration of ferric ions in solution above a pH of about 3.5 (Parker and Robertson, 1999). If the pH of a Fe^{3+} bearing solution is greater than approximately 3.5, the precipitation of ferric hydroxide occurs. Reaction 1.5 also contributes acid to the system and the accumulation of ferric hydroxides on the pyrite surface may inhibit further oxidation (Nicholson et al., 1988).

Experimental evidence shows that Fe^{3+} is the major pyrite oxidant in abiotic and biotic systems in acidic to near-neutral conditions (Bierens-de Haan, 1991; Moses et al., 1987; Singer and Stumm, 1970). After the cycle is initiated by Reaction 1.2, the main role played by O_2 is the regeneration of Fe^{3+} through Reaction 1.3, which is the slowest and therefore rate-determining step (Singer and Stumm, 1970).

The overall chemical reaction defining pyrite oxidation is often described in the literature as:

$$FeS_{2\,(s)} + 15/4O_{2(g)} + 7/2H_2O_{(l)} \rightarrow Fe(OH)_{3(s)} + 2H_2SO_{4(aq)} \qquad (1.6)$$

The Reactions 1.2 to 1.6 paint a deceptively simple picture. For example, Reaction 1.6 involves the transfer of 15 electrons, which cannot take place in a single step (Nordstrom and Alpers, 1999a). The overall reaction may be a combination of up to 15 separate steps. In addition, the reactions do not explain geochemical mechanisms or rates, the idealised nature of the reaction products, bacterial catalysis or the wide variety of factors that influence pyrite oxidation.

The literature contains numerous attempts to develop specific mechanisms for the oxidation of pyrite by oxygen (Reaction 1.2) and ferric iron (Reaction 1.4) through chemical kinetic experiments (Goldhaber, 1983; McKibben and Barnes, 1986; Moses et al., 1987; Moses and Herman, 1991, Nicholson et al., 1988, 1990), molecular orbital theory (Luther, 1987, 1990), surface studies (Nesbitt and Muir, 1994), isotopic studies (Taylor et al., 1984a,b), bacterial leaching experiments (Lizama and Suzuki, 1989; Palencia et al, 1990) and electrochemical theory (Lowson, 1982; Rimstidt and Vaughan, 2003; Williamson and Rimstidt, 1994).

Despite the extensive research into the subject, the exact mechanisms, rates and orders of pyrite oxidation by dissolved O_2 and ferric iron, by both biotic and abiotic processes, are still uncertain. It is agreed, however, that the process is a surface-controlled reaction involving the adsorption of the oxidant in the absence of bacteria and the intimate contact between the pyrite surface and bacteria in biotic systems (Evangelou and Zhang, 1995). Electron transfer then occurs either via a persulfido bridge (Luther, 1987) or through separate cathodic and anodic reactions at different locations on the pyrite surface (Rimstidt and Vaughan, 2003). Both mechanisms result in the eventual release of Fe^{2+} and thiosulphate to solution and the production of acid, which is in agreement with experimental observations (Evangelou, 1995b).

The oxidation mechanisms of the other metal sulphides are governed by the same general principles as pyrite (Rimstidt and Vaughan, 2003), although specific stoichiometry and kinetics differ greatly between minerals. The other metal sulphides may generate acid when oxidised, particularly if oxidised by ferric iron (Table 1.1). However, their main influence on mine drainage chemistry is generally the release of dissolved metals and metalloids into solution, although pyrrhotite may be the most important acid producer in some mine wastes (Nicholson and Scharer, 1994).

As with the specific mechanisms of sulphide oxidation, the kinetics of sulphide oxidation are also poorly understood. This is due to the large number of variables controlling sulphide oxidation rates, which on a microscopic level include mineralogy, morphology, crystallinity, surface area, impurities, bacterial catalysis, temperature, pH, oxidant concentrations and the nature of oxidation reaction products formed (Evangelou, 1995b). This dependence on such a large and complex set of variables has led some researchers to conclude that it may be impossible to derive single rate laws for the oxidation kinetics of sulphide oxidation (Evangelou and Zhang, 1995). Macroscopic variables must also be taken into account, the most important of which is the diffusion of O_2 through the mine waste (Ritchie, 1994). Other factors to be taken into account include hydrologic variables which influence the transport of products and reactants, climate, the physical structure and nature of the wastes in question (which affect diffusion and hydrologic transport) and the geomorphology of the terrain (Nordstrom and Alpers, 1999a).

