Chapter 5: Clay dissolution in saline-acidic solutions

Effect of pH, ionic strength and temperature on clay dissolution in saline-acid sulfate solutions

ABSTRACT

Significant amounts of sulfuric acid (H\textsubscript{2}SO\textsubscript{4}) rich saline waters can be produced in the inland acid sulfate soils (ASS) on sulfide mineral oxidation. The dissolution of phyllosilicate minerals is the only process that can provide long-term acid neutralisation in saline-ASS. It is therefore, imperative to investigate the dissolution behaviour of clay fraction of soil in saline-acidic solutions, to understand the neutralisation process in these systems. The dissolution behaviour of individual phyllosilicate minerals in acidic solutions has been explored in many previous studies which have helped to understand the reaction mechanism for the dissolution of these minerals. However, the dissolution behaviour of natural clays in highly saline and acidic conditions that exist in ASS has not been investigated. The clay fraction of soil cores from an inland ASS (i.e. Bottle Bend lagoon) in south-western New South Wales (NSW, Australia) was used in the dissolution experiments; the clay sample was comprised of smectite (40 %), illite (27 %), kaolinite (26 %) and quartz (7 %). The objective of this study was to investigate the effects of saline-acidic solutions (pH 1–4, ionic strengths = 0.01 and 0.25 M) on the extent of dissolution of soil clay, using flow-through reactors at 25°C; the experiments at pH 1 and 4 were also conducted at 35°C and 45°C to determine the effect of temperature on dissolution at the lowest and highest solution pH values. Acid-induced

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1 This chapter is in preparation for submission to *Geochimica et Cosmochimica Acta*, under the title ‘Kinetics of clay dissolution in sulphuric acid solutions: ionic strength and temperature effect’. Authors are Irshad Bibi, Balwant Singh and Ewen Silvester.
dissolution of the clay sample was rapid at the onset of experiments, as indicated by the fast release of cations (Si, Al, Fe, Mg) into the output solution. An enhanced concentration of Al was observed at the initial stage of experiments (pH 2–4) at the higher ionic strength (0.25 M) compared to the lower ionic strength (0.01 M). The highest release of cations (Si, Al, K, Fe, Mg) was observed in the experiments conducted at pH 1 and at 45°C. The dissolution rates of the clay sample derived from the steady state Si, Al and Fe concentrations \( R_{Si}, R_{Al}, R_{Fe} \) decreased with pH and increased with temperature. A slight increase in the \( R_{Si} \) values was observed with a decrease in the ionic strength across the pH range investigated, whereas a significant decrease in \( R_{Al} \) was observed at pH 4 with a decrease in the ionic strength at all temperatures. Apparent activation energies calculated for the clay sample decreased from 18.3 kcal mol\(^{-1}\) at pH 1 to 9.0 kcal mol\(^{-1}\) at pH 4. The individual mineral dissolution rates (kaolinite, illite and smectite) estimated on the basis of content of each mineral in the clay sample and released concentration of Si from the clay sample revealed dissolution rates in the order kaolinite > illite > smectite. The acid neutralisation capacity (ANC) of the clay sample was calculated on the basis of cation (Al, Fe, K, Mg) release from clay dissolution. The total ANC of clay calculated from cation release at pH 1 in 22 days period was 44.4 kg H\(_2\)SO\(_4\)/t, whereas a value of 13.1 kg H\(_2\)SO\(_4\)/t was calculated in 62 days period at pH 4. Such knowledge on the dissolution behaviour and acid buffering potential of soil clay minerals is vital for the management and rehabilitation of these soils.

### 5.1 Introduction

Iron sulfide rich sediments are referred to as acid sulfate soils (ASS) due to their potential to release sulfuric acid upon exposure to the atmosphere (Fitzpatrick et al., 1996). Minerals in the soil matrix can provide some acid neutralisation through mechanisms of mineral
dissolution (e.g. carbonate or oxide minerals) and chemical weathering (e.g. phyllosilicate minerals) (Totsche et al., 2003). The relative rates of acid production from sulfide oxidation and acid consumption from dissolution and weathering processes will control the pH trajectory of ASS and their resultant ecological impact.

The presence of large quantities of sulfidic sediments in inland wetlands of Murray-Darling Basin (MDB) have been identified (Fitzpatrick et al., 1996). The accumulation of sulfidic materials in these wetlands has been reported to have occurred from a combination of prolonged periods of inundation due to river regulation, and the intrusion of sulfate-rich saline water either from surface water from irrigation drainage or groundwater (Lamontagne et al., 2006). In a recent investigation into the wetlands of the MDB, it was established that sulfidic sediments were present in more than 20% of the wetlands at levels that could cause a potential damage to the soil environment (Hall et al., 2006).

Many wetland systems in the MDB, with limited or no carbonates have been acidified due to oxidation of sulfides in the recent past in response to natural or human-induced drying events (Bibi et al., 2011c; Glover et al., 2011). Under highly acidic conditions existing in ASS, the acid dissolution of phyllosilicate minerals is probably the only acid neutralisation pathway. The reaction of saline-acidic solutions with clay minerals is therefore of considerable interest in understanding the acid neutralisation process. Considerable effort has been devoted to study the dissolution behaviour of individual phyllosilicates under laboratory conditions (Amram and Ganor, 2005; Bibi et al., 2011a; Brandt et al., 2003; Cama and Ganor, 2006; Cama et al., 2002; Golubev et al., 2006; Kalinowski and Schweda, 2007; Kohler et al., 2003; Lawson et al., 2007; Metz et al., 2005b; Oelkers et al., 2008; Yang and Steefel, 2008; Zysset
and Schindler, 1996). These studies have helped to understand the dissolution reaction mechanisms of these minerals. The relationship between dissolution of minerals and pH, temperature, and surface and crystallographic characteristics of minerals has been evaluated in many of these studies. There are only few studies that have investigated the impact of acidic conditions on the dissolution of natural clay samples (Jurjovec et al., 2002; Salmon and Malmstrom, 2006; Shaw and Hendry, 2009). However, the solution conditions used in these studies were not representative of the highly-saline and acidic conditions prevailing in inland ASS. In addition, in many of these studies, the main objective was to compare the neutralisation potential of different mineral groups (such as carbonates, oxide minerals and aluminosilicates), whereas this study is designed to determine the dissolution behaviour and hence the neutralisation potential of clay minerals, the only major acid neutralisation mechanism in highly saline ASS systems.

The aim of this study was to investigate the dissolution behaviour of natural polymineralic clay fraction in solution conditions with high salinity combined with SO$_4^{2-}$ based acidity, which mimic the composition of inland ASS. The specific objectives of this study were (1) to measure the dissolution rates of natural clay in acidic solutions (sulfate based) at two ionic strengths (0.01 and 0.25 M), and (2) to evaluate the activation energy for the dissolution reaction.
5.2 MATERIALS AND METHODS

5.2.1 Clay sample

The clay sample used in this study was separated from soil cores collected from an inland wetland, Bottle Bend (BB), located adjacent to the Murray River in the south-west of NSW, Australia. The sediments at the BB wetland contain sulfidic material between a clay layer below and overlying oxidised (sulfuric) material (Appendix 3). The depth of the different layers in the soil core collected from the partially submerged section of the wetland was: sulfuric material 5 cm, sulfidic material 20 cm, clay layer 8 cm. The development of significant quantities of sulfidic sediments at the BB lagoon has been attributed to the long-term elevation of the water table, and sulfate-rich groundwater at the site (Lamontagne et al., 2006). Extended periods of drought over the period 2002-2010 resulted in highly saline conditions and exposure of sulfidic materials which were subsequently oxidised to produce highly acidic conditions (pH ~ 2) in conjunction with very high salinity (EC up to 216 dS/m).

5.2.2 Sample pre-treatment and characterisation

All experiments in this study were performed on the clay fraction of soil cores collected from BB site. The clay fraction (< 2 µm) was separated by a sedimentation-resuspension procedure and saturated with Na, following the procedure described elsewhere (Chapter 3) (Bibi et al., 2011a). A small fraction of the separated clay fraction was also saturated with Ca by repeated shaking with CaCl₂ solutions of decreasing concentration (0.1 and 0.01 M CaCl₂) followed by shaking with E-pure® water and ethanol. The Na- and Ca-saturated clay fractions of the BB sample were dried and stored in polyethylene bottles in a desiccator before further analyses.
and characterisation. The Ca-saturated clay sample was prepared for random powder XRD analysis for mineral quantification in the clay fraction.

