2

Review of Literature

2.1 Acid Sulfate Soils

Acid sulfate soils (ASS) are all those soils that may either contain sulfuric acid (H₂SO₄) or have the potential to form sufficient quantities of H₂SO₄ to affect the main soil characteristics (Pons, 1973). The most commonly found iron sulfide minerals in the natural environment include pyrite (FeS₂; cubic), pyrrohtite (Fe₁₋ₓS; where 0 < x < 0.125), mackinawite (FeS₀.₉), marcasite (FeS₂; orthorhombic), griegite (Fe₃S₄) and chalcopyrite (CuFeS₂) (Bigham and Nordstrom, 2000; Fanning et al., 2002; Thomas et al., 2001). The exposure of iron sulfide minerals to air and water results in oxidation of these minerals, and a subsequent release of acid sulfate water into the soil and associated water body.

Sulfidic material in most ASS have developed under mangroves and reed-swamps in tidal areas where a plentiful supply of organic matter and the constant addition of sulfate (SO₄²⁻) from seawater enhance the activity of SO₄²⁻-reducing bacteria to generate FeS and FeS₂ (Bigham and Nordstrom, 2000). Acid sulfate soils can be associated with a wide variety of anaerobic and/or drained environments because these environments provide favorable conditions for the formation of these soils. Some of the more common environments that
contain ASS include: coastal and estuarine areas, mangrove swamps, and inland lakes (Fitzpatrick and Shand, 2008).

In general, three broad types of ASS are recognised namely (i) potential, (ii) active, and (iii) post active ASS (Fanning, 2002).

(i) Potential ASS. The soils containing sulfide minerals that can oxidise to produce H$_2$SO$_4$ upon exposure to air and water are termed as potential ASS or (in Europe) unripe sulfidic soils (Dent and Pons, 1995; Fanning et al., 2002).

(ii) Active ASS. The soil materials that contain H$_2$SO$_4$ and also sulfidic material at shallow depths are termed active ASS (Fitzpatrick and Shand, 2008).

(iii) Post active or unripe ASS. These soils are indicative of the soils in which sulfides have been completely oxidised. These soils have conspicuous red mottles and may still be acidic with high soluble aluminium (Al) concentrations (Bigham and Nordstrom, 2000).

2.1.1 Iron sulfide formation and oxidation

Iron sulfide minerals such as pyrite are formed in anaerobic soil materials in contact with sea water or fresh water bodies, such as lakes and wetlands associated with rivers with unnaturally high water levels (due to river regulation), and occur in coal and lignite and associated rocks (Fanning et al., 2002; Holmer and Storkholm, 2001). The process through which sulfide minerals are formed in nature is termed as Sulfidization. Iron sulfide minerals require a source of sulfide and reactive iron (Fe) for their formation. The conditions necessary for SO$_4^{2-}$ reduction to sulfide (S$^2-$) include: (i) sulfate rich water (e.g. sea water), (ii) sulfate reducing microbes (e.g. Thiothrix ferrooxidans), (iii) an organic C source for microbial activity, and (iv) an anoxic environment (Fanning et al., 2002). The formation of iron sulfide
minerals also requires flushing action to remove the bicarbonate formed during the $\text{SO}_4^{2-}$ reduction process (equation 1). The first step involved in the iron sulfide mineral formation is the reduction of $\text{SO}_4^{2-}$ to $\text{S}^{2-}$ and can be expressed as:

$$\text{SO}_4^{2-} + 2\text{CH}_2\text{O} \rightarrow \text{H}_2\text{S} + 2\text{HCO}_3^- \quad (1)$$

In the next step if a reactive Fe source is available, particularly in the form of secondary iron (hydr)oxide minerals that are readily reduced in anoxic conditions to form ferrous iron (Fe(II)), iron sulfide minerals can form:

$$\text{H}_2\text{S} + \text{Fe}^{2+} \rightarrow \text{FeS} + 2\text{H}^+ \quad (2)$$

Iron sulfide minerals formed in this reaction (equation 2) may serve as precursors for the formation of disulfide minerals (i.e. FeS$_2$) or alternatively the disulfide minerals may also form directly by the reaction of Fe(II) and polysulfide ions:

$$\text{FeS} + S^0 \rightarrow \text{FeS}_2 \quad (3)$$

$$\text{Fe}^{2+} + S_x^{Y-} \rightarrow \text{FeS}_2 + (X - 2)S^{(Y-2)-} \quad (4)$$

where X is the number of moles of sulfur (S) and Y is the charge. The ingredients required for iron sulfide minerals formation (mentioned above) are found in several different environments (Fitzpatrick and Shand, 2008):

I. saline and brackish tidal flats and swamps;

II. bottoms of saline and brackish lagoons, seas and lakes;

III. inland valleys subject to an influx of $\text{SO}_4^{2-}$-rich water.
Soil materials enriched in iron sulfides are termed as *sulfidic materials* (Fitzpatrick et al., 1996). The sulfidic material is submerged, mineral or organic subsoil material containing oxidisable sulfur compounds; it has a pH of $\geq 4$ under field conditions and become acidic (pH $< 4$) when drained (Isbell, 1996).

The oxidation of iron sulfide minerals particularly pyrite has been the focus of many laboratory and field investigations in order to understand the mechanisms involved in the generation of acid sulfate waters in ASS and acid mine drainage (AMD) sites (Blodau, 2006; Blowes et al., 1998; Burton et al., 2006; Fitzpatrick and Shand, 2008; Glover et al., 2011; Gray, 1997).

**Sulfuricization.** The process through which sulfidic material is oxidised, minerals are weathered by the $\text{H}_2\text{SO}_4$ produced and new minerals are formed from the reaction products is known as *sulfuricization* (Fanning et al., 2002). The material formed on the oxidation of sulfidic material is known as *sulfuric material* and is characterised by an acidic pH of less than 4 (Fitzpatrick, 2008). The main focus of the previous field and laboratory studies has been the oxidation of pyrite (most common naturally occurring iron sulfide) to understand the mechanism involved in the generation of ASS and AMD systems containing acid sulfate waters (Bigham and Nordstrom, 2000). These studies describe the oxidation of pyrite by hydration, oxidation and hydrolysis reactions as well as a number of controls (Blodau, 2006). The process of pyrite oxidation is commonly described by the reaction as follows:

$$\text{FeS}_2 + 3.75\text{O}_2 + 2.5\text{H}_2\text{O} \rightarrow \text{FeOOH} + 2\text{H}_2\text{SO}_4$$

(5)
The process of pyrite oxidation described by this reaction (equation 5) is divided into several conceptual steps to understand the origin of many sulfate containing minerals formed at each step of the process (Fanning et al., 2002). In the first step, sulfide S is oxidised to form ferrous sulfate (FeSO₄) and sulfuric acid (H₂SO₄):

\[
\text{FeS}_2 + 3.5\text{O}_2 + \text{H}_2\text{O} \rightarrow \text{FeSO}_4 + \text{H}_2\text{SO}_4
\] (6)

Ferrous sulfate formed in this reaction (equation 6) is highly soluble in aqueous systems. If on drying it moves to the soil surface, it may form a variety of SO₄²⁻ containing minerals depending on the available water content (see Table 2.1 on next page).

Szomolnokite (FeSO₄·H₂O) is formed at low humidity, rozenite (FeSO₄·4H₂O) at an intermediate humidity, and melanterite (FeSO₄·7H₂O) is formed at high humidity values (Fanning et al., 2002). Ferrous iron (Fe(II)) is oxidised at relatively higher redox potential (Eₘ) values than sulfide S and forms ferric sulfate (Fe₂(SO₄)₃):

\[
\text{FeSO}_4 + 0.25\text{O}_2 + 0.5\text{H}_2\text{SO}_4 \rightarrow \text{Fe}_2(\text{SO}_4)_3 + 0.5\text{H}_2\text{O}
\] (7)

The hydrolysis of ferric sulfate to form Fe(III) oxyhydr(oxide) minerals, such as goethite; this step of pyrite oxidation is highly acidifying (equation 8).

\[
0.5\text{Fe}_2(\text{SO}_4)_3 + 2\text{H}_2\text{O} \rightarrow \text{FeOOH} + 1.5\text{H}_2\text{SO}_4
\] (8)
Table 2.1 Summary of the occurrence and distribution of secondary Fe oxides, sulfides, carbonates and salts in soil environment (modified from Fitzpatrick et al., 2008).