The generation of AMD from mine wastes is largely governed by the oxidation of pyrite, although the oxidation of other sulphides present in the mine waste will have an important influence on the drainage chemistry. The mechanisms and kinetics of sulphide oxidation remain poorly understood and are controlled by a wide range of variables. In a practical sense, however, the availability of O_2 to the mineral surface or to aqueous Fe^{2+} is the major factor governing acid generation in sulphidic mine wastes (Nicholson et al., 1990).

1.2.2 Acid neutralisation

In contrast to acid generation, the neutralisation of acidity in weathering mine wastes is a comparatively simple process. The dissolution of acid consuming minerals present in mine wastes provides the most acid buffering capacity. The formation and dissolution of various secondary mineral species, particularly hydroxides, may also consume acidity. Carbonate and silicate minerals commonly found in mine waste are listed according to their weathering reaction rate in Table 1.2.

Carbonates provide the most rapid buffering capacity, dissolving up to four orders of magnitude faster than pyrite in certain conditions (McKibben and Barnes, 1986). However, they are often only a minor component in mine wastes and may be quickly depleted (Stromberg and Banwart, 1999). Primary silicate minerals dissolve more slowly than carbonates (Table 1.2), though some rapidly weathering basic-silicate minerals may also consume significant acidity upon dissolution (Filipek et al., 1999). More resistant silicates may play an important long-term role in acid neutralisation after the exhaustion of the more reactive carbonates and silicates under low-pH conditions (Stromberg and Banwart, 1999). Silicate minerals are abundant in most rock-types and usually represent the largest capacity for acid consumption (Stromberg and Banwart, 1999). However the generally slow to very slow dissolution rates infers the effect of silicate minerals will be long term and, unless the rate of acid generation is relatively low, only partial neutralisation will be provided (Morin and Hutt, 1994).

Table 1.2. Grouping of minerals according to their weathering reaction rate (from Filipek et al., 1999).

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The exchange of base cations and protons between aqueous solutions and silicate mineral surfaces is another important acid-neutralising process in AMD (Stromberg and Banwart, 1999). Simply put, an H^+ in solution replaces a base cation on the silicate surface (Stromberg and Banwart, 1999):

$$R^{n-}X^{n+} + n\mathrm{H}^+ \leftrightarrow R^{n-}\mathrm{H}_n^+ + X^{n+} \tag{1.7}$$

where R = mineral species, X = Ca, Mg, Na or K.

The dissolution reactions of acid-consuming phases are independent of O_2 concentrations and may occur along the groundwater flow path limited only by mineral availability and solubility (Blowes et al., 1994a). The reactivities of carbonates and silicates are strongly dependent on the grain size and texture (i.e. surface area) of the mineral as well as the pH of the waters (Plumlee, 1999). Therefore, the physical nature of an ore-body may have as much influence on the drainage chemistry as the mineralogy. For example, fine-grained feldspars in volcanic rocks will weather more rapidly than the same minerals in coarse-grained granitic rocks (Plumlee et al., 1999).

The neutralisation of acid in mine waste material is governed mainly by the dissolution of carbonate and silicate minerals. These reactions consume acid, releasing CO_2 and aqueous alkalis into solution. The formation of secondary carbonates, silicates and sulphates may also occur. The overall drainage chemistry results from the interaction between the acid generating reactions and the acid neutralising reactions. The net composition is a function of the relative quantities of acid generating and acid consuming minerals and their rates of reaction.

1.2.3 Formation of secondary minerals

Secondary minerals are defined as those that form during weathering (Nordstrom and Alpers, 1999a). These minerals may be formed pre- or post-mining and have an important influence on the chemistry of mine waste drainage. The initial secondary phases formed are often metastable and poorly crystalline, altering to more stable species with time. Therefore, the more rapid processes operating in mine wastes will produce a different mineralogy than those found in the oxidised zones of mineral deposits (Nordstrom and Alpers, 1999a). The secondary mineralogy formed within mine wastes is a function of the drainage composition, temperature, moisture content and the process of formation (Nordstrom and Alpers, 1999a).