A sub sample of the Na-saturated BB sample was used for specific surface area (SSA) measurement using Quantachrome™ Autosorb 1 surface area analyser after outgasing at 110°C. The SSA of the clay sample was determined to be 104.5 m²/g by five-point N₂ Brunauer-Emmett-Teller (BET) method (Braunauer et al., 1938).

5.2.3 Chemical composition determination

Chemical composition of the Na-saturated sample was determined using Philips PW2400 X-ray fluorescence (XRF) spectroscopy (Norrish and Hutton, 1977). The detection limits of XRF for SiO₂, Al₂O₃, TiO₂, Fe₂O₃, MgO, CaO, K₂O, and Na₂O analyses were 0.006, 0.002, 0.003, 0.001, 0.006, 0.001, 0.001, and 0.016 wt%, respectively, and the accuracy of XRF results was better than 1%. Iron(II) content was determined by the 1, 10 phenanthroline colorimetric method (Amonette and Templeton, 1998). The uncertainty associated with Fe(II) analysis was ± 0.02 mg/L (i.e. standard deviation about mean, n = 3). The atomic ratios calculated from the chemical composition data of the Na-saturated clay (see Table 5.1) are presented in Table 5.2.

5.2.4 X-ray diffraction analysis

The mineralogy of the Na-saturated clay fraction of BB sample was determined using X-ray diffraction (XRD) (GBC MMA: CuKα radiation, λ = 1.5406 Å, operating conditions of 35 kV and 28.5 mA). Randomly oriented XRD patterns were collected from 4 to 75° 2θ at a step size of 0.02° 2θ and a scan speed of 1.0° 2θ min⁻¹. X-ray diffraction patterns of basally oriented
and K saturated specimens were obtained for the air-dried and the sample heated at 100, 330 and 550°C by scanning from 3 to 15° 20.

**Table 5.1 Bulk chemical composition (XRF) of Na-saturated Bottle Bend (BB) clay fraction.**

<table>
<thead>
<tr>
<th>Oxide</th>
<th>% (mass basis)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>49.17</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>23.75</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.91</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>7.13</td>
</tr>
<tr>
<td>FeO</td>
<td>1.16</td>
</tr>
<tr>
<td>MnO</td>
<td>0.02</td>
</tr>
<tr>
<td>MgO</td>
<td>1.08</td>
</tr>
<tr>
<td>CaO</td>
<td>0.03</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.71</td>
</tr>
<tr>
<td>K₂O</td>
<td>2.27</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>0.07</td>
</tr>
<tr>
<td>LOI</td>
<td>14.25</td>
</tr>
<tr>
<td>Total</td>
<td>100.55</td>
</tr>
</tbody>
</table>

**Table 5.2 Atomic ratios of major cations with Si for the BB clay calculated from X-ray florescence (XRF) analysis.**

<table>
<thead>
<tr>
<th>Atomic ratio</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al/Si</td>
<td>0.57</td>
</tr>
<tr>
<td>Fe/Si</td>
<td>0.13</td>
</tr>
<tr>
<td>K/Si</td>
<td>0.06</td>
</tr>
<tr>
<td>Mg/Si</td>
<td>0.03</td>
</tr>
</tbody>
</table>

The air-dried and ethylene glycol solvated oriented specimens after Mg saturation were scanned from 3 to 30° 20 and 3 to 15° 20, respectively (Brindley and Brown, 1980). The Greene-Kelly test was used to determine the origin of charge in smectite in the sample
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(Greene-Kelly, 1952). The oriented slides were scanned from 3 to 15° $2\theta$ after Li-saturation and heating at 300°C and for the same sample after glycerol solvation.

The quantitative analysis was performed on random powder XRD data of Ca-saturated sample using a combination of in-house developed XRD calibrations, TGA and XRF analyses; and Rietveld analysis using SIROQUANT (Taylor, 1991). The results were normalised to 100% as the analysis did not include the estimates of amorphous phases in the sample. The quantitative mineralogy results for the sample from two analyses matched very closely.

5.2.5 Transmission electron microscopic analysis

Crystal morphology of the original and the residual clay samples (i.e. following dissolution experiments) was determined by a Philips CM12 transmission electron microscope (TEM), operated at 120 kV. The specimens for TEM examination were prepared by dispersing a small amount of clay sample in E-pure® water using ultrasonication. A drop of the suspended sample was placed on a carbon-coated TEM Cu grid and was dried under light before the examination.

5.2.6 Flow-through reactor dissolution experiments

The dissolution experiments were carried out in flow-through reactors consisting of three chambers: the input solution of a fixed composition entered the reactor through the bottom chamber (Chapter 3). A fixed mineral mass of 0.1 g was placed into the middle chamber (the reaction chamber), which was separated from the bottom chamber by a fine nylon mesh and a filtration membrane (0.22 µm) assembly. The reaction chamber was also separated from the upper chamber by a filtration membrane (0.22 µm). An eight channel Gilson® peristaltic pump was used to deliver the input solution at a constant flow rate of 0.02 mL min$^{-1}$ in each experiment. The experiments were conducted at pH 1–4 at 25°C; the 35°C and 45°C
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experiments were conducted only at pH 1 and 4. The flow-through reactors were kept immersed in thermostatic water baths to maintain a constant temperature during the dissolution experiments. Input solution of two ionic strengths (0.01 or 0.25 M; NaCl) was used in the study and the pH of these solutions was adjusted between 1 and 4 using H$_2$SO$_4$. Each experiment was conducted until a steady state was reached; the steady state was confirmed when the concentration of Si and Al varied < 6% in six consecutive output samples (Chapters 3 and 4) (Bibi et al., 2011a; Rozalen et al., 2008).

5.2.7 Output solution analyses

An output solution sample was collected after every 24 hour and sample pH was measured immediately, using a pre-calibrated combined pH electrode (PHM 210 Radiometer pH meter, accuracy ± 0.02 pH units). Three replicates of a sample were analysed colorimetrically for Si and Al concentrations using molybdate blue (Koroleff, 1976) and catechol violet (Dougan and Wilson, 1974) methods, respectively. The output sample was also analysed for K, Mg and Fe using inductively coupled plasma atomic emission spectrometer (ICP-AES, Varian® Vista AX). Instrument detection limits were 0.005, 0.006 and 0.005 mg/L for K, Mg and Fe, respectively.

5.2.8 Geochemical speciation modelling

Geochemical speciation calculations were performed on the analytical results of steady state samples for each experiment using the geochemical speciation program PHREEQC (version 2.17) (Parkhurst and Appelo, 1999). The saturation state of the steady state solutions are presented in terms of Gibbs free energy of reaction, $\Delta G_r$, which were calculated as follows (Nagy, 1995):
\[ \Delta G_r = -RT \ln \left( \frac{IAP}{K_{eq}} \right) \]  

(1)

where \( IAP \) and \( K_{eq} \) are the ion activity product and the equilibrium constant, respectively, \( R \) is the gas constant, and \( T \) is the absolute temperature.

