MINERALOGY AND ACID NEUTRALISATION MECHANISMS IN INLAND ACID SULFATE ENVIRONMENTS

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A THESIS SUBMITTED TO THE FULFILMENT OF THE REQUIREMENTS
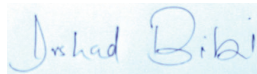FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

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CERTIICATE OF ORIGINALITY

I hereby declare that the text of this thesis is my own work, and that, to the best of my knowledge and belief, it contains no material that has been previously published or written by another person, nor any material that has been accepted as part of the requirements for any other degree or diploma in any university or other institute of higher learning, unless due acknowledgement has been made.

I also declare that the intellectual content of this thesis is original and the result of my own research and to the best of my knowledge and belief, any assistance I received in the experimentation presented, and all sources of information cited have been duly acknowledged.

Irshad Bibi

Declared at The University of Sydney

this 22nd day of March 2012

TO
MY PARENTS
AND FAMILY

ABSTRACT

Soils and sediments containing iron sulfides or the products of sulfide oxidation are known as acid sulfate soils (ASS). These soils possess significant environmental risks due to their potential capacity to produce copious amounts of sulfuric acid (H_2SO_4) on their exposure to atmosphere. The accumulation of large deposits of sulfidic material has been identified in the past 10 to 12 years in saline-inland wetlands in Australia. Extended periods of natural as well as human-induced drying events in many of these wetlands have resulted in highly saline conditions (e.g. dominated by NaCl and sulfate containing salts) and the exposure (oxidation) of sulfidic material. The oxidation of sulfidic material results in the release of H_2SO_4 and the precipitation of a range of secondary iron minerals (e.g. goethite, ferrihydrite, schwertmannite. Under highly acidic conditions (pH < 4) found in sulfuric material of the ASS, dissolution of layer silicates or phyllosilicate minerals is the only realistic process that can provide a long-term acid neutralisation in these soils; particularly in many Australian soils which have small quantities of weatherable primary minerals and carbonates. It is vital to investigate the mineralogical composition and dissolution mechanisms of layer silicates or phyllosilicate minerals existing in these ASS environments to develop effective management strategies for these soils.

The dissolution rate of illite, a common phyllosilicate mineral in Australian soil, was determined using flow-through reactors at $25 \pm 1°C$, in solutions with two different ionic strengths of 0.25 M and 0.01 M (maintained using NaCl), and pH ranging from 1–4.25 (H_2SO_4). The results from the illite dissolution experiments showed a rapid release of cations at the onset of the experiments and a relatively slower release at the steady state. Close to

stoichiometric dissolution of illite was obtained at pH 1–4 in the higher ionic strength solutions and at pH 1–3 in the lower ionic strength solutions. The experiment at pH 4.25 in the lower ionic strength solution exhibited $R_{Al} < R_{Si}$, resulting from a possible adsorption of dissolved Al on the illite surface. Illite dissolution rates showed strong pH dependence, with decreased dissolution rates with increasing pH. The proton reaction orders obtained for dissolution in the higher and lower ionic strength solutions were 0.32 and 0.36, respectively. From the relative cation release data, it was concluded that the dissolution of illite proceeded with the removal of interlayer K followed by the dissolution of octahedral cations, whereas the dissolution of Si was the rate limiting step in the dissolution process.

The dissolution rate of illite, kaolinite and montmorillonite was compared in flow-through reactors at 25 ± 1°C and at the two ionic strengths, as described earlier. Kaolinite dissolution rates were close to stoichiometric at pH 1 and 2 in the higher ionic strength solutions and at pH 1–4 in the lower ionic strength solutions. R_{Al} values greater than R_{Si} were obtained for kaolinite dissolution experiments at pH 3 and 4 in the higher ionic strength solutions. Kaolinite dissolution rates were strongly dependent on pH at pH ≤ 3, whereas kaolinite rates showed a little pH dependence at pH 3–4.25, and the point of zero charge (PZC) of the mineral appears to have affected the dissolution rate at these pH values. Kaolinite dissolution rates at pH 1 and 2 (H_2SO_4) in this study were greater than the previously reported rates in HCl and $HClO_4$ solutions, which was ascribed to the complexation of Al by sulfate ions in the solutions. For montmorillonite dissolution, R_{Al} values greater than R_{Si} were obtained in the higher ionic strength solutions at pH 1–4, whereas an opposite trend was observed in the lower ionic strength solutions at pH 2–4. A reduced R_{Al} in the lower ionic strength solutions from montmorillonite dissolution resulted from (apparent) adsorption of dissolved Al on

mineral exchange sites, possibly due to the availability of more interlayer exchange sites for Al re-adsorption and a decreased cation (Na^+) competition for exchange sites in these systems.