The important secondary mineral-forming processes in AMD environments are: (1) iron oxidation and hydrolysis, (2) reaction of acid solutions with primary minerals, (3) dilution of acid solutions and, (4) evaporation of acid solutions (Nordstrom and Alpers, 1999a).

The oxidation and hydrolysis of Fe^{2+} will lead to the precipitation of various Fe^{3+} oxides, hydroxides and hydroxysulphates. The product of this process is often represented as the idealised phase $Fe(OH)_3$, as shown in Reaction 1.5. The actual species that precipitate out of AMD waters are dependent on the pH, metal concentrations and sulphate concentration of the solution (Bigham et al., 1996b) and are often referred to as “yellow boy” or ochreous precipitates. The most important ochre minerals formed in AMD and their pH ranges of formation are ferrihydrite ($Fe_5HO_8{\cdot}4H_2O$ – ideal formula), forming at pH >5, schwertmannite [$Fe_8O_8(OH)_6(SO_4)$ – ideal formula], forming at pH 2.5–4.5, jarosite [$KFe_3(SO_4)_2(OH)_6$], forming at pH <3.5 and goethite (α-FeOOH), forming at pH >6.5 (Bigham et al., 1996a). Ferrihydrite and schwertmannite are metastable and will convert to goethite or hematite with time, explaining the predominance of the latter two minerals in the weathered zone of mineral deposits (Nordstrom and Alpers, 1999a). Ferric species similar to these minerals have been observed to form on pyrite during oxidation experiments (Nicholson et al., 1990; Todd et al., 2003). The accumulation of a surface oxidation layer may reduce further oxidation rates significantly (Zhang and Evangelou, 1996).

The behaviour of Al in acidic mine waters is very different to iron. The fact that Al^{3+} tends to behave conservatively at pH <4.5 (Nordstrom and Ball, 1986) results in a paucity of Al species in AMD precipitates. The neutralisation of AMD waters to pH >5 may lead to the precipitation of Al hydroxides, generally distal from the AMD source (Nordstrom and Alpers, 1999a).

Dilution of AMD waters may also promote the sorption of dissolved metals into/onto ochre minerals. “Adsorption” is the two-dimensional accumulation of a sorbate at a solid surface, whereas “absorption” involves diffusion of the sorbate into the solid phase (Smith, 1999). These sorption processes probably limit metal and metalloid mobility in most natural systems (Smith, 1999). The most important control on metal/metalloid sorption is pH, increasing pH favouring metal sorption and metalloid oxyanion desorption. Other variables include mineral speciation and surface area, solution composition, presence of organics and temperature (Bowell and Bruce, 1995; Levy et al., 1997; Smith, 1999). Iron ochres are considered the primary adsorbent for metals in oxic environments, particularly goethite, and are an important factor in the natural attenuation of metals from acidic waters (Swedlund and Webster, 2001). The relatively weak sorption of some metals (e.g. Zn, Cd and Ni), results in elevated concentrations of these metals in AMD waters when other metals have been attenuated by ochreous precipitates. Desorption and recycling of metals back into the environment is also an important factor in mine water chemistry. If there are changes in the water pH, temperature or moisture content, metals may be desorbed off or out of the ochres back into solution (Smith, 1999).

Evaporation of AMD waters will concentrate acid, sulphate, alkalis and metals until they reach mineral saturation and form efflorescent sulphate salts that are generally highly soluble (Nordstrom and Alpers, 1999a). As the iron sulphides pyrite and pyrrhotite are the most abundant sulphide minerals in mine waste, it follows that the most abundant efflorescent sulphates are iron sulphates (Alpers et al., 1994a). In weathering solutions with sufficient Fe^{2+} concentrations, the divalent metals such as Cu, Zn, Ni, Mg and Mn are likely to be incorporated into iron sulphates (Alpers et al., 1994b). In certain conditions, however, there are a large number of sulphates of other elements beside iron that may form as efflorescent minerals in weathering mine waste environments, such as oxidising, base-metal sulphide-rich, Fe sulphide-poor mine wastes (Nordstrom and Alpers, 1999a). Alternatively, waters from which the Fe^{2+} has been removed, particularly by oxidation to Fe^{3+} and subsequent precipitation of ochres, may become enriched with other metals and precipitate out sulphates upon evaporation (Alpers et al., 1994a).