### 5.2.9 Clay dissolution rates

The dissolution reaction of the clay sample exposed to acidic solution (\( \text{H}_2\text{SO}_4 \)) can be expressed as:

\[
\text{Clay (smectite, illite, kaolinite, etc.)} + \text{H}_2\text{SO}_4 = [\text{Al}] + [\text{Si}] + [\text{K}] + [\text{Fe}] + [\text{Mg}] + \ldots \]

(2)

The dissolved Al, Si or Fe concentration \( C_j \) (mol/L) at the steady state in each experiment, initial sample mass, \( M \) (g), specific surface area, \( S \) (m\(^2\)/g) and fluid flow rate, \( F \) (L/s) were used to measure the dissolution rate, \( R_j \) (mol m\(^{-2}\) s\(^{-1}\)) of the clay in each experiment using the expression:

\[
R_j = \frac{F}{SM} (C_j)
\]

(3)

### 5.3 RESULTS

The XRD analysis showed the presence of smectite, illite and kaolinite (Fig. 5.1) (Moore and Reynolds, 1989). The XRD pattern of the Li-saturated and 300°C heated specimen showed smectite reflection move to 10 Å and on glycerol solvation a large part of the peak shifted to ~18 Å (Fig. 5.1). These results show that the charge in smectite has originated in both tetrahedral and octahedral sheets and a greater proportion of charge appeared to have originated in the tetrahedral sheet. The results are consistent with various studies on soil smectites including samples from Australia (Singh and Heffernan, 2002).
The quantitative analyses of the random powder XRD pattern of Ca-saturated sample showed that the sample was dominated by smectite (40 %) with nearly equal amounts of kaolinite (26 %) and illite (27 %). A considerable amount of quartz (6 %) was also present in the sample along with minor amounts of anatase (1 %). The chemical analyses of the Na-saturated clay (see Table 5.1) showed a Si/Al+Mg+Fe atom ratio of 1.48 which is also consistent with the presence of a mixture of 1:1 and dioctahedral 2:1 phyllosilicates as this ratio is equal to 1 for a 1:1 layer, and equal to 2 for a 2:1 dioctahedral layer (Moussa et al., 1992). The TEM examination of the clay sample showed the abundance of platy smectite particles of variable sizes (Fig. 5.2). Large euhedral crystals of kaolinite and illite were also observed in the micrographs.

**Fig. 5.1 X-ray diffraction patterns of the oriented specimens of Bottle Bend clay sample (< 2 µm). Mg air-dried (Mg-AD); Mg ethylene glycolated (Mg-EG); K heated at 550°C (K 550°C); Li heated at 300°C (Li 300°C); Li heated at 300°C and glycerol solvated (Li-300-Gly).**
Fig. 5.2 Transmission electron microscopic image of a pre-treated Bottle Bend clay sample showing three different mineral (particle) types. Smectite particles – irregular to a globular shape, thin layered structure; illite particles – platy shape; kaolinite particles – hexagonal shape.

The release rate of Si in all experiments showed a distinct variation from a rapid release at the onset of experiments to a significantly lower release at the steady state (Appendix 3). The initial and steady state concentrations of Si increased with a decreasing pH and increasing temperature. The highest initial Si release (613 µM) was obtained at pH 1 and 45°C, nearly
three times higher than the value observed at the same pH at 25°C (230 µM). The steady state Si concentrations were slightly higher for the lower ionic strength solution than the higher ionic strength solution under similar pH and temperature systems (Table 5.3, on next page).

Aluminium concentrations also tended to decrease with elapsed time except in the experiments conducted at the lower ionic strength of solutions at pH 3 and 4 at 25°C, and at pH 4 at higher (35°C and 45°C) temperatures (Appendix 3). Aluminium concentrations in the lower ionic strength experiment (pH 3 and 25°C) increased from a low value of 1.5 µM at the onset of experiment to 3.2 µM at the steady state (Appendix 3). Slow Al release (< 1µM) continued throughout the duration of experiments at pH 4 at the lower ionic strength at all temperatures (data not shown). Similar to Si, the highest initial and steady state Al release was observed at the lowest pH (pH 1) and the highest temperature (45°C).

The release rate of Fe at the higher ionic strength (at all temperatures) followed the same trend as Si, with higher release rates at the initial stage of the experiments and slower rates at the steady state (Appendix 3). The experiments at pH 3 and 4 at the lower ionic strength demonstrated a slow Fe release over the duration of experiment. The initial and steady state Fe concentrations increased with increasing temperature.

Potassium (K) release in all experiments followed a similar trend to the other cations, with a rapid initial release and a relatively slower release at the steady state. Similar K release was obtained at pH 1 for the two ionic strengths, whereas a higher K release was observed in the higher ionic strength solutions at pH 2–4 than the lower ionic strength (data not shown). There was no trend in the steady state K concentrations with pH at the higher ionic strength (at 25°C) (Table 5.3). At the lower ionic strength the steady state K concentrations decreased with increasing pH (Table 5.3).
### Table 5.3 Summary of experimental conditions, steady state concentrations (µmol/L) of Si, Al, K, Fe and Mg and elemental ratios calculated from the dissolution experiments at pH 1–4, at \( I = 0.25 \) M and 0.01 M at 25–45°C.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Final Mass (g)</th>
<th>Steady state duration (h)</th>
<th>Flow rate (mL min(^{-1}))</th>
<th>Output solution</th>
<th>Log rate(^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>pH</td>
<td>Si</td>
<td>Al</td>
<td>K</td>
<td>Fe</td>
</tr>
<tr>
<td>(25^\circ\mathrm{C})</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BB-0.25-1</td>
<td>0.0699</td>
<td>700</td>
<td>0.022</td>
<td>1.11</td>
<td>41.47</td>
</tr>
<tr>
<td>BB-0.25-2</td>
<td>0.0680</td>
<td>1270</td>
<td>0.0237</td>
<td>2.08</td>
<td>17.44</td>
</tr>
<tr>
<td>BB-0.25-3</td>
<td>0.0962</td>
<td>2015</td>
<td>0.0246</td>
<td>3.00</td>
<td>4.15</td>
</tr>
<tr>
<td>BB-0.25-4</td>
<td>0.0689</td>
<td>1700</td>
<td>0.0217</td>
<td>4.01</td>
<td>2.20</td>
</tr>
<tr>
<td>BB-0.01-1</td>
<td>0.0758</td>
<td>700</td>
<td>0.0222</td>
<td>1.13</td>
<td>44.53</td>
</tr>
<tr>
<td>BB-0.01-2</td>
<td>0.0877</td>
<td>1100</td>
<td>0.0236</td>
<td>2.05</td>
<td>26.41</td>
</tr>
<tr>
<td>BB-0.01-3</td>
<td>0.0850</td>
<td>1300</td>
<td>0.0218</td>
<td>3.05</td>
<td>6.23</td>
</tr>
<tr>
<td>BB-0.01-4</td>
<td>0.0880</td>
<td>1500</td>
<td>0.0238</td>
<td>4.05</td>
<td>2.20</td>
</tr>
<tr>
<td>(35^\circ\mathrm{C})</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BB-0.25-1</td>
<td>0.0660</td>
<td>600</td>
<td>0.0222</td>
<td>1.09</td>
<td>111.79</td>
</tr>
<tr>
<td>BB-0.25-4</td>
<td>0.0800</td>
<td>1100</td>
<td>0.0211</td>
<td>4.00</td>
<td>3.49</td>
</tr>
<tr>
<td>BB-0.01-1</td>
<td>0.0655</td>
<td>700</td>
<td>0.0220</td>
<td>1.13</td>
<td>146.14</td>
</tr>
<tr>
<td>BB-0.01-4</td>
<td>0.0958</td>
<td>900</td>
<td>0.0254</td>
<td>4.05</td>
<td>5.11</td>
</tr>
<tr>
<td>(45^\circ\mathrm{C})</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BB-0.25-1</td>
<td>0.0318</td>
<td>570</td>
<td>0.0234</td>
<td>1.09</td>
<td>274.69</td>
</tr>
<tr>
<td>BB-0.25-4</td>
<td>0.0664</td>
<td>1350</td>
<td>0.0220</td>
<td>3.99</td>
<td>5.63</td>
</tr>
<tr>
<td>BB-0.01-1</td>
<td>0.0188</td>
<td>670</td>
<td>0.0238</td>
<td>1.12</td>
<td>230.23</td>
</tr>
<tr>
<td>BB-0.01-4</td>
<td>0.0892</td>
<td>1330</td>
<td>0.0260</td>
<td>4.07</td>
<td>4.66</td>
</tr>
</tbody>
</table>

\(^a\)Log rate Si, Al and Fe (mol m\(^{-2}\)s\(^{-1}\)) are the dissolution rates calculated from the steady state release rates of Si, Al and Fe, respectively.