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Soil environment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hematite [Fe$_2$O$_3$]</td>
<td>Aerobic soils of tropical and sub-tropical regions, and Mediterranean climate. Greater amounts formed at higher temperatures and lower organic matter content</td>
</tr>
<tr>
<td>Goethite [$\alpha$-FeO(OH)]</td>
<td>At all weathering regimes, greater amounts associated with wet climates and higher organic matter content</td>
</tr>
<tr>
<td>Lepidocrocite [$\gamma$-FeO(OH)]</td>
<td>Seasonally anaerobic, non-calcareous soils of cold, temperate weather conditions</td>
</tr>
<tr>
<td>Ferrihydrite [5Fe$_2$O$_3$.9H$_2$O]</td>
<td>Soils subjected to rapid Fe(II) oxidation in the presence of organic matter</td>
</tr>
<tr>
<td>Maghemite [$\gamma$-Fe$_2$O$_3$]</td>
<td>Highly weathered soils of tropical and sub-tropical regions derived from mafic rocks containing magnetite as the precursor for its formation and/or organic matter rich soils subjected to burning</td>
</tr>
<tr>
<td>Schwertmannite [Fe$_8$O$_8$.OH$_6$.SO$_4$.2]</td>
<td>Sulfuric material of both coastal and inland ASS areas; frequently formed from pyrite oxidation in mines, spoils and tailings</td>
</tr>
<tr>
<td>Jarosite [K,Na$_3$.Fe$_3$.SO$_4$.2.(OH)$_6$]</td>
<td>Sulfuric material of ASS in both coastal and inland regions; mines, spoils and tailings</td>
</tr>
<tr>
<td>Sideronatrite [Na$_2$.Fe(SO$_4$)$_2$.OH.3H$_2$O]</td>
<td>Sulfuric material of ASS of inland and coastal areas; also found in mines, spoils and tailings</td>
</tr>
<tr>
<td>Green Rust [Fe(OH)$_2$]</td>
<td>Strongly hydromorphic soils.</td>
</tr>
<tr>
<td>Akaganéite [$\beta$-FeO(OH)]</td>
<td>Strongly hydromorphic and sub-aqueous soils; *sulfuric material of wetland rich in organic matter</td>
</tr>
<tr>
<td>Iron monosulfides [FeS]</td>
<td>Strongly hydromorphic and sub-aqueous soils</td>
</tr>
<tr>
<td>Iron disulfides or pyrite [FeS$_2$]</td>
<td>Strongly hydromorphic and sub-aqueous soils</td>
</tr>
<tr>
<td>Greigite [Fe$_3$S$_4$]</td>
<td>Strongly hydromorphic and sub-aqueous soils.</td>
</tr>
<tr>
<td>Calcite [CaCO$_3$]</td>
<td>Calcareous soils</td>
</tr>
<tr>
<td>Dolomite [CaMg(CO$_3$)$_2$]</td>
<td>Calcareous soils</td>
</tr>
<tr>
<td>Gypsum [CaSO$_4$.2H$_2$O]</td>
<td>Saline and saline-acid sulfate soils</td>
</tr>
<tr>
<td>Quartz [SiO$_2$]</td>
<td>Sandy soils</td>
</tr>
<tr>
<td>Halite [NaCl]</td>
<td>Saline and saline acid sulfate soils</td>
</tr>
</tbody>
</table>

*Occurrence in the oxidised surface horizon of an abandoned lead smelter site (organic soil) in Indiana, the USA (Gao and Schulze, 2010).
However, if ferric sulfate formed in the above reaction (equation 7) is only partially hydrolysed it may result in the formation of schwertmannite or jarosite and a small amount of acidity is generated compared to that involved in Fe(III) oxyhydr(oxide) formation:

$$4\text{Fe}_2(\text{SO}_4)_3 + 14\text{H}_2\text{O} \rightarrow \text{Fe}_8\text{O}_8(\text{OH})_6\text{SO}_4 \text{(schwertmannite)} + 11\text{H}_2\text{SO}_4 \quad (9)$$

$$1.5\text{Fe}_2(\text{SO}_4)_3 + 6\text{H}_2\text{O} + \text{K}^+ \rightarrow \text{KFe}_3(\text{SO}_4)_2(\text{OH})_6 \text{(jarosite)} + 2.5\text{H}_2\text{SO}_4 + \text{H}^+ \quad (10)$$

Jarosite is a much more crystalline mineral than schwertmannite and persists in the soil in oxygenated conditions for longer periods of time. In addition to the other soil characteristics indicative of the fact that sulfuricization is no longer active, the presence of jarosite is also an evidence of post active ASS (Fanning et al., 2002).

### 2.1.2 Factors determining types of secondary iron minerals in ASS

The mineralogy of precipitates formed from the hydrolysis of Fe(III) (equation 8) depends on the solution pH, \(\text{SO}_4^{2-}\) concentration, microbial activity, presence of base cations and the chloride (\(\text{Cl}^\)−) concentration of the acid sulfate solution. A schematic diagram representing the precipitation of Fe minerals and the necessary conditions for their formation in soil systems is shown in Figure 2.1.

Soil pH is considered to be the most important factor in determining the type of the Fe(III) minerals to be precipitated in an acid sulfate system (Bigham, 1990; Bigham, 1996; Bigham et al., 1996; Carlson et al., 2002). At low pH (< 2.5), high \(\text{SO}_4^{2-}\) ion concentration (> 3000 mg L\(^{-1}\)) and in the presence of base cations, jarosite \([\text{K, H, Na}]\text{Fe}_3(\text{OH})_6(\text{SO}_4)_2\) is precipitated (Regenspurg et al., 2004).
The microbial mediation of the pyrite oxidation process leading to jarosite formation has been suggested due to the frequent formation of jarosite onto submerged rock surfaces or its formation in association with microbial biofilms (Kawano and Tomita, 2001). Schwertmannite forms at an acidic pH range of 2.8–3.2 and it also requires high SO$_4^{2-}$ concentrations for its formation (1000–3000 mg L$^{-1}$) (Bigham et al., 1996). The formation of schwertmannite in acid sulfate solutions has also been linked to the microbially catalysed
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oxidation of Fe(II) (Bigham, 1994; Gu and Wong, 2004; Regenspurg et al., 2004; Xiong et al., 2008). Slightly acidic to alkaline pH conditions and high concentrations of dissolved Fe are favorable for ferrihydrite formation (see Figure 2.1). In addition, ferrihydrite also requires very low levels of $\text{SO}_4^{2-}$ for its precipitation (Bigham, 1994; Blodau, 2006). Goethite is the thermodynamically most stable secondary Fe mineral and mostly forms under similar pH conditions to that of ferrihydrite; it may also form through the transformation of less stable phases such as schwertmannite, ferrihydrite and jarosite (Murad and Rojik, 2005).

2.1.3 Secondary iron minerals associated with pyrite oxidation

Following the oxidation of Fe(II) to Fe(III), a variety of secondary Fe minerals may form depending on the prevailing conditions and solution (geo)chemistry, in particular goethite, jarosite, ferrihydrite and schwertmannite (Bigham, 1990). The type of secondary mineral formed from the Fe released during pyrite (or other iron sulfide minerals) oxidation is important, as it governs the amount of acidity released per unit of pyrite oxidised (Dold and Fontbote, 2001). For example, if the hydrolysis of Fe(III) produces goethite or ferrihydrite, then 3.0 moles of $\text{H}^+$ are produced per mol of Fe(III) hydrolysed (Sullivan and Bush, 2004). However, if an incomplete hydrolysis of Fe(III) results in jarosite formation then only around 2.0 moles of $\text{H}^+$ are released per mole of Fe(III) (Van Breemen, 1976). Schwertmannite precipitation leads to the release of ~ 2.6 moles of $\text{H}^+$ for every mole of Fe(III) (Peine et al., 2000). As the incomplete hydrolysis of Fe(III) results in the formation of jarosite and schwertmannite, the transformation of these minerals to goethite proves to be an additional source of acidity that was once stored in these minerals on their precipitation. Therefore, the transformation of these minerals can have severe consequences for the surrounding environment (Dold and Fontbote, 2001).
Schwertmannite is a secondary Fe mineral that forms in acidic, Fe and \(\text{SO}_4^{2-}\) rich waters (Murad and Rojik, 2003). Since the first report of its formation by Bigham, (1990) schwertmannite has been found in several different environments impacted by acidity generation resulting from iron sulfide mineral (especially pyrite) oxidation. Schwertmannite has been frequently identified as the product of sulfide oxidation in environments impacted by acid mine drainage (Acero et al., 2006; Bigham et al., 1996; Murad, 2003; Regenspurg et al., 2004).