The soluble sulphates act as an important sink for metals, alkalis and, in the case of iron sulphates, acidity (Nordstrom and Alpers, 1999a). The efflorescences store the acid, alkalis and metals during dry periods. On contact with water, normally supplied through rainfall, the soluble efflorescences dissolve, releasing the acidity and ions into solution (Cravotta, 1994). This process is particularly important in arid regions (Keith et al., 1999).

Although the majority of secondary sulphates are highly soluble, a number of species are poorly soluble (Alpers et al., 1994a). The most common of these are barite ($BaSO_4$), anglesite ($PbSO_4$) and celestite ($SrSO_4$) (Nordstrom and Alpers, 1999a). These minerals, through their low solubilities, tend to immobilise the elements Ba, Pb and Sr respectively in mine drainage environments. Anglesite in particular is important for its apparent control of Pb concentrations in AMD and mine tailings pore waters (Blowes et al., 1991; Boorman and Watson, 1976).

Carbonate minerals are common in mineral deposits, both as primary and secondary phases (Alpers et al., 1994a). The dissolution of carbonates is the most important acid neutralising mechanism in mine wastes (Blowes and Ptacek, 1994). However, carbonate minerals may also have an important influence on the concentrations of dissolved metals in AMD waters by precipitation and adsorption of metals on mineral surfaces (Al et al., 2000). Metal carbonates and hydroxyl-bearing metal carbonates may form in oxidised mine wastes and act as metal sinks (Nordstrom and Alpers, 1999a). These species generally do not control the metal concentrations in AMD waters as their abundances are normally too low. An exception is the iron carbonate siderite ($FeCO_3$), which has been observed as a precipitate in oxidised mine tailings (Al et al., 2000; Ptacek and Blowes, 1994).

The formation of secondary minerals in mine waste has an important influence on the overall geochemistry of the drainage formed by the oxidation of mine wastes. Precipitation and dissolution of secondary minerals often control the concentration of metal ions and anionic species in AMD waters. The mechanisms which are involved in this control are sorption processes (Smith, 1999) and the precipitation/dissolution of secondary minerals, either through evaporation/re-dissolution reactions or through changes in the mineral saturation state in the solution (Alpers et al., 1994a). Over a period of time, the differing reaction/dissolution rates of minerals in a mine waste impoundment may lead to the development of different geochemical zones or subregions within the mine waste (Ptacek and Blowes, 1994). Thus, the drainage chemistry of mine waste is also a function of time, as well as the site-specific character of the mine waste.

1.2.4 AMD control methods and phosphate stabilisation

The scale of the environmental problem posed by AMD has promoted the research and development of a number of remediation and prevention techniques. At sites where AMD is being generated and released into local waters, the collection and treatment of the leachate is the usual management strategy. However, prevention of AMD generation is more cost-efficient and a preferred closure solution.

The AMD prevention technologies currently utilised in the mining industry are designed to change either the biological, chemical and/or the physical nature of the mine waste. Bactericide addition limits sulphide oxidation by slowing the bacterial catalysis, particularly of the oxidation of ferrous iron to ferric iron. The addition of alkaline material aims to neutralise the acidity produced by sulphide oxidation. The alteration of the physical nature of the mine waste aims to reduce permeability and access of oxygen and/or water to the sulphides, preventing oxidation and therefore acid generation.

Limitations exist with all of these approaches. Bactericides suppress sulphide oxidation for relatively short periods and require continual re-application (Blowes et al., 1994b). Alkaline addition raises the buffering capacity of the waste but does not prevent the sulphide oxidation and therefore often requires re-application, particularly if the alkaline material becomes armoured by iron oxides (Evangelou and Zhang, 1995). Physical methods are limited by climatic and geographic conditions (wet covers), may be prohibitively expensive and possibly ineffective over the long term due to deterioration (dry covers; oxygen inhibiting covers) or require specific mine waste characteristics and infrastructure (selective handling and isolation) (Parker and Robertson, 1999).