Note: In the first column, BB represents sample name (Bottle Bend clay), second term (0.25 M or 0.01 M) is the ionic strength and third term is the experimental pH.
The stoichiometry of clay dissolution was assessed by comparing the elemental ratios in the output solutions to the elemental ratios in the original clay sample. Figs. 5.3–5.6 show variation in elemental ratios (Al/Si, K/Si, Fe/Si and Mg/Si) over the experimental period; the black line running parallel to the x-axis in the figures corresponds to the elemental ratios in the original clay sample. The Al/Si ratio of the output solution decreased with time until the steady state was achieved in all experiments at the higher ionic strength (Fig. 5.3). The Al/Si ratio of the output solution in the lower ionic strength solutions decreased with time only at pH 1, whereas in experiments at pH 2–4, the Al/Si ratio increased from a slow initial value and became stoichiometric at the steady state at pH 2 and 3 and was well below stoichiometric value at pH 4. Steady state Al/Si ratios at the higher ionic strength were close to the Al/Si ratio of the original clay sample; the steady state Al/Si ratio at pH 1 for the lower ionic strength system was also close to stoichiometric ratio (Fig. 5.3a). The Al/Si ratio in lower ionic strength systems at pH 2 and 3 was initially lower than the ratio of the original clay sample, however, it increased with time and attained a value close to the Al/Si ratio of the original clay sample at the steady state (Fig. 5.3c,e). The lower ionic strength experiments at pH 4 showed an Al/Si ratio of the output solution much lower than the Al/Si ratio of the original clay sample (0.57) at all temperatures (data not shown).

The K/Si ratio of the output solutions was greater than the original clay in all the experiments except for the lower ionic strength experiments at pH 1 and at 35°C and 45°C, which showed a stoichiometric K/Si ratio in the steady state solutions (Fig. 5.4). The difference in the K/Si ratios of the steady state solutions and the original sample was greater at the higher ionic strength than at the lower ionic strength (Fig. 5.4).
Fig. 5.3 Change in Al/Si ratio with time in the experiments conducted at the two ionic strengths (0.25 and 0.01 M) and pH 1–4. (a,c,e,g) 25°C; (b,d) 35°C; (f,h) 45°C. Al/Si ratio in experiments conducted at pH 4 at I = 0.01 M at all temperatures are not shown because of a very low Al release (< 1 µM) throughout the experimental duration.
Fig. 5.4 Variation in K/Si ratio with time in the experiments conducted at the two ionic strengths (0.25 and 0.01 M) and pH 1–4. (a,c,e,g) 25°C; (b,d) 35°C; (f,h) 45°C.
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The Fe/Si ratio of the steady state solution was more than Fe/Si ratio of the original clay in the experiments at pH \( \leq 3 \) at both ionic strengths, with the Fe/Si ratio reaching close to the stoichiometric ratio in the experiments at pH 1 at the highest temperature (Fig. 5.5f). The experiments at pH 4 at all temperatures showed Fe/Si ratio of the steady state solution less than the Fe/Si ratio of the original clay except for the lower ionic strength experiment at 45°C (Fig. 5.5h).

The Mg/Si ratio in the steady state solution was equal to the original clay at pH 1 for both ionic strengths at all three temperatures (Table 5.3, Fig. 5.6a,b,f). The Mg/Si ratio of the steady state solution was also close to the Mg/Si ratio in the original sample at pH 3. However, the Mg/Si ratio of the steady state solution was greater than the original sample at pH 2 (Table 5.3, Fig. 5.6c). Similarly at pH 4, the Mg/Si ratio of the steady state solution was greater than the original sample in 25°C experiments at both ionic strengths, and at the lower ionic strength in 35°C experiments (Fig. 5.6d,g). The 45°C experiments at pH 4 showed the steady state Mg/Si ratio close to the original sample (Fig. 5.6h).

The clay dissolution rates, \( R_{Si} \), \( R_{Al} \) and \( R_{Fe} \) in each experiment were calculated using equation 3 and the log-normalised dissolution rates are presented in Table 5.3. The dissolution rates derived from steady state Si concentrations (\( R_{Si} \)) decreased with increasing pH and decreasing temperature (Table 5.3; Fig. 5.7). The \( R_{Si} \) values were slightly higher at the lower ionic strength than at the higher ionic strength. The reaction order (\( n \)) obtained from the linear regression of the plot of \( R_{Si} \) versus pH from 25°C experiments at both ionic strengths was 0.45. Similar to \( R_{Si} \), the \( R_{Al} \) values also decreased with an increasing pH and a decreasing temperature.
Fig. 5.5 Change in Fe/Si ratio with time in the experiments conducted at the two ionic strengths (0.25 and 0.01 M) and pH 1–4. (a,c,e,g) 25°C; (b,d) 35°C; (f,h) 45°C.
The $R_{AI}$ values for the two ionic strength systems were similar except for pH 4 where a low Al concentration in the lower ionic strength solution throughout the experiments resulted in much lower $R_{AI}$ than the higher ionic strength solution (Table 5.3).

Fig. 5.6 Change in Mg/Si ratio with time in the experiments conducted at the two ionic strengths (0.25 and 0.01 M) and pH 1–4. (a,c,e,g) 25°C; (b,d) 35°C; (f,h) 45°C.
Fig. 5.7 Arrhenius plot illustrating the variation in steady state clay dissolution rate, $\log R_{Si}$ (mol m$^{-2}$s$^{-1}$) against 1000 times reciprocal temperature, $T$ (K$^{-1}$) for the experiments performed at pH 1 and 4. Simple linear regression equations for the plotted data (log rate vs. $1000/T$ (K$^{-1}$)) is also presented: $\log R_{Si} = -3.996x + 1.472$ ($R^2 = 1$), and $\log R_{Si} = -1.959x - 6.656$ ($R^2 = 0.99$) at pH 1 and 4, respectively.

Speciation calculations of the steady state solutions predicted undersaturation with respect to the phyllosilicate minerals-kaolinite, illite and smectite (Table 5.4). The steady state solutions were also undersaturated with respect to secondary Fe minerals, such as akaganéite, goethite and hematite at pH 1 to 3; however, the experiments at pH 4 were close to saturation with respect to goethite and hematite ($\Delta G_r = -1.67$ and -0.46 for goethite and hematite, respectively, at $I = 0.01$ M and 45°C). The steady state solutions were close to saturation with respect to gibbsite and quartz at pH 4 and 1, respectively ($\Delta G_{gibbsite} = -4.41$ to $-2.47$ at pH 4, $\Delta G_{quartz} = -0.94$ to $-0.19$ at pH 1). The value of $\Delta G_r$ showed an increasing trend with pH and a decreasing trend with the experimental temperature. In the case of quartz and SiO$_2$, the value of $\Delta G_r$ decreased with increasing pH (Table 5.4).
### Table 5.4 Saturation state of the steady state solutions at $I = 0.25$ M and $0.01$ M and at pH 1–4 at a solution temperature range of 25–45°C.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Gibbsite</th>
<th>Goethite</th>
<th>Hematite</th>
<th>Akaganéite</th>
<th>Kaolinite</th>
<th>Illite</th>
<th>K-mica</th>
<th>Smectite</th>
<th>Quartz</th>
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<td></td>
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<td>-2.66</td>
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<td>-38.78</td>
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<td>-4.04</td>
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<tr>
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<td>-14.14</td>
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<td>-51.77</td>
<td>-53.14</td>
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<td>-20.67</td>
<td>-2.68</td>
<td>-4.23</td>
<td>-19.85</td>
</tr>
</tbody>
</table>

Note: In the first column, BB represents sample name (Bottle Bend clay), second term (0.25 M or 0.01 M) is the ionic strength and third term is the experimental pH.
5.4 DISCUSSION

5.4.1 Initial release of Si, Al, K, Fe and Mg

A relatively fast dissolution of minerals during the early stages of clay dissolution experiments as observed in this study possibly resulted from several processes including (i) rapid dissolution of ultra-fine particles present in the mineral sample; (ii) enhanced availability of highly reactive sites on the mineral surfaces created during sample pre-treatment procedures; and (iii) dissolution of cations from highly strained areas on large particles or defects (Stillings and Brantley, 1995). The wide range in the particle size of minerals constituting the clay sample and the presence of ultra-fine particles was also evident in the TEM images of the clay (Fig. 5.2). Previous laboratory studies of pure phyllosilicate dissolution in acidic solutions suggest that aqueous Al concentrations exceed Si concentrations at the onset of experiments due to relative ease of breaking of Al–O bonds compared to Si–O bonds (Chapter 3) (Bibi et al., 2011a; Kohler et al., 2003). This behaviour of phyllosilicate dissolution in acidic solutions can be explained by taking into account the dissolution rates of quartz and Al (oxy)hydroxide. The dissolution rates of quartz are slower compared to Al (oxy)hydroxide at acidic pH (Oelkers et al., 2008). In the current study, Al was also released at a higher rate compared to Si at the initial stage of the experiments at pH 1–4 in the higher ionic strength solutions and at pH 1 in the lower ionic strength solutions (Fig. 5.3). The preferential leaching of cations from phyllosilicate dissolution has also been linked to the valence of the cations. Based on single oxide/hydroxide dissolution studies, there is a clear evidence which suggests that the dissolution of single (hydr)oxides proceeds via metal for proton exchange reactions, and the number of protons required for these reactions equals the valence of the cation. A comparison of dissolution rates of various (hydr)oxides at
pH 2 have suggested that SiO$_2$ which contains tetravalent Si dissolved at a slower rate compared to the single (hydr)oxides containing divalent or trivalent cations (Oelkers, 2001).