Schwertmannite has also been recognised in Fe precipitate accumulations linked to the drainage induced pyrite oxidation in coastal lowlands (Burton et al., 2006; Sullivan and Bush, 2004). Sullivan and Bush (2004) determined the mineralogy and morphology of twenty-seven Fe precipitate accumulations from coastal ASS sites in Australia. Schwertmannite was found to be the most common and widespread Fe(III) mineral in the surface environments of disturbed ASS on the east coast of Australia. Goethite was the only secondary Fe mineral that formed along with schwertmannite. As schwertmannite was found in abundance at these sites and the morphology of goethite formed at these sites was very similar to that of schwertmannite, it was suggested that the goethite at these sites had been formed from the transformation of schwertmannite. Schwertmannite has also been identified to precipitate along with ferrihydrite and goethite in inland ASS in the Mount Lofty Ranges, South Australia (SA) (Fitzpatrick et al., 1996).
The estimated thermodynamic stability constants for the formation of schwertmannite range between $\log K_{sp} = 7.09 \pm 0.09$ and $\log K_{sp} = 18.0 \pm 2.5$ (Blodau, 2006). Schwertmannite has a structure similar to that of akaganéite (Table 2.1). Both of these minerals consist of Fe octahedra forming a tunnel structure; however the tunnels are filled by different anionic species in akaganéite and schwertmannite. In akaganéite, $\text{Cl}^-$, (fluoride) $\text{F}^-$ or (hydroxyl) $\text{OH}^-$ occupy every second cavity to provide structural stability to the mineral. The tunnel space in the case of schwertmannite is filled by $\text{SO}_4^{2-}$ ions, with extra $\text{SO}_4^{2-}$ ions absorbing onto the mineral surface sites (Jonsson et al., 2005). The larger size, $\text{SO}_4^{2-}$ ions cannot occupy the tunnel spaces in the schwertmannite structure without sharing the oxygen (O) atoms with surrounding Fe atoms (Fukushi et al., 2003). Thus the unit cell of schwertmannite is severely distorted which gives it a very poor crystallinity compared to much more ordered akaganéite structure (Bigham, 1990). Accordingly the habit of schwertmannite crystals is also markedly different from that of akaganéite and is characterised by long, thin needles which agglomerate to give ‘hedgehog’ like crystals compared with ‘cigar’ or ‘spindle’ shaped morphology of akaganéite crystals (Bigham, 1990).

2.1.4 Transformation of metastable iron minerals to goethite

Schwertmannite is a poorly crystalline oxyhydroxysulfate mineral that may transform to goethite over timescales of weeks to months (Burton et al., 2006; Yu et al., 1999). Transformation takes place through dissolution of schwertmannite followed by re-precipitation of goethite (Schwetmann, 2005). The transformation of schwertmannite to goethite releases acidity and $\text{SO}_4^{2-}$ and results in lowering the pH of the system (Fanning et al., 2002). Bigham et al. (1996) found that synthetic schwertmannite transformed to goethite over a time period of 543 days, resulting in lowering the solution pH from 3.9 to 2.4. The
formation of trace quantities of goethite was observed by Acero et al. (2006) from natural schwertmannite within 105 days at pH 2–3. Previous studies have also revealed that the transformation of schwertmannite to goethite proceeded at a faster rate at a higher pH. For instance, Jonsson et al. (2005) reported a complete transformation of schwertmannite to goethite within 187 days at pH 9, whereas the transformation was incomplete even after 514 days at pH 6.

A number of studies documented the pH control on schwertmannite transformation rates to goethite (Bigham et al., 1996; Regenspurg et al., 2004; Schwetmann, 2005). The increase in pH from 3 to 5 increased the transformation rates by approximately 6 times (Knorr and Blodau, 2007). The transformation rates were also reported to depend on temperature, \( \text{SO}_4^{2-} \) concentration and dissolved organic carbon (DOC) concentration of the pore water (Blodau, 2006). The transformation rates increased with an increase in temperature and a decrease in the \( \text{SO}_4^{2-} \) concentration (Bigham et al., 1996; Knorr and Blodau, 2007). A combination of low pH, high \( \text{SO}_4^{2-} \) and DOC concentrations, and low temperatures inhibited schwertmannite transformation to goethite (Knorr and Blodau, 2007) (equation 11).

\[
\text{Fe}_8\text{O}_8(\text{OH})_6\text{SO}_4 + 2\text{H}_2\text{O} \rightarrow 8\text{FeOOH} + \text{SO}_4^{2-} + 2\text{H}^+
\]

Studies of in-situ sediment profiles show that over time, schwertmannite tends to be replaced by goethite. Gagliano et al. (2004) determined the mineralogy and geochemical stability of ochreous sediments accumulated in a compost wetland constructed near Carbondale in Athens County, Ohio, the USA for AMD treatment. The predominant phase formed in the upper
portion of the column sediments collected from the study site, was schwertmannite which transformed to goethite with depth.

In another study conducted on ochreous precipitates and water samples collected from the surroundings of seven closed sulfide mines, schwertmannite and goethite were found to be the most dominant secondary iron minerals formed (Kumpulainen et al., 2007) as a result of sulfide oxidation. The authors found that at most of these sites, schwertmannite and goethite were found as mixtures and they occurred at sites with similar pH and \( \text{SO}_4^{2-} \) solution concentrations. They indicated that ferrihydrite was found at the sites, either not affected by AMD or AMD waters containing high organic matter content; and jarosite was present only at one site. Kumpulainen et al. (2007) collected samples at different time periods during a year and characterised them for mineralogical and geochemical composition. Based on the mineralogical and geochemical evidence, they suggested that Fe was precipitated as schwertmannite initially following the snowmelt in spring, and then partially transformed to goethite in the warm summer months accompanied by Fe and \( \text{SO}_4^{2-} \) release into the solution and a decrease in the solution pH.

Peine et al. (2000) have described the presence of a clear boundary between acidic schwertmannite-rich surface sediment and a deeper goethite-rich, \( \text{SO}_4 \)-reducing, sub-surface sediments in an acid mining lake. Peretyazhko et al. (2009) determined the mineralogy and chemistry of sediments from two AMD sites in northern Pennsylvania, the USA using chemical extractions, X-ray diffraction (XRD), Scanning Electron Microscopy (SEM) and Fourier Transform Infra red (FTIR) spectroscopy. Schwertmannite and goethite were found to
be major Fe(III) minerals at both sites. In-situ transformation of schwertmannite to goethite was also observed in sediments from one site and the laboratory incubation experiments conducted on sediments from the study sites revealed the central role of schwertmannite on AMD water chemistry.

Similar results on sediment accumulation in waterways linked to acidified coastal lowlands have been reported by Burton et al. (2006). In another study, Burton et al. (2008) conducted batch experiments using synthetic schwertmannite suspensions to quantify the catalytic effect of Fe(II) on transformation of schwertmannite to goethite at slightly acidic to neutral pH conditions. The transformation rate of schwertmannite to goethite was quantified by the SO$_4^{2-}$ released into the solution on the addition of Fe(II) in conjunction with the mineralogical characterisation of the products formed using XRD. The results from the study conducted by Burton et al. (2008) showed that fast SO$_4^{2-}$ release observed on Fe(II) addition to schwertmannite suspensions was accompanied by the formation of goethite. The authors revealed that transformation process was several orders of magnitude faster in the suspensions containing dissolved Fe(II) than those without Fe(II) addition. Rapid transformation of schwertmannite to goethite results in reduced availability of Fe(III) in solid form thus providing a benefit to SO$_4^{2-}$-reducing bacteria. This process may help in the formation of iron sulfide minerals like mackinawite, instead of further release of acidity to the soil system (Burton et al., 2008).
Fitzpatrick et al. (2008b) demonstrated that the minerals precipitated in the drains of the Western Australian wheat-belt on pyrite oxidation were indicative of the specific geochemical conditions at the site. The bright yellow precipitates of natrojarosite were found to be precipitating in clay rich sulfuric horizons in the pH range 3.5–4, whereas orange colored mottles consisting of precipitates of schwertmannite and akaganéite (first reported occurrence of akaganéite in the soil environment) were formed from Fe(II) oxidation in the pH range of 4–5 (Fitzpatrick et al., 2008b).

