

Non-Steady State and Steady State Silicate Dissolution: Non-Carbonate Acid Neutralisation for Long-Term Acid and Metalliferous Drainage Control

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Abstract: The dissolution of silicate minerals has been largely examined under steady state conditions. The primary aim of this study was to understand the potential of the non-steady state dissolution of silicate minerals in treatment of acid and metalliferous drainage (AMD) resulting predominantly from pyrite oxidation. To this end, flow-through dissolution cell experiments were carried out using selected silicate minerals (biotite, chlorite, olivine and K-feldspar), all commonly found in AMD environments, under various pH and flow rate conditions, for comparison to pyrite dissolution carried out under the same conditions. Both acid generation rate (pyrite) and steady-state and non-steady state acid neutralisation rates (silicates) were calculated and compared. Results showed that the non-steady state acid neutralisation rates due to silicate dissolution were greater than the steady-state neutralisation rates and that all silicate minerals investigated in this study, except K-feldspar, can provide acid neutralisation rates to match the acid generation rate due to pyrite dissolution under certain conditions.

Keywords: Acid and metalliferous drainage, Flow-through dissolution, Non-steady state dissolution, Pyrite oxidation, Steady-state dissolution, Silicate minerals.

1. INTRODUCTION

Silicate minerals commonly exist in acid and metalliferous drainage (AMD)-forming waste rocks and tailings. The dissolution of silicate minerals can potentially provide aqueous silicates for development of silicate-stabilised iron (oxy)hydroxide surface passivation layers on sulfide minerals [1-3] for AMD control at-source. In addition, the dissolution of silicates, albeit relatively slow as compared to that of carbonate minerals (e.g. calcite CaCO_3), has shown potential application in neutralisation of low acid generation rates [4]. For AMD remediation, the rates of dissolution of minerals (e.g. $\text{mol m}^{-2} \text{s}^{-1}$) are usually converted into acid generation and neutralisation rates, AGR and ANR (e.g. $\text{mg H}_2\text{SO}_4 \text{ kg}^{-1} \text{ week}^{-1}$), for comparison. Several methods have been developed to calculate the non-carbonate ANR (ANRnc) of silicate components present within AMD wastes, based on e.g. sample mineralogy and the dissolution rates of individual silicate minerals [5, 6]. Miller *et al.* [7] demonstrated, using column leaching, that some silicate minerals can provide ANRnc to match AGR at

$\approx 10 \text{ mg H}_2\text{SO}_4 \text{ kg}^{-1} \text{ week}^{-1}$, buffering leachate pH to around 3 to 4.

It is noted that most silicate dissolution rates (e.g. quartz, albite, anorthite, K-feldspar, leucite and forsterite) have been determined using commonly the concentration of dissolved silica under steady-state and various temperature and pH conditions; the kinetic rate parameters such as *Arrhenius* pre-exponential factor, rate constant and activation energy have been compiled and reported in Palandri and Kharaka (2004) [8]. Only several studies have examined the non-steady state dissolution of silicate minerals including brucite, albite and illite [9-11]. The initial non-steady state dissolution rates of silicate minerals remain largely unexplored. The primary aim of this study was, therefore, to understand (1) the dissolution kinetic behaviours of selected silicate minerals (biotite, chlorite, K-feldspar and olivine) in the initial reaction stages and their acid neutralisation rates and (2) their potentials in providing neutralisation capacities for control of AMD resulting from pyrite dissolution. These four selected silicate minerals are all commonly found in AMD environments, but investigation of their dissolution behaviours has been focused on steady state dissolution (see Ref [8] for compiled rate parameters and references therein) rather than non-

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steady state dissolution. Therefore, examination of the non-steady state dissolution kinetics of the four common silicate minerals will generate new knowledge about their dissolution behaviours and also enable a comparison between the non-steady state ARNnc and AGR due to pyrite dissolution.

2. EXPERIMENTAL METHODOLOGY

2.1. Flow-Through Dissolution Experiments

Each dissolution experiment was conducted using a polytetrafluoroethylene (PTFE) flow-through reaction cell under the conditions of 25 ± 1 °C, pH 2 (HCl) or 4 (HCl), and the flow-rates of 4 or 12 L day⁻¹ kg⁻¹. Each experiment contained 10 g of a silicate mineral (biotite, chlorite, olivine or K-feldspar; 38–75 µm) or pyrite (38–75 µm), with two 0.45 µm PTFE filter papers placed above and below the sample within the sample compartment of each flow-through cell. The pH of effluent for each experiment was measured regularly and flow rates were also measured daily and, if necessary, adjusted. Solutions were pumped through each PTFE flow-through vessel using a Gilson MINIPULS 3 peristaltic pump (Figure 1).