A reverse trend in the initial concentrations of Al and Si in the effluent solution was observed at pH 2–4 at the lower ionic strength. A close examination of the initial Al/Si ratios reveals that the Al/Si ratio decreased with an increasing pH of the input solution (Fig. 5.3). Mineral dissolution tended to proceed at the highest rate during the initial 3–4 days of the experiments at both ionic strengths as indicated by the higher dissolved concentrations of other cations, particularly Si. This suggests that the release rate of Al should also be similar to the release rates of other cations. However, the results showed a slow initial Al release from the lower ionic strength experiments at pH 2–4 which could be attributed to the adsorption of Al on mineral surfaces under these experimental conditions. In a recent study Bibi et al. (2010) (Chapter 4) observed a slower Al release rate than that of Si for montmorillonite dissolution at 0.01 M ionic strength and pH 2–4. In the present study, smectite is the predominant mineral and the clay sample showed similar dissolution behaviour, with minimal Al release at the onset of experiments in the lower ionic strength solutions. In a batch experiment study conducted on polymineralic samples including illite, kaolinite, smectite and quartz, a greater Si release compared to Al was observed at pH 3 and 5 in H$_2$SO$_4$ solutions (Shaw and Hendry, 2009). Although the clay samples used by these authors contained considerable amounts of quartz, the difference in initial Al and Si concentrations was attributed to reduced Al release from phyllosilicate dissolution (not due to the enhanced Si release from quartz dissolution). In several other studies, it was reported that even in extremely acidic solutions (pH ~3.5), quartz remained relatively unaffected during acidic dissolution, and the Si released during these
experiments was mainly resulting from phyllosilicates dissolution (Belver et al., 2002; Komadel, 2003; Madejova et al., 1998).

Metz et al. (2005a) investigated the dissolution of smectite and suggested that Si concentrations initially exceeded Al concentrations due to the fast dissolution of amorphous silica particles present as an impurity in the mineral sample. Rozalen et al. (2009b) also observed high initial Si and low Al concentrations from acidic dissolution of montmorillonite sample and attributed a greater initial Si release to the dissolution of amorphous Si phase present as an impurity in the montmorillonite sample. However, in the current work two different trends were observed in the initial Al and Si concentrations at the higher and lower ionic strengths, as described earlier.

Although the clay sample used in this study contained about 5% quartz, based on the dissolution kinetics of quartz in acidic solutions reported in previous studies, we assume that quartz remained comparatively intact during the dissolution experiments, with Si release predominantly resulting from phyllosilicate dissolution (Belver et al., 2002; Komadel, 2003). Moreover, a linear relationship between Si release and \([\text{H}^+]\) also suggests that the Si release rates are not influenced by the presence of quartz in the sample; the dissolution kinetics of quartz shows very little dependence on \(\text{H}^+\) concentration in the acidic pH range (Brady and Walther, 1990; Zysset and Schindler, 1996). In various batch reactor dissolution experiments conducted on smectite in highly acidic solutions (pH \(\leq 1.0\)), it was observed that following the exchange of \(\text{H}^+\) with the interlayer cations, \(\text{H}^+\) was replaced by the polyvalent ions especially \(\text{Al}^{3+}\) released by the mineral dissolution (Janek and Komadel, 1993). The Al/Si ratio in the lower ionic strength experiments at pH 2–3 gradually increased from an initial low release to
a maximum value in 600 to 800 hour and became stable at the steady state (Fig. 5.3b,c). The slow Al release at the onset of experiments at pH 2–3 may have resulted from the exchange of dissolved Al$^{3+}$ for H$^+$ in the interlayer sites of 2:1 phyllosilicate minerals. Initially, the diffusion controlled exchange reactions take place at the greatest speed, evident from the fast release of interlayer cations into the solution and possibly a fast exchange of dissolved Al from the solution into the interlayer at the lower ionic strength. As the rate of diffusion controlled exchange reactions becomes slower with time because of a reduced flux of ions with an increase in the length of the diffusion path (Kalinowski and Schweda, 2007), the concentration of Al in the output solution increases and attains a maximum value before becoming stable at the steady state (Fig. 5.3 and Appendix 3). The slower Al release throughout the experimental duration at pH 4 in the lower ionic strength solutions is more likely due to the adsorption of dissolved Al on the mineral surfaces as the speciation calculations indicate under-saturation with respect to gibbsite under all conditions (see Table 5.4).

The release rates of cations were influenced by their position in the mineral structure which was shown clearly by the initial rapid release of K (by ion-exchange reactions) over Si in all the experiments (Fig. 5.4). The release rate of K was also affected by the ionic strength of the input solution as the rates were higher in the higher ionic strength solutions than in the lower ionic strength solutions, mainly at pH 2–4. A similar effect of ionic strength on the release rate of interlayer cation was observed in the earlier work conducted on illite dissolution (Chapter 3) (Bibi et al., 2011a). It was suggested that the release rate of K at pH 2–4 was mainly controlled by Na for K exchange; however, H$^+$ for K exchange resulted in similar release rates at pH 1 at both ionic strengths. The results from this study showed a small
difference in the K release rates at pH 1 at the two ionic strengths at 25°C. However, at higher (35°C and 45°C) temperatures the difference in the release rates was more predominant at pH 1 (Fig. 5.4). The results also suggest that the difference in release rates of K at the two ionic strengths increased with increasing pH; the greatest difference was observed at pH 4 at all temperatures. This suggests that the high concentration of Na in the higher ionic strength solutions played a pivotal role in a greater release of K compared to the lower ionic strength solutions.

5.4.2 Stoichiometry of clay dissolution at steady state

The experiments at pH ≤ 3 attained the values of Al/Si ratio close to the Al/Si ratio of the original clay (Fig. 5.3). Similar results were reported for pure mineral phyllosilicate dissolution studies in highly acidic solutions (pH 1–3) (Rozalen et al., 2009b). However, in slightly acidic-neutral solutions (pH 4–6), a decrease in the Al/Si ratio due to possible adsorption of dissolved Al on the montmorillonite surface or the precipitation of Al minerals was reported (Rozalen et al., 2009b). These authors reported a nearly stoichiometric Al/Si ratio in all the experiments at acidic to neutral pH at 70°C. In the current study, the experiments performed at pH 4 in the lower ionic strength solution at all temperatures showed an Al/Si ratio significantly smaller than that in the original clay. However, no such effect was observed at the higher ionic strength at all temperatures and the corresponding pH (Table 5.3). Zysset and Schindler (1996) conducted dissolution experiments on K-saturated montmorillonite in 0.03, 0.1 and 1 M KCl solutions. A comparison of $R_{Si}$ and $R_{Al}$ at the two lower ionic strengths (0.1 and 0.03 M KCl) revealed that $R_{Si}$ values were similar at both ionic strengths, whereas $R_{Al}$ was significantly higher in 0.10 M KCl than in 0.03 M KCl (Zysset and Schindler, 1996); the difference between the two ionic strengths was more evident with an increase in solution pH. The $R_{Si}$ values in the current study were also not influenced by the
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ionic strength of the solution, whereas a difference in $R_{Al}$ values at the two ionic strengths ($I = 0.01$ and $0.25$ M) was observed at pH 4. Similar results have also been reported for illite dissolution in input solutions of two different ionic strengths in the previous work (Bibi et al., 2011a) (Chapter 3).