Smelter operations produce large quantities of waste materials that often contain significant quantities of pyrite, galena and arsenopyrite (FeAsS). Gao and Schulze (2010) investigated precipitates from the surface horizon of an organic soil in Indiana, USA, at a site which previously hosted a lead (Pb) smelter. Goethite and akaganéite were found to be the main Fe(III) minerals at the site; schwertmannite and jarosite were also recognised occasionally, especially in samples collected during dry periods. Akaganéite was identified by Fitzpatrick et al. (2008b) for the first time in the soil environment. However, Gao and Schulze (2010) gave a detailed description of the characteristics of akaganéite formation in soil by Fe(II) oxidation using XRD, SEM, synchrotron based micro-XRD and micro X-ray fluorescence (µ-XRF) spectroscopy. The authors suggested that the unique conditions at the study site, such as acidic solution pH and the presence of Cl\(^-\) favored the precipitation of akaganéite. They also reported that the poor crystallinity and the presence of mixtures of schwertmannite, akaganéite and goethite is an indication that goethite had not directly precipitated from sulfide mineral oxidation, and is the product of transformation of schwertmannite and/or akaganéite.
Jarosite is a metastable mineral which in the continued presence of water may either dissolve (pH < 2) (Dutrizac and Jambor, 2000) or transform to Fe(III) minerals, such as schwertmannite, hematite (Fe$_2$O$_3$) or goethite depending on prevailing conditions (Acero et al., 2006; Dutrizac and Jambor, 2000). The transformation of jarosite to goethite in AMD systems is observed at pH > 2.5 (Murad and Rojik, 2005) (equation 12).

\[
\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6 \rightarrow 3\text{FeOOH} + \text{K} + 2\text{SO}_4^{2-} + 3\text{H}^+ 
\] (12)

There are several studies that have documented the co-existence of jarosite and other secondary Fe minerals, such as goethite and schwertmannite from ASS and AMD environments. Poch et al. (2009) used light microscopy and SEM microscopy to determine the morphology of products from pyrite oxidation of two contrasting coastal ASS environments (St Kilda and Gilman) in SA, Australia. They investigated the compositional changes and weathering pathways accompanying the oxidation process in these ASS environments. In the undrained mangrove soils at St Kilda, pyrite oxidation led to the formation of gypsum due to the presence of calcium (Ca) in the environment. Whereas in the case of the drained environment at Gilman with very little acid neutralising capacity, the oxidation of pyrite resulted in the formation of thick coatings of jarosite and Fe oxides during aeration periods. However, from the morphological features of the Fe oxides formed at the site, the authors suggested that the Fe oxides have formed directly from the pyrite oxidation process and there were no signs of transformation of jarosite which formed at the site of pyrite occurrence.
Kacourková et al. (2011) investigated a waste rock pile with high initial sulfide and low carbonate content in two profiles using XRD, electron microprobe analysis, bulk composition analysis and Mössbauer spectroscopy. The predominant secondary Fe(III) mineral identified at the excavation profile was goethite, whereas jarosite was found at the base of the profile; melanterite was also found at the deep zone of the excavation profile. The authors proposed that the downward movement of acid water via macropores or the presence of an oxidation layer related to the break-in-deposition has caused the formation of jarosite at the base of the profile. Jarosite group minerals were major Fe(III) phases formed at the outcrop profile along with the presence of scorodite; however, Fe(II) minerals such as melanterite were not found in the outcrop profile.

In a study, Kawano and Tomita (2001) investigated the mineralogy and geochemistry of acidic spring waters (flowing down on the surfaces of hydrothermally altered andesitic rocks) in Japan. The authors revealed that schwertmannite and jarosite were preferentially formed as products of the pyrite oxidation process instead of the more stable Fe mineral goethite. However, the results from the geochemical modelling predicted that the spring water was super-saturated with respect to schwertmannite and also goethite and jarosite and under-saturated with respect to ferrihydrite. The authors concluded that the bulk solution chemistry slightly deviated into the stability field of goethite instead of jarosite, and that \( \text{SO}_4^{2-} \) rich acidic waters in contact with the rock surfaces may be more acidic than the bulk solution. This may ultimately result in the precipitation of jarosite as a preferred Fe(III) mineral over goethite.
2.2 **Extent and Distribution of ASS: Worldwide and in Australia**

Significantly large areas of coastal floodplains, swamps and wetlands throughout the world have developed sulfidic sediments during the Holocene age. Holocene sediments were deposited in the last 10,000 years (White et al., 1997). Over the years these areas have been increasingly drained for agricultural, aquacultural and numerous other uses. Many coastal floodplains with sulfidic sediments were drained for land use particularly in agriculture in Australia (Sammut et al., 1996), the Netherlands (Pons, 1973), Vietnam’s Mekong Delta (Tuong, 1993), China’s Pearl River Delta (Lin and Melville, 1994), South Kalimantan, Indonesia (Hamming and van den Eelaart, 1993), and Finland (Palko and Yli-Halla, 1993), with significant environmental damage. The global extent of coastal ASS is between \(10^7\) and \(10^8\) ha, with large deposits in Southeast Asia, the far-east, Africa, and North and South America (Brinkman, 1981); however, the global extent of inland ASS is not well known.

Australia contains a wide range of types of ASS in different physical settings which is due to changes in the hydrology and biogeochemistry in different parts of the country (Fitzpatrick, 2008). These soils are prevalent around coastal Australia, occur to an unknown scale in inland areas and are often associated with certain mining activities, such as waste rock accumulations and tailing impoundments (Fitzpatrick et al., 1998). Fresh coastal rivers are expected to have low \(\text{SO}_4^{2-}\) levels (< 10 mg L\(^{-1}\)), and significant quantities of sulfidic sediments are not found in river systems with fluvial outflows much larger than the tidal exchange. The tidal stretch in eastern Australia is about 2 m and the coastal rivers have small
catchments and low outflow; thereby these areas become primary sites for sulfidic sediment development.

![Diagram of coastal ASS development](image)

Fig. 2.2 A schematic soil landscape cross section representing the development of saline-acidic land with sulfuric materials, removed vegetation, reduction of wetland biodiversity, poor water quality, and ground subsidence, in an estuary in South Australia (Australia) (modified from Fitzpatrick and Shand 2008)

Fig. 2.2 shows a schematic soil-landscape cross-section of the development of coastal ASS in an estuary in SA (Australia). Exclusion of seawater from the original sulfidic material underlying this area has caused the surface to dry and oxidise the sulfide minerals to produce H$_2$SO$_4$ (Fitzpatrick and Shand, 2008). The development and accumulation of sulfidic sediments is also very well correlated with mangrove communities (Figure 2.2) (Simpson and Pedini, 1985). Currently, Australia has the third largest area of mangroves in the world and had even more in the early Holocene period. The sulfidic sediments in Australia were expected to form in the (White et al., 1997):
Chapter 2: Review of literature

I. coastal lowlands and estuary floodplain Holocene sediments;

II. estuarine sediments with surface altitude of < 10 m Australian Height Datum;

III. bottom sediments of estuaries and tidal lakes;

IV. deep Pleistocene estuarine sediments.

The criteria mentioned above and models of the coastal geomorphology were used to develop ASS risk maps for New South Wales (NSW), Australia (Naylor et al., 1998). According to Naylor et al. (1998), there are about $0.6 \times 10^6$ ha of estuarine sulfidic sediments in NSW. In SA, coastal ASS with sulfuric and sulfidic materials occupy over $2410$ km$^2$ and have an estimated acid reservoir of $2$ Mt (Poch et al., 2009). The sulfidic sediments in the remainder of Australia are yet to be mapped; however, they occur in every state of Australia and cover in excess of $3 \times 10^6$ ha (Lin and Melville, 1992), containing over 1 billion tonnes of pyrite (i.e. approximately 10% by area of world sulfidic sediments) (White et al., 1997). The total extent of ASS that has been mapped in Australia is about $2.2 \times 10^6$ ha, of which about $0.6 \times 10^6$ ha is coastal and $1.6 \times 10^6$ ha is inland (Fitzpatrick et al., 2008a; Fitzpatrick et al., 2010). In the coastal zone, $4.1 \times 10^6$ ha are exposed at some point during the tidal cycle, with the remaining $1.7 \times 10^6$ ha being permanently subaqueous. More than $126$ km$^2$ of coastal ASS with sulfuric material have been mapped, however, this is a significant underestimate which will be modified with future work.