A new prevention technique currently under development involves encapsulating sulphide surfaces in stable, impermeable coatings of phosphate, silicate or organic ligands. Initially several researchers observed that coatings of ferric hydroxide formed on pyrite during oxidation experiments inhibited oxidation of the mineral (Nicholson et al., 1988, 1990). It was proposed that the coatings formed a barrier for oxygen diffusion and that impermeable coatings of phosphate and silicate could be induced to form on sulphide surfaces to provide long-term oxidation prevention (Evangelou, 1995a). The coatings are produced by leaching the sulphides in a solution containing an oxidant (hydrogen peroxide [H_2O_2] or calcium hypochlorite [$Ca(OCl)_2$]), a buffer (sodium acetate [NaOAC]) and potassium di-hydrogen orthophosphate (KH_2PO_4), sodium metasilicate (Na_2SiO_3) (Fytas et al., 1999; Zhang and Evangelou, 1998) or organic ligands (Chen et al., 1999; Matlock et al., 2003). Ferric ions are produced by sacrificial oxidation of the sulphide surface, which complex with the phosphate or silicate ions to form the stable coating. The process using phosphate to coat pyrite is represented by Reaction 1.8 (Fytas and Evangelou, 1998), and is represented schematically by Figure 1.1.

$$FeS_{2(s)} + 15/2H_2O_{2(aq)} + H_2PO_4^-{}_{(aq)} \rightarrow FePO_{4(s)} + 2SO_4^{2-}{}_{(aq)} + 3H^+{}_{(aq)} + 7H_2O_{(l)} \qquad (1.8)$$

Using column leaching experiments, the coatings formed have successfully slowed and, in some cases, halted further oxidation of the AMD generating sulphides (Evangelou, 1995a; Fytas and Evangelou, 1998; Georgopoulou et al., 1996; Nyavor and Egiebor, 1995). To date published studies of this technique have been limited to laboratory studies on the sulphide minerals pyrite and pyrrhotite, three experiments on pyritic coal waste (Evangelou, 1996, 2001; Matlock et al., 2003) and an ongoing field column experiment using pyritic tailings and coal waste (Vandiviere and Evangelou, 1998). Unpublished laboratory studies by Woltmann (2001) demonstrated the effectiveness of the technique to inhibit oxidation of chalcopyrite and arsenopyrite. In contrast, the geochemical interactions and validity of this technique within poly-metallic mine wastes bearing multiple sulphide phases, including gangue minerals, are unknown.

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Figure 1.1. Schematic diagram of phosphate stabilisation of pyrite (from Evangelou, 2001).

A similar method has been utilised for the remediation of metal-contaminated soils by *in situ* conversion of unstable metal-bearing phases to relatively insoluble, stable, metal-bearing phosphate species (Cotter-Howells and Caporn, 1996; Ma et al., 1993; Ruby et al., 1994; Zhang et al., 1998). This research has concentrated on the immobilisation of Pb in contaminated soils, taking advantage of the rapid formation and extremely low solubility product of pyromorphite [$Pb_5(PO_4)_3Cl$] (Nriagu, 1983). Pyromorphite has been found to replace anglesite, galena, cerrusite and Pb adsorbed onto goethite in soils after apatite addition, reducing the soluble Pb concentrations in the soils (Zhang and Ryan, 1998, 1999a,b; Zhang et al., 1997; Zhang et al., 1998). An example of this process is the transformation of anglesite to chloropyromorphite in the presence of hydroxyapatite (Zhang and Ryan, 1998):

$$Ca_5(PO_4)_3OH_{(s)} + 5PbSO_{4(s)} + Cl^-_{(aq)} + H^+_{(aq)} \rightarrow Pb_5(PO_4)_3Cl_{(s)} + 5Ca^{2+}_{(aq)} + 5SO_4^{2-}{}_{(aq)} + H_2O_{(l)} \quad (1.9)$$