The $K/Si$ ratio of the steady state solutions showed a preferential release of $K$ over $Si$ in all the experiments. The stoichiometry of $K$ release at the two ionic strengths ($I = 0.01$ and $0.25$ M) in this study followed the trend similar to pure illite dissolution as described previously (Chapter 3) (Bibi et al., 2011a). An increase in the ionic strength of the input solution resulted in an enhanced $K$ release, particularly at pH 2–4 in the 25°C experiments. The ionic strength had a pronounced effect on the released $K$ concentrations even at pH 1 at the higher temperatures (35°C and 45°C) (Fig. 5.4b,f).

Lower $Fe/Si$ ratios than the original clay were observed in most of pH 4 experiments; the speciation calculations of the steady state solutions in these experiments showed that the solutions were close to saturation with respect to secondary Fe minerals, such as hematite and goethite (see Table 5.4). A stoichiometric release of $Mg$ was observed in most of the experiments as indicated by the $Mg/Si$ ratio of the steady state solutions that was similar to the original clay sample (Table 5.3). The exceptions were the experiments at pH 2 and 4 at both ionic strengths at 25°C, and at pH 4 and the lower ionic strength system at 35°C where $Mg/Si$ ratio was higher than the original clay, which could be due to faster dissolution of octahedral cations in clay. Several previous studies on phyllosilicate dissolution have reported a stoichiometric or preferential $Mg$ release in the acidic pH range (Golubev et al., 2006; Rozalen et al., 2009b). Rozalen et al. (2008) ascribed the preferential $Mg$ release from
montmorillonite dissolution to the ion-exchange reactions involved in a rapid Mg release. A preferential Mg release observed in some experiments in this study could also be attributed to the rapid exchange of Mg from octahedral sheet for cations in the solution (Na$^+$ or H$^+$).

### 5.4.3 Effect of pH on clay dissolution rate

The dissolution rates of the clay sample calculated from the steady state release rates of Si, Al, and Fe showed a decreasing trend with an increasing pH (from 1 to 4) (Table 5.3). A similar effect of pH was observed for pure phase phyllosilicate dissolution in many previous investigations (Amram and Ganor, 2005; Bibi et al., 2011a; Cama et al., 2002; Rozalen et al., 2009b). A steady increase in the dissolution rates of three polymineralic natural clay samples with a decrease in pH (from 5 to 1) was reported in batch dissolution experiments (Shaw and Hendry, 2009). The dissolution of minerals occurs at the mineral surface and is controlled by proton adsorption on the mineral surface under acidic conditions. The fast proton adsorption step is followed by a slow hydrolysis step which results in the release of cations into the solution (Cama et al., 2002). The dissolution rates of minerals are affected by solution pH in two ways. The pH of solution affects the dissolution rate by its direct effect on the concentration of protons adsorbing on the mineral surface. The direct effect of pH on dissolution rate also helps in understanding the reaction mechanism. The indirect effect of pH on dissolution rate is through its effect on the degree of saturation of the solution which in this case was determined by calculating the value of $\Delta G_r$. The effect of degree of saturation on dissolution rate is minimised by conducting experiments under ‘far from equilibrium’ dissolution plateau region (Amram and Ganor, 2005).

Under far from equilibrium conditions, the pH dependence of the dissolution rate of clay can be described by the rate law (Zysset and Schindler, 1996):
where $R$ is the clay dissolution rate (mol m$^{-2}$s$^{-1}$), $k$ is the reaction constant, $[H^+]$ is the activity of protons, and $n$ is the reaction order; plotting log $R$ vs. pH allows the $n$ to be determined.

The reaction orders obtained from the linear regression of the plot of log-normalised dissolution rates vs. pH (Appendix 3) showed that $R_{Al}$ ($n = 0.42$) was slightly less affected by each unit change in pH compared to $R_{Si}$ ($n = 0.45$) and $R_{Fe}$ ($n = 0.46$). Kalinowski and Schweda (1996) obtained $H^+$ dependent fractional reaction order ranging between 0.35 and 0.61 for biotite and phlogopite dissolution in the pH range of 1–4 and at room temperature. Rozalen et al. (2008) calculated reaction order of 0.40 for montmorillonite dissolution under acidic conditions (pH < 4.5) which closely matches the reaction order obtained for clay dissolution in this study.

5.4.4 Effect of temperature on clay dissolution rate

At constant pH, the clay dissolution rates increased with increasing temperature (Table 5.3). Arrhenius equation was used to describe the temperature dependence of reaction rates at constant pH.

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

where $A$ (mol cm$^{-2}$s$^{-1}$) is the pre-exponential factor also known as the frequency factor, $E_{app}$ (kcal mol$^{-1}$) is the apparent activation energy, $R$ and $T$ are the gas constant and absolute temperature, respectively. To obtain $E_{app}$ value, at pH 1 and 4 the experiments were performed at 25°, 35° and 45°C while all the other variables (i.e. pH, ionic strength) were kept constant in these experiments. By plotting log dissolution rates ($R_{Si}$) from these experiments against $1/T$, $E_{app}$ values at pH 1 and 4 were calculated using equation 5 from a
least-squares estimate of the slope of the plots in Fig. 5.7. Apparent activation energy values
of 18.3 kcal mol\(^{-1}\) and 9.0 kcal mol\(^{-1}\) were obtained at pH 1 and 4, respectively. The
dependence of \(E_{\text{app}}\) of clay dissolution on pH has also been reported in previous pure mineral
dissolution studies (Kohler et al., 2003; Lawson et al., 2007). Carroll and Walther (1990)
reported the dependence of \(E_{\text{app}}\) on solution pH in kaolinite dissolution experiments. Cama et
al. (2002) developed a model to determine the combined effect of pH and temperature on
kaolinite dissolution. The assumptions of this model were (i) proton-promoted dissolution of
kaolinite consists of fast adsorption of proton followed by slow hydrolysis step, and (ii)
proton adsorption on a surface site can be explained by Langmuir adsorption isotherm. The
formulation of the Langmuir adsorption isotherm includes an energy term which explains the
variation of proton surface coverage with temperature. Based on this model, Cama et al.
(2002) suggested that the temperature dependence of the \(E_{\text{app}}\) observed by Carroll and
Walther (1990) was an artifact of the difference in the pH dependence of the proton surface
coverage at different temperatures. Although many previous studies have determined the
effect of pH and temperature on phyllosilicates dissolution, the results from the current work
are very similar to the values reported by Rozalen et al. (2009b), who determined the
dissolution rates of montmorillonite at 25°C, 50°C and 70°C, using flow-through reactors.
The authors calculated an \(E_{\text{app}}\) value of 19.3 kcal mol\(^{-1}\) at pH 1 and 5.3 kcal mol\(^{-1}\) for the pH
range 4–7. They suggested that the rate constants and reaction orders increased with
temperature and the increase was higher for proton and hydroxyl promoted dissolution than
for \(\text{H}_2\text{O}\) assisted dissolution. As the increase in temperature from 25°C to 70°C has a very
small impact on the surface charge of montmorillonite, the increase in the value of reaction
order with temperature in the acidic and alkaline pH range cannot be solely attributed to the
surface charge effects (Rozalen et al., 2009a; Rozalen et al., 2009b). These authors concluded
that the hydrolysis of metal-oxygen bonds controlled the overall dissolution reaction and metal-oxygen bonds became increasingly sensitive to temperature change under acidic and basic pH conditions.

### 5.4.5 Dissolution rates of individual minerals

The first step involved in the calculation of structural formulae was the partitioning of the elemental oxide constituents to each mineral (except smectite), according to their percentage content in the sample and the chemical composition of idealised quartz, kaolinite and Fithian illite samples (Appendix 3) (Hover and Mowatt, 1966; Mermut and Cano, 2001). Soil kaolinites are known to contain structural iron in Fe$^{3+}$ form; 2.5% Fe$_2$O$_3$ was allocated to octahedral sheet of kaolinite based on the chemical composition reported for soil kaolinites in Australia (Singh and Gilkes, 1992). The sum of the elemental oxides allocated to quartz, kaolinite and illite was subtracted from the original elemental oxide composition of the clay sample and the difference was normalised to 100%, constituting the elemental oxide composition of smectite (Appendix 3). The calculation of structural formula was based on 44 ideal total negative charges, and the formula of smectite was calculated following the method reported by Cicel and Komadel (1994) (Appendix 3).