Major occurrences of inland ASS have been documented in river and wetland systems (e.g. the Murray River, Lower Lakes and Coorong in SA), artificially drained landscapes (e.g. Western Australian wheat-belt cropping region) and upland landscapes experiencing altered
groundwater drainage (e.g. Mount Lofty Ranges, South Australia, and Dundas Tablelands, Victoria) (Fitzpatrick, 2008).

2.2.1 Development of inland ASS in Australia

The development of sulfidic sediments from accumulation of Fe and S in inland systems has received very less attention compared with the well-known coastal wetlands (Baldwin and Fraser, 2009). The concentration of \( \text{SO}_4^{2-} \) in inland wetlands is assumed to be low and therefore, \( \text{SO}_4^{2-} \) reduction is not considered to be an important process (Hall et al., 2006). Several recent investigations into the development of sulfidic sediments in inland systems indicate that they are a major environmental concern in ecosystems of high conservation value (Fitzpatrick et al., 1996). Hall et al. (2006) investigated the extent of sulfidic sediments in freshwater wetlands of the Murray Darling Basin, using the methods developed for the analysis of coastal ASS. Out of 81 wetlands tested by the authors, 17 contained sulfidic sediments at concentrations that could cause potential hazard due to the generation of acidity and other harmful effects associated with the presence of these sediments (i.e. foul odours associated with the drying of these wetlands, deoxygenation of the water column following sediment resuspension, \( \text{H}_2\text{S} \) toxicity). In another study conducted on nine floodplain wetlands representing a salinity gradient from fresh to hyper-saline, it was determined that surface sulfide sediment concentrations varied from \(< 0.05\%\) to \(~1\%\) (Lamontagne et al., 2006).

River regulation in Australia has resulted in increased periods of overflow of floodplain wetlands due to (i) weirs elevating surface and subsurface water levels (ii) un-seasonally excessive riverine flows for irrigation distribution (McCarty et al., 2006). The
implementation of a drying phase is becoming increasingly common in order to restore the original drying/wetting cycles of some of these wetlands (Casanova and Brock, 2000; McCarthy et al., 2006); however, drying of the wetlands in some cases may have some unforeseen outcomes in the form of acidity generation ($H_2SO_4$) and a mobilization of metal(loid)s from the sediments (Sullivan et al., 2002). For instance, the partial drying of a wetland in the south-western NSW, Bottle Bend (BB) lagoon in 2002 resulted in the release of highly saline-acidic solution ($EC = 30,000\ \mu S\ cm^{-1}$ and $pH < 3$), which resulted in an extensive fish-kill in the wetland (McCarthy et al., 2006). Approximately, 8 ha of previously submerged wetland was exposed to aeration and showed Fe discoloration characteristic of ASS (McCarthy et al., 2006). The presence of sulfidic material in the sediments of BB lagoon was confirmed (Hicks et al., 2003; Lamontagne et al., 2004) and it was suggested that an elevated and $SO_4^{2-}$ rich groundwater table under conditions favorable for $SO_4^{2-}$ reduction would have resulted in the sulfide mineral formation (Fitzpatrick et al., 1996; Lamontagne et al., 2004). The reason for the acidification at BB lagoon indicated that the sediments of the wetland had low capacity to neutralise the acidity generated on sulfide mineral oxidation (Glover et al., 2011; McCarthy et al., 2006). The released Fe(III) from iron sulfide oxidation in inland wetlands may precipitate in the form of oxyhydr(oxides), hydroxides, oxyhydroxysulfates and oxides of Fe, depending on the prevailing biogeochemical conditions (Fitzpatrick and Shand, 2008). An important consideration should be given to the mineralogical composition of the products of the sulfide mineral oxidation process as these products may either enhance or neutralise the acid generating potential of these soils. For example, when the process forms secondary Fe minerals, such as jarosite or schwertmannite – these phases may serve as stores of acidity. Thus any assessment on the acid generating
potential of these soils needs to include the possibility of the presence of these mineral phases (Fitzpatrick and Shand, 2008). While considerable research effort has been focussed on the characterisation of Fe minerals precipitated as a result of sulfide minerals oxidation in coastal ASS (Burton et al., 2006; Sullivan and Bush, 2004) and AMD systems (Bigham, 1994; Singh et al., 1999), there is a need to understand the geochemistry and mineralogy of inland ASS.

2.3 ACID NEUTRALISATION PROCESSES IN ASS

A soil becomes acidic when the acid neutralising processes in the soil consume less acidity than is being produced by the acid generating processes (Fitzpatrick and Shand, 2008). The components of the soil with the capacity to neutralise acidity generated during various processes include the soil solution, minerals, and exchange complexes (Essington, 2003). Primary soil minerals neutralise acidity by consuming protons during weathering processes, whereas secondary mineral precipitation reactions release protons and are detrimental chemical reactions in regards to the production of acid soils (Essington, 2003).

2.3.1 Carbonate and silicate dissolution

Dissolution of carbonates and silicates changes the chemical composition of the acidic soil solutions by consuming protons and releasing metal cations such as $\text{Ca}^{2+}$, $\text{Mg}^{2+}$, $\text{K}^+$ and $\text{Al}^{3+}$ (Blodau, 2006). The carbonate minerals with the highest acid neutralisation potential include calcite, dolomite and magnesite (Paktunc, 1999). Surface normalised dissolution rates of carbonates are strongly dependent on the pH of the solution. An increase in solution pH from 0 to 5 decreased the dissolution rate by about 4 orders of magnitude; however, temperature
changes had little to no effect on the carbonate dissolution rates (Gautelier et al., 1999). Particle size, i.e. mineral surface area, further controls carbonate dissolution rates (Stromberg and Banwart, 1999). The carbonate buffered systems show much higher pH values compared to silicate buffered systems. Circumneutral pH values were maintained in carbonate rich tailings and dumps in ore and coal mining areas by carbonate dissolution while much lower pH values were shown by dumps and tailings devoid of carbonates (Blodau, 2006; Hoth et al., 2001; Rolland et al., 2001). In a recent investigation on comparing the pH buffering properties of two wetlands, namely Bottle Bend (BB) and Psyche Bend (PB) (Australia), anaerobic titration experiments were performed on sulfidic sediments from the two wetlands (Glover et al., 2011). In these experiments, very little buffering was provided by BB sediment while much more buffering was provided by PB sediment, i.e. almost an order of magnitude higher than the acid generation potential of the sediment. The high acid buffering provided by PB sediment matched closely the formation of aqueous Ca$^{2+}$, resulting from the dissolution of aragonite (Glover et al., 2011).

The acid neutralisation potential of silicates depends on their stoichiometric composition, and the products of dissolution reactions (Sherlock, 1995). In the case of congruent dissolution of silicates more protons per formula unit are consumed (Blodau, 2006). The acid neutralisation reactions of carbonates and silicates are different in terms of the pH values developed as a result of the dissolution process. Silicate dissolution often results in lower pH values because of the release of Fe$^{3+}$, Mn$^{2+}$ and Al$^{3+}$ into the solution. The cations released as a result of silicate dissolution may re-precipitate in the form of oxyhydr(oxides), releasing additional acidity to the system (Hammarstrom, 2005; Totsche et al., 2003). Irrespective of their slower
dissolution rates as compared to the carbonates, silicates still play a very important role in providing acid neutralisation on a long-term basis because of their presence in soil in large quantities and high reactive surface areas (Sherlock, 1995).