Although research has concentrated on Pb in soils, phosphates of other metals (e.g. Zn, Cu, Cd, Ni, Al and U) are highly insoluble and are often the most stable form in which the metal can exist in ambient conditions (Hodson et al., 2000b). The formation of hopeite [$Zn_3(PO_4)_2.4H_2O$] on addition of apatite to a Zn^{2+}-rich aqueous solution was observed by Chen et al., (1997) with the resultant removal of Zn from the solution. Phosphate addition to metal-contaminated soils in experiments by Cotter-Howells and Caporn (1996) and Hodson et al., (2000a) formed unidentified Zn-phosphate minerals and significantly reduced Zn release from the soils.

The potential of phosphate stabilisation to successfully remediate metal-contaminated soils implies that it may also be an effective technique for the remediation of mine wastes. Experiments involving the addition of phosphate to metal-rich mine tailings by Eusden et al., (2002) identified the formation of pyromorphite and relatively insoluble unidentified tertiary metal (Cu, Pb, Zn) phosphates. These phases resulted in significant reduction in concentrations of Pb^{2+}, Zn^{2+}, Cd^{2+} and Cu^{2+} in pH-controlled mine waste leaching experiments.

The addition of soluble phosphate to partly-oxidised mine waste could provide a doubly effective technique for the prevention of AMD. Firstly, the formation of stable, insoluble phosphate coatings on sulphide surfaces would prevent further sulphide oxidation and hence acid generation. Secondly, the formation of relatively insoluble metal phosphate phases, either as coatings or precipitates, would attenuate metals from solution, resulting in reduced metal release into mine drainage waters.

1.3 Definitions

The following definitions are either generally accepted definitions of chemical processes referred to in the thesis or are specific definitions of terms utilised to describe methodology, observations and interpretations of the experiments outlined in the thesis, particularly Chapter 3, and as such are specific to the thesis.

Acid mine drainage (AMD): the formation of a low pH, usually metal-rich, leachate through the oxidation of sulphide minerals contained within a waste produced by a mining or mineral processing operation (Nyavor and Egiebor, 1995).

Acid neutralising capacity (ANC): A measure of the amount of acid a sample of mine waste can neutralise. Reported as kilograms of sulphuric acid consumption per tonne of waste (Lottermoser, 2003).

Amorphous: Lacking crystalline order (McNaught and Wilkinson, 1997). Material defined as amorphous in chapter 3 appears to have no crystalline order under scanning electron microscope observation, however, the material may be crystalline at a grain size too fine for observation.

Coalescence: A layer/layers of phosphate precipitates which have coalesced into an interconnected covering on a mineral surface.

Coated columns: Columns containing mine waste to which a coating solution is applied during the coating stage of the phosphate stabilisation experiments.

Coating: A layer/layers of phosphate on a sulphide mineral which is interpreted to be chemically connected to the sulphide mineral.

Coating solution: The solution which is applied to the columns during the coating stage in order to promote phosphate development on the mine wastes within the columns. The coating solutions contain phosphate, a buffer and usually an oxidant.

Coating stage: The first stage of the phosphate stabilisation experiments, in which a coating solution is applied to mine waste contained within a column in order to develop phosphate phases on the mine waste.

Control column: A column containing mine waste identical to that contained within the coated columns but which has not had a coating solution applied to it. The control column has an oxidising solution applied to it during the dissolution stage of the phosphate stabilisation experiments.

Dissolution stage: The second stage of the phosphate stabilisation experiments, in which an oxidising solution is applied to the coated columns and a control column in order to test the ability of any phosphate phases formed during the coating stage to inhibit acid generation and metal release within the columns.

Efflorescence: A mineral formed by the evaporation of a solution (Jambor et al., 2000).

Leachate: The solution which has passed through a column during either the coating stage or dissolution stage.

Net acid production potential (NAPP): The difference between the maximum potential acidity of a sample of mine waste (weight % of sulphur converted to kilograms of sulphuric acid per tonne of waste) and the acid neutralising capacity (Lottermoser, 2003).

Oxidation: The complete, net removal of one or more electrons from a molecular entity (McNaught and Wilkinson, 1997).