The dissolution reactions of kaolinite, illite and smectite in acidic system (H$_2$SO$_4$) can be expressed by equations 6, 7 and 8:

**Equation 6**

$$(\text{Al}_{1.92}\text{Fe}_{0.08})[\text{Si}_2]_\text{O}_5(\text{OH})_4 + 6\text{H}^+ \rightarrow 1.92\text{Al}^{3+} + 0.08\text{Fe}^{3+} + 2\text{H}_4\text{SiO}_4 + \text{H}_2\text{O} \quad (6)$$

**Equation 7**

$$\text{K}_{1.20}\text{Na}_{0.05} (\text{Al}_{2.82}\text{Fe}_{0.46}\text{Fe}_{0.19}\text{Mg}_{0.56}) [\text{Si}_{6.78}\text{Al}_{1.22}]\text{O}_{20}(\text{OH})_4 \rightarrow 15.88\text{H}^+ + 3.12\text{H}_2\text{O} \rightarrow 1.20\text{K}^+ + 0.05\text{Na}^+ + 4.04\text{Al}^{3+} + 0.46\text{Fe}^{3+} + 0.19\text{Fe}^{2+} + 0.56\text{Mg}^{2+} + 6.78\text{H}_4\text{SiO}_4 \quad (7)$$

**Equation 8**

$$\text{K}_{0.18}\text{Na}_{0.52} (\text{Al}_{2.28}\text{Fe}_{3.16}^{3+}\text{Fe}_{0.23}^{2+}\text{Mg}_{0.19}) [\text{Si}_{6.96}\text{Al}_{1.04}]\text{O}_{20}(\text{OH})_4 \rightarrow 16.16\text{H}^+ + 3.84\text{H}_2\text{O} \rightarrow 0.18\text{K}^+ + 0.52\text{Na}^+ + 3.32\text{Al}^{3+} + 1.56\text{Fe}^{3+} + 0.23\text{Fe}^{2+} + 0.19\text{Mg}^{2+} + 6.96\text{H}_4\text{SiO}_4 \quad (8)$$
Chapter 5: Clay dissolution in saline-acidic solutions

The dissolution rate of a given mineral \( (i) \) was obtained from the cation release (Si or Al) using the following expression:

\[
R_i = -\frac{1}{V_{ij}} \frac{F}{S_i M_i} (C_j)
\]  \hspace{1cm} (9)

where \( V_{ij} \) is the stoichiometric coefficient of element \( j \) in the dissolution reaction of mineral \( i \) (given in equation 6, 7 or 8) and \( C_j \) is the concentration of element \( j \) released from clay dissolution, divided by the content of mineral \( i \) in the clay sample. A SSA value of 40 \( m^2/g \) was used for both kaolinite and illite for dissolution rate calculations, whereas a SSA value of 83.3 \( m^2/g \) was used for smectite dissolution rate calculation, which was obtained by subtracting the SSA values of kaolinite and illite (based on their content in the clay fraction) from the SSA of the clay sample (104.5 \( m^2/g \)). The estimated dissolution rates of kaolinite, illite and smectite derived using equation 9 are presented in Table 5.5. The dissolution rates of minerals calculated from Si and Al release followed the sequence \( R_{\text{kaolinite}} > R_{\text{illite}} > R_{\text{smectite}} \) (Table 5.5). A comparison of the kaolinite dissolution rates with standard kaolinite dissolution rates from a previous dissolution study (Cama et al., 2002) suggests faster rates for soil kaolinite compared to standard kaolinite (Fig. 5.8). The dissolution rates of natural illite estimated in this study are faster than standard mineral rates (Chapter 3) (Bibi et al., 2011a) at pH 1 and 2, however, the rates are similar to the standard mineral rates at pH 3 and 4. The dissolution rates for soil smectite from this study present a great similarity to standard mineral rates previously calculated under similar experimental conditions (Fig. 5.8). (Bibi et al., 2011b) (Chapter 4) It is important to mention here that the stoichiometric coefficients (for Si and Al) and the SSA values of kaolinite and illite used in the rate calculations for these minerals were based on the data available in literature for standard minerals. In contrast to the dissolution rate results obtained in this study, Salmon and Malmström (2006) reported up to two orders of magnitude slower dissolution rates for aluminosilicate minerals from
polymineralic samples than the pure mineral dissolution rates in batch dissolution experiments and attributed this effect to the underestimation of surface area for minerals in the polymineralic samples or the particle size differences between the pure and natural (polymineralic) samples.

### Table 5.5 Estimated dissolution rates (mol m\(^{-2}\) s\(^{-1}\)) of kaolinite, illite and smectite at pH 1–4 at 25°C and at pH 1 and 4 at 35°C and 45°C.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Smectite</th>
<th>Illite</th>
<th>Kaolinite</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(R_{Si})</td>
<td>(R_{Al})</td>
<td>(R_{Si})</td>
</tr>
<tr>
<td><strong>25°C</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.25-1</td>
<td>-12.65</td>
<td>-12.65</td>
<td>-12.29</td>
</tr>
<tr>
<td>0.25-2</td>
<td>-12.96</td>
<td>-12.91</td>
<td>-12.63</td>
</tr>
<tr>
<td>0.01-1</td>
<td>-12.58</td>
<td>-12.60</td>
<td>-12.25</td>
</tr>
<tr>
<td>0.01-2</td>
<td>-12.78</td>
<td>-12.77</td>
<td>-12.45</td>
</tr>
<tr>
<td>0.01-3</td>
<td>-13.44</td>
<td>-13.41</td>
<td>-12.11</td>
</tr>
<tr>
<td>0.01-4</td>
<td>-13.86</td>
<td>-14.54</td>
<td>-13.53</td>
</tr>
<tr>
<td><strong>35°C</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.01-1</td>
<td>-12.07</td>
<td>-12.08</td>
<td>-11.74</td>
</tr>
<tr>
<td>0.01-4</td>
<td>-13.46</td>
<td>-14.21</td>
<td>-13.13</td>
</tr>
<tr>
<td><strong>45°C</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.25-1</td>
<td>-11.77</td>
<td>-11.76</td>
<td>-11.44</td>
</tr>
<tr>
<td>0.01-1</td>
<td>-11.84</td>
<td>-11.82</td>
<td>-11.51</td>
</tr>
<tr>
<td>0.01-4</td>
<td>-13.49</td>
<td>-14.11</td>
<td>-13.16</td>
</tr>
</tbody>
</table>

Note: In the first column, first term is the ionic strength (M) and second term represents the solution pH.
Fig. 5.8 A plot of log $R_{Si}$ values estimated for individual minerals (kaolinite, illite and smectite) based on the content of each mineral in the bulk clay sample as a function of pH (1–4) and at $I = 0.25$ M in this study; and a comparison of these rates with log $R_{Si}$ values from previous studies on pure mineral samples of kaolinite, illite and smectite.

### 5.4.6 Acid neutralisation capacity of clay

The acid neutralisation capacity (ANC) of clay from dissolution experiments was calculated from the released concentrations of neutralising cations during the experimental period. However, the release of Si, which is the major structural cation in the structure of phyllosilicate minerals (kaolinite, illite and smectite) was not considered for these calculations; as the final dissolution step relating to the release of partially attached Si atoms (equation 10) involves H₂O adsorption rather than a Si for H⁺ exchange reaction (Oelkers, 2001; Weber, 2003).

$$\equiv \text{Si–O–Si} \equiv + \text{H}_2\text{O} \rightarrow \text{(Si–O–Si–OH}_2^+) \rightarrow 2\equiv \text{Si–O–H} \quad (10)$$
The ANC for the clay sample was determined from the quantity of Al, Fe, K and Mg dissolved from the clay during the experimental period. Previous studies suggest that the ANC calculations should not be based on the release of Al and Fe due to the possibility of release of acidity from the hydrolysis of these cations (Weber et al., 2005). However in the highly acidic conditions prevailing in ASS, very little Al or Fe hydrolysis is expected.