2.3.2 Precipitation of secondary mineral phases

With respect to the acidity balance of the acidic systems (acid sulfate systems in ASS and AMD), the precipitation of secondary minerals is important since these processes sequester metals and \( \text{SO}_4^{2-} \) (Cornell and Schwertmann, 2003; Hammarstrom, 2005). Precipitation reactions also change the ratio of the protons to metal ions (Hammarstrom, 2005) in the acidity generated in the soil as a result of different acid generating processes and have great potential to reduce the trace metal load by co-precipitation reactions (e.g. co-precipitation of trace metals with Fe hydroxides). In comparison to mineral dissolution, the precipitation reactions are kinetically faster and often achieve equilibrium with respect to some particular mineral phases (Nordstrom and Alpers, 1999). Precipitation of Fe(II) or Al with the anion of a strong acid (e.g. \( \text{H}_2\text{SO}_4 \)) to produce minerals (melanterite or halotrichite) decreases the acidity load in the pH range of 2.5 to 3.5 (Blowes et al., 1991). However, the precipitation of Fe(II) or Al with anions of weak acids is an acidity neutral reaction. Precipitation of oxidised metal ions as oxyhydroxides or oxyhydroxysulfates, e.g. ferrihydrite or schwertmannite does not change the acidity concentration of the discharged acidic solution (Blodau, 2006). Gypsum also frequently precipitates from acid sulfate solutions. Although the process has less impact on the proton balance of the system, it is important for limiting the mineralisation of acidic waters and \( \text{SO}_4^{2-} \) export (Blodau, 2006).
2.3.3 Dissolution of phyllosilicate minerals in saline acidic solutions

Phyllosilicate minerals constitute a subgroup of silicate minerals. Due to their large surface area and reactivity, phyllosilicate minerals control a number of chemical and physical processes in soils and groundwater (Sposito, 1989). Kaolinite, illite and montmorillonite are the most abundant phyllosilicate minerals in soils worldwide (Dixon, 2002). A brief summary of the results from dissolution studies on kaolinite, illite and smectite under acidic conditions is presented in Table 2.2 (see next page).

The oxidation of iron sulfide minerals to form \( \text{H}_2\text{SO}_4 \) causing the soil pH to drop from around neutral to below 4, causes the dissolution of layer silicates or phyllosilicates in the soil (Fitzpatrick and Shand, 2008). The dissolution of phyllosilicate minerals becomes a major acidity consumption process in ASS (pH ≤ 4) (Fig. 2.3).

Quantification of phyllosilicate dissolution rates is important for understanding and managing environmental impact from ASS, AMD and acid deposition from other processes. The dissolution rates of minerals can be calculated from the field-scale measurements (involving mass balanced approaches in soil profiles and watersheds) and in the laboratory from batch, column and flow-through reactor experiments. One of the most direct methods to determine the impact of acid input on acid loading of soil is based on the experimental investigation of the effect of pH on phyllosilicate dissolution, as the data on the effect of acidification on natural dissolution rates are uncertain (White and Brantley, 1995).
Table 2.2 Selected log normalised dissolution rates (based on Si and/or Al release) and reaction orders \((n)\) of kaolinite, illite and smectite at 25°C.

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Solution pH</th>
<th>Dissolution rate Si (mol m(^{-2}) s(^{-1}))</th>
<th>Dissolution rate Al (mol m(^{-2}) s(^{-1}))</th>
<th>Reaction order ((n))</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>3.02–4.04</td>
<td>–12.17 to –12.62</td>
<td>–12.07 to –12.70</td>
<td>0.5</td>
<td>Ganor et al. (1995)</td>
</tr>
<tr>
<td></td>
<td>0.95–4.73</td>
<td>–12.73 to –13.81</td>
<td>–12.70 to –13.82</td>
<td>0.5</td>
<td>Huertas et al. (1999)</td>
</tr>
<tr>
<td></td>
<td>0.5–4.5</td>
<td>–12.94 to –13.94</td>
<td>–12.97 to –14.05</td>
<td>0.3</td>
<td>Cama et al. (2002)</td>
</tr>
<tr>
<td></td>
<td>4.0</td>
<td>–</td>
<td>–12.94</td>
<td>–</td>
<td>Yang and Steefel (2008)</td>
</tr>
<tr>
<td>Illite</td>
<td>1.6–4.7</td>
<td>–12.5 to –14.5</td>
<td>–</td>
<td>–</td>
<td>Kohler et al. (2003)</td>
</tr>
<tr>
<td></td>
<td>1.0–4.0</td>
<td>–11.44 to –12.20</td>
<td>–11.82 to –13.58</td>
<td>0.2–0.3</td>
<td>Zysset and Schindler (1996)</td>
</tr>
<tr>
<td></td>
<td>1.0–4.0</td>
<td>–11.34 to –12.41</td>
<td>–11.66 to –12.90</td>
<td>0.2–0.3</td>
<td>Zysset and Schindler (1996)</td>
</tr>
<tr>
<td></td>
<td>1.0–4.0</td>
<td>–10.52 to –11.57</td>
<td>–10.85 to –11.99</td>
<td>0.2–0.3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.0–4.5</td>
<td>–10.70 to –12.12</td>
<td>–10.70 to –12.21</td>
<td>0.6</td>
<td>Amram and Ganor (2005)</td>
</tr>
<tr>
<td></td>
<td>1.1–5.5</td>
<td>–13.89 to –14.77</td>
<td>–13.89 to –14.84</td>
<td>0.2</td>
<td>Golubev et al. (2006)</td>
</tr>
<tr>
<td></td>
<td>0.97–3.98</td>
<td>–12.83 to –13.84</td>
<td>–12.81 to –13.88</td>
<td>0.4</td>
<td>Rozalen et al. (2008)</td>
</tr>
</tbody>
</table>

\(^a\)Yang and Steefel (2008) performed kaolinite dissolution experiments at 22°C; \(^b\)KCl concentration = 0.03 M;\(^c\)KCl = 0.1 M; \(^d\)KCl = 1.0 M

However, the effects of pH alone cannot be considered in applying measured dissolution rates to natural acidification problems. For example, a change in the ionic strength of the solution due to an increase or decrease in the salt concentration of the input solution may accelerate or inhibit the dissolution rate of one structural cation of the mineral over another (Zysset and Schindler, 1996).
There is an extensive literature available on the dissolution rates of minerals obtained from laboratory experiments in different experimental settings that are potentially useful for understanding the dissolution behaviour of minerals subjected to different input solutions (Amram and Ganor, 2005; Kohler et al., 2003; Oelkers et al., 2008; Rozalen et al., 2009).

Kaolinite is a phyllosilicate mineral consisting of an Al octahedral sheet bonded to a Si tetrahedral sheet. Pure kaolinite has no layer charge, however a small amount of permanent charge may result from Al substitution for Si in the tetrahedral sheet (Nagy, 1995). A significant amount of work has been done on the dissolution kinetics of kaolinite in last few years that has helped us understand the reaction mechanism and the impact of various
environmental factors (Table 2.2). Kaolinite dissolution rates were determined from pH 0.5 to 12 by Carroll-Webb and Walther (1988) and Carroll and Walther, (1990) at 25, 60 and 80°C. Wieland and Stumm, (1992) determined kaolinite dissolution rates from pH 2 to 6.5 at 25°C. Based on slightly incongruent dissolution where Al was released at a slightly lower rate than Si at 25°C, Carroll-Webb and Walther, (1988) and Wieland and Stumm, (1992) suggested the removal of Al to be the rate limiting step in acidic solutions. Ganor et al. (1995) hypothesised that the rate limiting step in acidic solutions was the dissolution of the Al–O–Si bond only. Huertas et al. (1999) determined kaolinite dissolution rates in batch reactor experiments at room temperature from pH 1 to 13 and combined the dissolution rate data with the results from surface speciation data obtained from titration experiments to explain the dissolution mechanism. These authors suggested that the rate limiting step was the breaking of Si–O–Al bonds and was thus associated with the adsorption of a proton on an Al centre, the detachment of Al and a subsequent detachment of Si. The combined effect of pH and temperature on the kaolinite dissolution rate was investigated by flow-through reactor experiments conducted at the pH values ranging between 0.5 and 4.5 and at temperatures ranging between 25 and 70°C (Cama et al., 2002). The rate of kaolinite dissolution was suggested to be controlled by two independent parallel reaction mechanisms; however, the sites of these reaction mechanisms were not identified by these authors. The first reaction mechanism was suggested to be controlling the dissolution of kaolinite at pH $\geq 2.5$ and the second mechanism controlled the dissolution reaction at pH less than 0.5. Between pH 0.5 and 2.5, both reaction mechanisms were suggested to be controlling the dissolution rate (Cama et al., 2002). In a recent investigation, kaolinite dissolution rates were determined as a function of Gibbs free energy of reaction ($\Delta G_r$), at an acidic pH 4 and at 22°C (Yang and Steefel, 2008). A slightly
incongruent release of Si over Al was observed which was reported to have resulted from the re-adsorption of dissolved Al; and a variation in the input Al concentration from 0 to 60 µM was not suggested to inhibit kaolinite dissolution rate.