The dissolution rate of the clay fraction of soil cores from an inland ASS at Bottle Bend (BB) in south-western New South Wales (NSW, Australia) was determined under similar experimental conditions to pure minerals described earlier. Clay dissolution experiments were also conducted at 35 and 45°C at pH 1 and 4 to determine the effect of temperature on dissolution rates. The clay sample comprised of smectite (40 %), illite (27 %), kaolinite (26 %) and quartz (6 %), with a minor impurity of anatase (1 %). Clay dissolution rates decreased with an increasing pH and a decreasing temperature. A strong reduction in the initial Al release resulted from clay dissolution in the lower ionic strength solutions at pH 2 to 4, whereas a preferential initial Al release was obtained in the higher ionic strength solutions. A slight increase in the R_{Si} values was observed at the lower ionic strength across the pH range investigated, whereas a significant decrease in R_{Al} was found at pH 4 with a decrease in the ionic strength, at all temperatures. An apparent activation energy value of 18.3 kcal mol^{-1} was calculated at pH 1 that decreased to 9.0 kcal mol^{-1} at pH 4. The individual mineral dissolution rates estimated from bulk release rate of Al and Si showed fastest dissolution rates for kaolinite followed by illite and smectite. Smectite dissolution rates obtained for soil clay showed close similarity to pure montmorillonite rates obtained under similar conditions. The acid neutralisation capacity (ANC) of the clay sample was calculated from the release rates of cations (Al, Fe, K, Mg). The ANC values of 44.4 and 13.1 kg H_2SO_4/tonne of clay sample were estimated from the cation release over a period of 22 and 62 days at pH 1 and 4, respectively. An enhanced release of Al from phyllosilicate dissolution in the highly saline-

acidic systems could possibly be a contributing factor to the ecological disturbance caused by increased Al concentrations in the soil and water systems.

Morphology of the oxidised surface (5 cm) sediments collected from a highly saline inland ASS at the BB site was characterised by X-ray diffraction (XRD), transmission electron microscopy (TEM) and scanning transmission electron microscopy combined with energy dispersive X-ray spectroscopy (STEM-EDS). Halite (NaCl), gypsum ($CaSO_4.2H_2O$) and akaganéite (β-FeOOH) were identified as the major phases with minor amounts of K-jarosite in some sediment samples. Akaganéite is rarely found in the soil environments and mainly forms as a product of corrosion of iron in chloride-rich environment. The precipitation of akaganéite at the study site resulted from the natural occurrence of the unique solution conditions (*in situ* pH as low as 2 and EC as high as 216 dS/m) at the site. The chemical analysis of the akaganéite found in these sediments revealed an average Fe/Cl mole ratio of 6.7 and a structural formula of $Fe_8O_8(OH)_{6.8}(Cl)_{1.2}$ which is consistent with the composition of pure akaganéite. Saline-acidic conditions with significantly higher chloride over sulfate levels provided the necessary conditions for akaganéite formation at the study site. The precipitation of akaganéite in the ASS environment necessitates detailed investigation to determine the competitive formation and stability of this mineral relative to stable secondary iron minerals commonly precipitated in ASS environments.

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PUBLICATIONS

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1. Bibi I, Singh B, Silvester E (2011) Dissolution of illite in saline-acidic solutions at 25°C. *Geochimica et Cosmochimica Acta* 75 (11):3237–3249.

2. Bibi I, Singh B, Silvester E (2011) Akaganéite (β-FeOOH) precipitation in inland acid sulfate soils of south-western New South Wales (NSW), Australia. *Geochimica et Cosmochimica Acta* 75 (21):6429–6438.

3. Bibi I, Singh B, Silvester E (2012) A comparative study of the dissolution kinetics of kaolinite, illite and montmorillonite under acid sulfate conditions. *Clay Minerals* (To be Submitted).

Refereed scientific journals (In preparation)

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