Oxidising solution: The solution which is applied to the columns during the dissolution stage. The oxidising solution is composed of 0.01 M H_2O_2 in all phosphate stabilisation experiments.

Phosphate stabilisation: The *in situ* conversion of unstable metal-bearing phases to relatively insoluble, stable metal-bearing phosphate phases. In the case of sulphides this ideally involves the formation of an impermeable stable coating of metal phosphate on the sulphide surface which prevents further oxidation of the sulphide.

Precipitate: A solid formed by sedimentation from a liquid solution in which the material is present in amounts greater than its solubility in the liquid (McNaught and Wilkinson, 1997). In chapter 3 the term specifically applies to phosphate or sulphate phases formed in the columns which are interpreted to have no chemical connection with the mineral they have as a substrate; cf. **Coating**.

Sacrificial oxidation: The oxidation of a small amount of sulphide by the oxidant in the coating solution (Evangelou, 1995b). This releases cations from the sulphide surface which react with the phosphate in solution and form phosphate coatings or precipitates.

Sorption: The removal of a solute from solution to a contiguous solid phase by an unknown removal mechanism (Smith, 1999).

[X] – where X represents a chemical symbol: Abbreviation for the aqueous concentration of X.

1.4 Project Aims

1.4.1 Primary objective

The primary objective of the project is presented in the form of a research question:

Is it possible to use the phosphate stabilisation technique to inhibit acid generation and attenuate metals released from partly oxidised, polymінerallic mine waste on a laboratory scale?

In an attempt to answer the research question, three column leach experiments were conducted, adapted from Fytas and Evangelou (1998). Mine waste material for use within the column leach experiments was sourced from the abandoned, AMD generating, Montalbion silver mine, Atherton Tablelands, north Queensland. The partly oxidised, polymineralllic nature of the waste at the Montalbion mining area was ideally suited to meet the project's objective.

1.4.2 Specific aims

A number of specific aims were proposed to enable complete understanding of the complex geochemical processes operating within the column leach experiments.

- Characterisation of the acid-generating and metal attenuation mechanisms occurring within the waste dumps and local surface waters of the Montalbion mining area.

- Application of the understanding gained from the characterisation of the Montalbion mining area to determine the interactions of the waste material with the phosphate coating solution.

- Determination of the chemistry, morphology, stability and sulphide oxidation inhibiting capability of any phosphate phases formed by interaction of the waste material with the phosphate coating solution.

The project expands on the work of Evangelou (2001), and is the first known investigation of the phosphate stabilisation technique on partly oxidised, polyminerallic mine wastes that include sphalerite, chalcopyrite, tetrahedrite and arsenopyrite. A positive answer to the research question widens the possible applications of phosphate stabilisation as a technique for AMD prevention in polyminerallic mine wastes and remediation of abandoned, partly oxidised, polyminerallic mine wastes.

1.5 Thesis Outline

The thesis is comprised of five chapters, including the introduction and conclusion. Specifically, the introduction summarises the processes of AMD generation and neutralisation, the influences of secondary minerals on mine drainage and the theory behind phosphate stabilisation. The main objectives of the project are also outlined.

The second chapter details the investigation into the environmental geochemistry and mineralogy of the Montalbion mining area and receiving surface waters. The chapter is adapted from Harris et al., (2003) and as such contains contributions by Dr B.G. Lottermoser and Dr J. Duchesne.

The third chapter describes the methods, results and specific discussions of the three column leach experiments. Each experiment is dealt with in a separate section showing the morphology and chemistry of phosphate phases formed during the experiments as well as the column leachate chemistry. Interpretations of the results of each experiment are described in each section, with an overall summary concluding the chapter.

Chapter four forms the discussion of the phosphate stabilisation experiments. Potential limitations of the technique in relation to the existing literature and future research required to expand upon and answer questions raised by this study are outlined. The chapter concludes with a summary of contributions to previous research made by the phosphate stabilisation experiments.

The final section is the conclusion to the thesis, summarising all the former chapters above in context with current knowledge of AMD processes and prevention methods.

Accompanying appendices contain supplementary data and extra details of experimental procedures.