Illite is a non-expanding, dioctahedral phyllosilicate mineral that consists of two tetrahedrally coordinated sheets and one octahedrally coordinated sheet and contains K in the interlayer sites. In comparison to kaolinite dissolution that has been the topic of many recent investigations, the dissolution rates of illite were determined in only one batch experiment study conducted by Kohler et al. (2003) on a natural illite sample from France at a pH range of 1.4 to 12.4 and at a temperature range of 5 to 50°C. Illite dissolved stoichiometrically in experiments conducted at 4 > pH > 11 whereas, a non-stoichiometric dissolution of illite occurred at 4 < pH < 11 due to the precipitation of secondary mineral phases. The dissolution rate of illite decreased with an increase in pH of the input solution in the acidic pH range, was minimal at near to neutral pH, and increased with an increase in pH in the alkaline pH range.

Smectite is a phyllosilicate mineral with two tetrahedrally coordinated sheets and one octahedrally coordinated sheet. Montmorillonite is the most abundant smectite in nature. Its permanent surface charge ranges from 0.2 to 0.6 and thus it can have complex cation composition in both tetrahedral and octahedral sheets (Nagy, 1995). The structural charge resulting from tetrahedral and octahedral substitution is compensated by the exchangeable interlayer cations. Zysset and Schindler, (1996) conducted both batch and flow-through reactor experiments to study the proton promoted dissolution kinetics of a K-saturated
montmorillonite sample. The dissolution experiments were carried out in 1 M, 0.10 M and 0.03 M KCl solutions and the pH of the solutions was adjusted using HCl. From a linear regression of log$R_{Si}$ vs. pH, the fractional reaction orders with respect to protons ranging between 0.24 and 0.35 were obtained. A congruent dissolution of K-saturated montmorillonite was obtained in 1.0 and 0.10 M KCl solutions, whereas a preferential Si over Al release was observed in 0.03 M KCl solutions. Montmorillonite dissolution rate increased with KCl concentration and decreased with pH. The observed element release rate ratio (i.e. $R_{Si}/R_{Al}$) was observed to depend on both pH and KCl concentration. The results from experiments conducted by Zysset and Schindler, (1996) also showed the inhibition effect of input Al on montmorillonite dissolution rate at pH $\geq 3$.

The effect of deviation from equilibrium in terms of Gibbs free energy of reaction ($\Delta G_r$) on smectite dissolution rate was studied by Cama et al. (2000) at pH 8.8 and 80°C. The results from this study showed that the dissolution rate of smectite was independent of deviation from equilibrium in the range of $\Delta G_r \leq -30$ kcal mol$^{-1}$. Amram and Ganor (2005) studied the dissolution of smectite under far from equilibrium conditions and proposed a rate law to describe the combined effects of pH (1–4.5) and temperature (25–70°C), based on the application of a Langmuir model for proton adsorption on reactive edge sites. Dissolution rates decrease with increasing pH, having a fractional reaction order with respect to protons of 0.57. The proposed dissolution rate law is a function of proton activity in solution and temperature-dependent adsorption equilibrium. These authors (Amram and Ganor, 2005) normalised the dissolution rates to mineral mass or edge surface area instead of BET determined surface area. Golubev et al. (2006) studied the effect of pH and organic ligands on
the kinetics of montmorillonite dissolution at 25°C. Dissolution rates in ligand-free, carbonate solutions show the expected profile as function of pH, with reaction orders ($n$) of 0.21 and 0.33 in acidic and basic conditions, respectively. Rozalen et al. (2008) determined the effect of pH on K-saturated montmorillonite dissolution rate in batch and flow-through reactor experiments at 25°C. A non-stoichiometric dissolution of montmorillonite was observed at pH ranging between 5 and 10 due to the adsorption of dissolved Al onto the mineral surface. They suggested a dissolution mechanism involving an inward movement of a dissolution front from particle edges based on the results from the study. Rozalen et al. (2008) normalised the dissolution rates to both BET surface area as well as the mineral mass and have not suggested a single procedure to normalise the montmorillonite dissolution rates.

2.3.3.1 Effect of temperature

The temperature dependence of clay minerals dissolution at a given pH typically follows the Arrhenius law:

$$Rate = -A \exp \left( \frac{E_{app}}{RT} \right)$$  \hspace{1cm} (13)

where $A$ is a pre-exponential factor, $E_{app}$ is the apparent activation energy of the overall mineral dissolution reaction (kcal mol$^{-1}$), $R$ is the gas constant and $T$ is the absolute temperature. Summary of activation energies for kaolinite, illite and smectite dissolution under acidic conditions is given in Table 2.3.
Table 2.3 Activation energies for dissolution kinetics of kaolinite, illite and montmorillonite under acidic conditions.

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Temperature range (°C)</th>
<th>$E_{\text{app}}$ (kcal mol$^{-1}$)</th>
<th>pH range</th>
<th>Solution composition</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kaolinite</td>
<td>25–80</td>
<td>16.0–1.70</td>
<td>1.0–7.0</td>
<td>pH buffers, $I = 0.05$ M</td>
<td>Carroll and Walther (1990)</td>
</tr>
<tr>
<td></td>
<td>25–80</td>
<td>7.0</td>
<td>3.0–4.0</td>
<td>HClO$_4$</td>
<td>Ganor et al. (1995)</td>
</tr>
<tr>
<td></td>
<td>25–70</td>
<td>23.0</td>
<td>0.5–4.5</td>
<td>HClO$_4$, NaClO$_4$</td>
<td>Cama et al. (2002)</td>
</tr>
<tr>
<td>Illite</td>
<td>5–50</td>
<td>11.0</td>
<td>&lt; 6.0</td>
<td>HCl</td>
<td>Kohler et al. (2003)</td>
</tr>
<tr>
<td>Smectite</td>
<td>25–70</td>
<td>17.0</td>
<td>1.0–4.5</td>
<td>HClO$_4$</td>
<td>Amram and Ganor (2005)</td>
</tr>
<tr>
<td></td>
<td>25–70</td>
<td>19.3</td>
<td>1.0</td>
<td>HNO$_3$</td>
<td>Rozalen et al. (2009)</td>
</tr>
</tbody>
</table>

Carroll and Walther, (1990) and Ganor et al. (1995) determined $E_{\text{app}}$ for kaolinite dissolution at temperature from 25 to 80°C. Carroll and Walther, (1990) observed that the value of $E_{\text{app}}$ varied with pH, with a minimum value at neutral pH. Conversely, Ganor et al. (1995) observed that over the limited pH range of 3 to 4, $E_{\text{app}}$ was constant from 25°C to 80°C at a value of 7 kcal mol$^{-1}$. Cama et al. (2002) conducted kaolinite dissolution experiments at 25°C, 50°C and 70°C in acidic solutions (pH 0.5–4.5) under far from equilibrium conditions. They separated the direct and indirect effects of variables (i.e. pH and temperature) on the kaolinite dissolution rate. According to these authors, the direct effect of a variable was related to the surface processes and one that could be used to understand the reaction mechanism. The direct effect of pH on dissolution rate was ascribed to the effect of adsorbed proton on bond strength (which was independent of temperature, the second variable) whereas, an indirect effect of pH was its effect on dissolution rate (temperature dependent effect) as a result of change in the degree of saturation with pH change. Cama et al. (2002) proposed a model based on the Langmuir equation to explain the effect of pH and temperature on the kaolinite dissolution rate. The authors suggested that two separate and independent
mechanisms controlled the dissolution reaction under acidic conditions, the first mechanism controlled the operation at pH \( \geq 2.5 \) while the second mechanism controlled the reaction below pH 0.5. A pH independent \( E_{\text{app}} \) for the two reaction paths was calculated by plotting an Arrhenius plot of the rate coefficients \( (k_1', k_2') \) at 25°C, 50°C and 70°C, which were obtained by fitting of the experimental data to the proposed model. The obtained \( E_{\text{app}} \) values were 23±1 kcal mol\(^{-1}\) and 23±2 kcal mol\(^{-1}\) for the first and second reaction mechanisms, respectively.