The ANC of clay from the release of a metal cation, M in a flow-through reactor was determined by the expression (Weber, 2003):

\[
ANC = \frac{(M \times Vol) \times m_c \times 49 \times T_d}{1000 \times Mw_m \times wt(g) \times S_d}
\]

where ANC is in kg H$_2$SO$_4$/t, M is the cation concentration (mg/L) in solution, Vol is the volume of solution, Mw$_m$ is the atomic weight of metal cation, m$_c$ is the ionic charge of the metal cation M, wt(g) is the weight of the sample in the reaction vessel (0.1 g), 49 is the conversion factor to convert moles of hydrogen ions into kg H$_2$SO$_4$/t; T$_d$ is the time duration in hours since the previous sample was collected, and S$_d$ is the sample duration in hours. The multiplication of the calculated ANC by T$_d$/S$_d$ will provide an estimate of the ANC over a particular time interval during the experiment, and a cumulative sum of the ANC values calculated by the equation 11 will provide the value of the total ANC over the experimental period. The initial fast release stage in each experiment was not included in the ANC calculations, as the initial stage has a much faster dissolution rate due to the dissolution of ultra-fine particles and/or dissolution from highly reactive surface sites, and it is not a true representative of the clay dissolution rate over longer time periods.

The cumulative ANC values calculated for the individual metal cation released from clay dissolution over the experimental duration (excluding the initial rapid release stage) at the pH
range of 1–4 and at 0.25 M ionic strength (in 25°C experiments) are shown in Table 5.6. The data show that an ANC of 44.4 kg H$_2$SO$_4$ will be provided by the dissolution of 1 tonne of BB clay at pH 1 in a period of 22 days, whereas the total ANC provided by the dissolution of same amount of clay at pH 4 will be 13.1 kg H$_2$SO$_4$ in 62 days.

### Table 5.6 The acid neutralisation capacity (ANC) values in kg H$_2$SO$_4$/t of clay sample calculated from the cation release at pH 1–4 and $I = 0.25$ M.

<table>
<thead>
<tr>
<th>pH</th>
<th>Time duration (days)</th>
<th>ANC$_{Al}$</th>
<th>ANC$_{Fe}$</th>
<th>ANC$_{K}$</th>
<th>ANC$_{Mg}$</th>
<th>Total ANC</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10–31</td>
<td>26.2</td>
<td>10.7</td>
<td>5.2</td>
<td>2.3</td>
<td>44.4</td>
</tr>
<tr>
<td>2</td>
<td>11–56</td>
<td>22.6</td>
<td>2.9</td>
<td>7.5</td>
<td>6.2</td>
<td>39.2</td>
</tr>
<tr>
<td>3</td>
<td>28–81</td>
<td>5.7</td>
<td>2.1</td>
<td>7.7</td>
<td>0.3</td>
<td>15.8</td>
</tr>
<tr>
<td>4</td>
<td>16–77</td>
<td>4.0</td>
<td>0.5</td>
<td>8.1</td>
<td>0.5</td>
<td>13.1</td>
</tr>
</tbody>
</table>

#### Maximum acid neutralisation capacity of clay (ANC$_{\text{max}}$)

The maximum acid neutralisation capacity (ANC$_{\text{max}}$) of phyllosilicate minerals can be determined by (Paktunc, 1999):

$$
\text{ANC}_{\text{max}} = \frac{H}{\sum_{i=1}^{k} x_i \times y_n}
$$

where $x_i$ includes cations in the mineral structure other than Si, and $H$ is the number of hydrogen ions in 1 mole H$_2$SO$_4$, $x_i$ is the number of i ions present in the phyllosilicate mineral available to neutralise 1 mol H$_2$SO$_4$, $y_n$ is the charge of ion $x_i$, and $k$ is the number of neutralising cations in the silicate mineral. As an example the ANC$_{\text{max}}$ of BB smectite can be calculated as:

$$
\text{MNC} = \frac{2}{\text{Na}(0.26) + \text{Al}(1.66 \times 3) + \text{Fe}^{3+}(3 \times 0.78) + \text{Fe}^{2+}(2 \times 0.12) + \text{Mg}(2 \times 0.09)} = \frac{2}{8.01} = 0.25 \text{ mole}
$$

(13)
Thus 0.25 mole of smectite is required to neutralise 1 mole of $\text{H}_2\text{SO}_4$. Similarly, according to equation 13, 0.33 and 0.25 moles of kaolinite and illite, respectively will be required to neutralise 1 mol of $\text{H}_2\text{SO}_4$, whereas, 1 mol of calcite is required to neutralise 1 mol of $\text{H}_2\text{SO}_4$ (Jambor et al., 2002; Weber et al., 2005).

$$\text{CaCO}_3 + 2\text{H}^+ \rightarrow \text{Ca}^{2+} + \text{CO}_2 + \text{H}_2\text{O} \quad (14)$$

The values of $\text{ANC}_{\text{max}}$ provide an insight into the maximum neutralisation potential of the minerals constituting the clay sample under investigation; however, the dominant influence on the actual ANC of minerals is determined based on their dissolution rates determined at different acidic pH values in this study. Although the dissolution rates of clay sample determined in this study ($10^{-12}$ to $10^{-14}$ mol m$^{-2}$ s$^{-1}$) and in many previous investigations on pure phyllosilicate minerals are slower than carbonate minerals (dissolution rates in the order of $10^{-5}$ to $10^{-8}$ mol m$^{-2}$ s$^{-1}$); the overall ANC of phyllosilicate minerals per mol is greater than the carbonate minerals (as discussed above), the ANC of phyllosilicate minerals is realised in the long-term dissolution of these minerals (Paktunc, 1999). The presence (and dominance) of these minerals in the clay fraction of most soils enhances their significance in the neutralisation of acidity generated in the soils.

### 5.5 Conclusions

The release of cations from clay dissolution showed a decreasing trend with increasing solution pH. The exceptions to this trend included K release in the higher ionic strength solutions and Mg release at both ionic strengths at 25°C. At the initial stage of the experiments, an enhanced Al over Si release occurs at pH 1–4 in the higher ionic strength solutions and at pH 1 at the lower ionic strength. An inhibited Al release resulted from clay dissolution at the initial stage of the experiments at pH 2–4 in the lower ionic strength
solutions, which continued for the experimental duration at pH 4. These results show that the phyllosilicate dissolution under highly saline and acidic conditions ($I = 0.25 \text{ M}$, particularly at pH 4) results in an enhanced dissolved concentration of Al compared to low ($I = 0.01 \text{ M}$) or non-saline acidic solutions. This might have an adverse effect on the associated systems in the form of $\text{Al}^{3+}$ toxicity and/or other adverse effects resulting from the leaching of high dissolved Al concentrations into water systems associated with ASS. Clay dissolution rates obtained from steady state Si, Al and Fe release decreased with increasing solution pH and decreasing temperature. The pH dependent reaction order values obtained from the linear regression of the plots of $R_{Si}$, $R_{Al}$ and $R_{Fe}$ versus pH were 0.45, 0.42 and 0.46, respectively. The apparent activation energy values obtained for clay dissolution at pH 1 and 4 were 18.3 kcal mol$^{-1}$ and 9.0 kcal mol$^{-1}$, respectively.

The individual mineral dissolution rates obtained from the steady state cation release (Si, Al) and the content of each mineral in the clay fraction suggested highest dissolution rates for kaolinite followed by illite and smectite. The dissolution rates obtained for soil smectite in this study showed strong resemblance to standard mineral rates reported previously.

The amount of neutralising cations released during clay dissolution was used to estimate the ANC of clay in solutions having similar composition to saline-ASS solution. According to these estimates the total ANC provided by the dissolution of 1 tonne clay will be 44.4 kg $\text{H}_2\text{SO}_4$ and 13.1 kg $\text{H}_2\text{SO}_4$, respectively at pH 1 (22 days) and 4 (62 days). Such information is important in the determination of acidity balance of ASS systems and need to be considered in the planning of management strategies needed for the rehabilitation of these soils.
5.6 REFERENCES


Chapter 5: Clay dissolution in saline-acidic solutions


Chapter 5: Clay dissolution in saline-acidic solutions


Kohler S. J., Dufaud F. and Oelkers E. H. 2003. An experimental study of illite dissolution kinetics as a function of pH from 1.4 to 12.4 and temperature from 5 to 50°C. 


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