Kohler et al. (2003) studied illite dissolution in batch reactors at pH values ranging from 1.4 to 12.4 and temperatures ranging from 5 to 50°C. Using the empirical Arrhenius equation \( E_{\text{app}} \) values of 11, 3, and 16 kcal mol\(^{-1}\) were obtained at acidic, neutral and alkaline pH conditions, respectively. The reason for the variation in \( E_{\text{app}} \) with pH obtained from the empirical expression was not explained by Kohler et al. (2003).

Amram and Ganor, (2005) described the combined effect of pH (1 to 4.5) and temperature (25 to 70°C) on smectite dissolution. A simple model using the Langmuir equation was used to describe the effect of variables on the smectite dissolution rate. According to the model developed by Amram and Ganor (2005) the dependence of the smectite dissolution rate on temperature was affected by the activation energy and the adsorption enthalpy. The value of \( E_{\text{app}} \) obtained from the fitting of the experimental data to the developed model was 17±2 kcal mol\(^{-1}\) and an enthalpy value of −11±2 kcal mol\(^{-1}\) was obtained. Rozalen et al. (2009) determined the effect of pH and temperature on the montmorillonite dissolution rate in flow-through reactor experiments. The activation energy values obtained at acidic, neutral and alkaline conditions were 19.3, 5.3 and 20.3 kcal mol\(^{-1}\), respectively which is similar to the pH.
dependence of $E_{app}$ values obtained for kaolinite and illite, previously (Carroll and Walther, 1990; Kohler et al., 2003).

### 2.3.3.2 Effect of saturation

Chemical affinity, $A$ and Gibbs free energy of reaction, $\Delta G_r$ are two ways to express the deviation from equilibrium in a chemical state (Nagy, 1995). Chemical affinity, $A$ is expressed by the equation:

$$A = \left( \frac{\partial G}{\partial \xi} \right)_{T,P} = -\sum v_i \mu_i$$  \hspace{1cm} (14)

where, $G$ is the Gibbs free energy of reaction, $\xi$ is the extent of reaction, $v_i$ and $\mu_i$ are the stoichiometric coefficients and chemical potentials, respectively, of the reactants and products. The Gibbs free energy of reaction, $\Delta G_r$ is given by:

$$\Delta G_r = -RT \ln \left( \frac{IAP}{K_{eq}} \right)$$  \hspace{1cm} (15)

where $R$ is the gas constant, $T$ is the absolute temperature, $IAP$ is the ion activity product and $K_{eq}$ is the equilibrium constant. For a dissolution reaction, both of these parameters (i.e. chemical affinity and $\Delta G_r$) have the same absolute value, but have opposite sign. Reaction affinity is a positive while $\Delta G_r$ is negative (Nagy, 1995). Among the variables that control the dissolution reaction of a mineral, the degree of saturation (expressed in the form of chemical affinity or $\Delta G_r$) needs to be given special attention. Most of the environmental parameters that have a direct effect on the mineral dissolution rate (e.g. pH, temperature, concentration of dissolved species, ionic strength) affect the degree of saturation as well and as a result have an indirect effect on the dissolution rate (Cama et al., 2000). Only a few studies have been
conducted to assess the affect of saturation state on the dissolution rates of phyllosilicate minerals. In general, the dissolution rates of minerals slow down as equilibrium is approached. However, the exact functionality of the dissolution rate change with chemical affinity or $\Delta G_r$ varies from mineral to mineral and is also a function of the solution composition (Nagy, 1995).

Transition State Theory (TST) is a formulation for kinetic rate laws that provides an important relationship between the thermodynamic driving force and the rates of kinetic geochemical processes. It has been widely applied by geochemists in the form given in equation 16 to describe the dissolution rates of phyllosilicate minerals.

$$ f(\Delta G_r) = (1 - \exp(\frac{\Delta G_r}{RT})) $$

Equation 16 can be generalised to (Cama et al., 2000):

$$ f(\Delta G_r) = (1 - \exp(\frac{\Delta G_r}{\sigma \cdot RT})) $$

where, $\sigma$ is Temkin’s average stoichiometric number which is the ratio of the rate of destruction of the activated complex involved in the rate limiting reaction step with the rate of the overall dissolution reaction (Yang and Steefel, 2008). The application of equation 17 assumes that a single rate limiting step controls the overall rate of reaction, that steady-state conditions are met, and that the magnitude of $\Delta G_r$ for each elementary reaction is not much greater than $RT$. The equation 17 predicts that under near to equilibrium conditions, the dissolution rate will be a linear function of $\Delta G_r$ (Lasaga et al., 1994).
Nagy et al. (1991) determined the rate dependence of kaolinite dissolution (pH 3, 80°C) on saturation state using TST:

\[ R_{\text{diss}} = -1.2 \pm 0.12 \times 10^{-12} \left[ 1 - \exp\{(0.85 \pm 0.24) (\Delta G_r/RT)\} \right] \]  \hspace{1cm} (18)

According to Nagy et al. (1991) the dissolution plateau for kaolinite at 80°C is reached for \( \Delta G_r < 2 \) kcal mol\(^{-1}\), i.e., for \( \Delta G_r \) below \(-2 \) kcal mol\(^{-1}\) the kaolinite dissolution rate is not directly affected by the degree of under-saturation. Yang and Steefel (2008) studied the dissolution kinetics of kaolinite at pH 4 and at 22°C. These authors fitted the dissolution rate data from the flow-through experiments into TST using a Temkin coefficient of 2. There were two apparent regions in the fit of the dissolution rate data, a far from equilibrium region (< \(-2.6 \) kcal mol\(^{-1}\)) independent of the chemical affinity and a region close to equilibrium (> \(-2.6 \) kcal mol\(^{-1}\)) where the rates were dependent on chemical affinity, with the width of the region determined by the Temkin coefficient.

Metz (2001) studied the effect of saturation state on the smectite dissolution rate under acidic conditions. According to Metz (2001), near equilibrium (\( 0 \geq \Delta G_r \geq -20 \) kcal mol\(^{-1}\)) the rates increased gradually with increasing under-saturation. Under far from equilibrium conditions (\( \Delta G_r \leq -30 \) kcal mol\(^{-1}\)), the dissolution rate was much faster and was independent of the degree of saturation.
2.3.3.3 Effect of ionic strength

Raising the ionic strength of the solution has been shown to accelerate the dissolution rates of quartz. Studies have also shown that the nature of the cation in the solution also affects the dissolution rate due to its effect on the reaction path for the detachment of Si (White and Brantley, 1995). However, only a few researchers have investigated the impact that ionic strength may have on the dissolution rates of most of the phyllosilicate minerals. And due to the limited number of studies performed on determining the ionic strength effect on phyllosilicate dissolution, there is controversy surrounding this aspect of the dissolution process. Zysset and Schindler (1996) performed batch dissolution experiments on K-saturated montmorillonite in 1 M, 0.10 M and 0.03 M KCl solutions at an acidic pH range of 1 to 4. The results from their study showed a congruent dissolution of the mineral occurred in 1 M and 0.10 M KCl solutions, whereas a Si/Al ratio of the output solution greater than that of the original mineral sample was obtained in 0.03 M KCl solutions. They suggested that the adsorption of dissolved Al on cation exchanger sites resulted in incongruent dissolution of montmorillonite in solutions with the lowest KCl concentration. Cama et al. (2002) and Amram and Ganor, (2005) performed experiments on kaolinite and smectite dissolution, respectively, which were designed to determine the effect of ionic strength on the dissolution rate in addition to other variables (such as pH and temperature). An insignificant effect of ionic strength on mineral dissolution rate was reported by these authors. Most of the researchers who examined the effect of ionic strength on mineral dissolution rates obtained mixed results. The controversy about the effect of ionic strength on dissolution rates of phyllosilicate minerals remains; a detailed set of experiments is required in order to make the application of the dissolution rate laws from laboratory experiments applicable to the natural
systems with variable salt concentrations, and in addition to other environmental variables.

Furthermore, most of the earlier work on phyllosilicate dissolution has focussed on determining the impact of environmental variables, such as pH, temperature and saturation state etc. on dissolution rates under different experimental settings. The impact of acidity generated as a result of sulfide oxidation in ASS on dissolution behaviour of phyllosilicate minerals is still unclear and needs to be investigated in detail. The data obtained from the dissolution of mono and polymineralic phyllosilicate samples will be useful in order to determine the acidity neutralisation resulting from these long term processes and the impact of these processes on the geochemistry of these systems.
2.4 References


Chapter 2: Review of literature


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