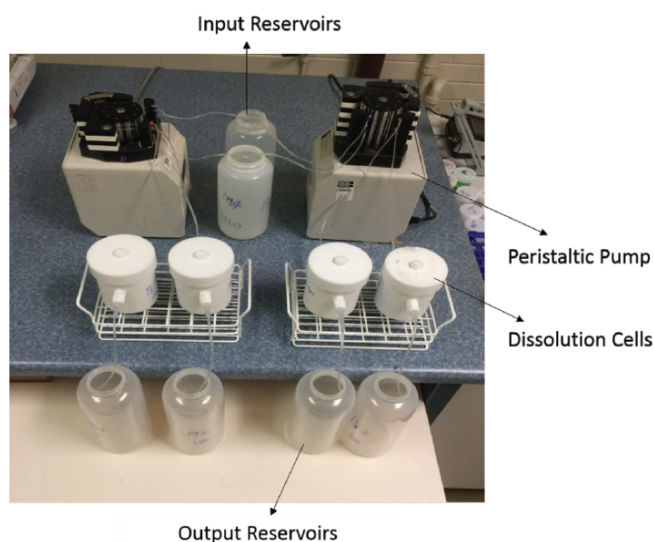


Figure 1: Setup of flow-through kinetic dissolution cell experiments.

2.2. Instrumental Analyses

All silicate samples were examined using powder X-ray diffraction (XRD) analysis (Bruker's D4 diffractometer with Co K α radiation). XRD data collection and analysis (identification of mineral species and quantification) were carried out as per Qian *et al.* [12].

Scanning electron microscopy (SEM) was carried out, using a ZEISS Merlin field emission SEM equipped with energy dispersive spectrometry (EDS), to obtain surface morphologies and identify predominant mineral species in the samples. The operating voltage was set to 15 kV. All samples were carbon-coated prior to SEM analysis.

An electron probe micro-analyser (EPMA; CAMECA SXFive) with wavelength dispersive spectrometers, was also used to quantify the elemental compositions of all silicate samples.

A 5-point, N₂ Brunauer-Emmett-Teller (BET) surface area analysis was carried out, using a Micromeritics Gemini 2375 instrument, to determine the specific surface areas (m² g⁻¹) of silicates and pyrite (all in the particle size range of 38–75 µm): 0.85 $\pm$ 0.01 (pyrite), 1.49 $\pm$ 0.02 (chlorite), 0.75 $\pm$ 0.01 (K-feldspar), 1.35 $\pm$ 0.02 (olivine) and 1.29 $\pm$ 0.02 (biotite).

Solution samples (10 ml) were collected periodically and filtered through 0.45 µm membrane filters (Millipore, USA) for analysis of S, Si, K, Na, Ca, Mg, and Al concentrations using solution inductively coupled plasma mass spectrometry (solution ICP-MS; Agilent 7500ce).

3. RESULTS AND DISCUSSION

3.1. Mineralogical Composition of Silicate Minerals and Pyrite

The mineralogical and elemental compositions of silicate samples were determined using quantitative XRD (QXRD) and EPMA analyses, respectively. The chemical formula of the major species within the silicate samples, derived from EPMA analysis, and the QXRD results are presented in Table 1. All samples contained ≤ 10 wt.% impurities, except for chlorite with 19 wt.% impurities. Pyrite sample used for the flow-through cell dissolution experiments has been found in our recent work to contain no crystalline impurity phases detectable by XRD; the elemental composition of the pyrite is also reported therein [13].

3.2. Flow-Through Kinetic Dissolution of Silicates

The flow-through dissolution tests of each silicate sample were performed at pH 2 and 4 and at 4 and 12 L day⁻¹ kg⁻¹ flow rates for calculation of ANRnc. The calculated ANRnc values were then compared against the measured AGR due to pyrite dissolution under otherwise identical conditions.

Table 1: Mineralogical Compositions of Silicate Samples

Biotite Sample wt.% ^a		K-Feldspar Sample wt.% ^a	
biotite ^b $K_{0.96}Na_{0.04}Mg_{2.72}Fe_{0.28}AlSi_3O_{10}(F,OH)_2$	93(5)	K-feldspar ^b $(K_{0.79}Na_{0.21})AlSi_3O_8$	94(5)
phlogopite	7(2)	albite	6(2)
Olivine Sample wt.% ^a		Chlorite Sample wt.% ^a	
olivine ^b $(Ca_{0.05}Mg_{1.79}Fe_{0.16})SiO_4$	90(5)	chlorite ^b $(Mg_{2.78}Fe_{2.22})Al_2Si_3O_{10}(OH)_8$	81(5)
enstatite	10(2)	biotite	12(2)
		albite	7(2)

^aUncertainties (given in parentheses) at the 95% confidence level for QXRD were estimated based on $\chi^{0.35}$ where χ is the wt.% of each component [14, 15];

^bSpecific elemental compositions (given as formula) of the main phases of silicate samples were determined by EPMA.

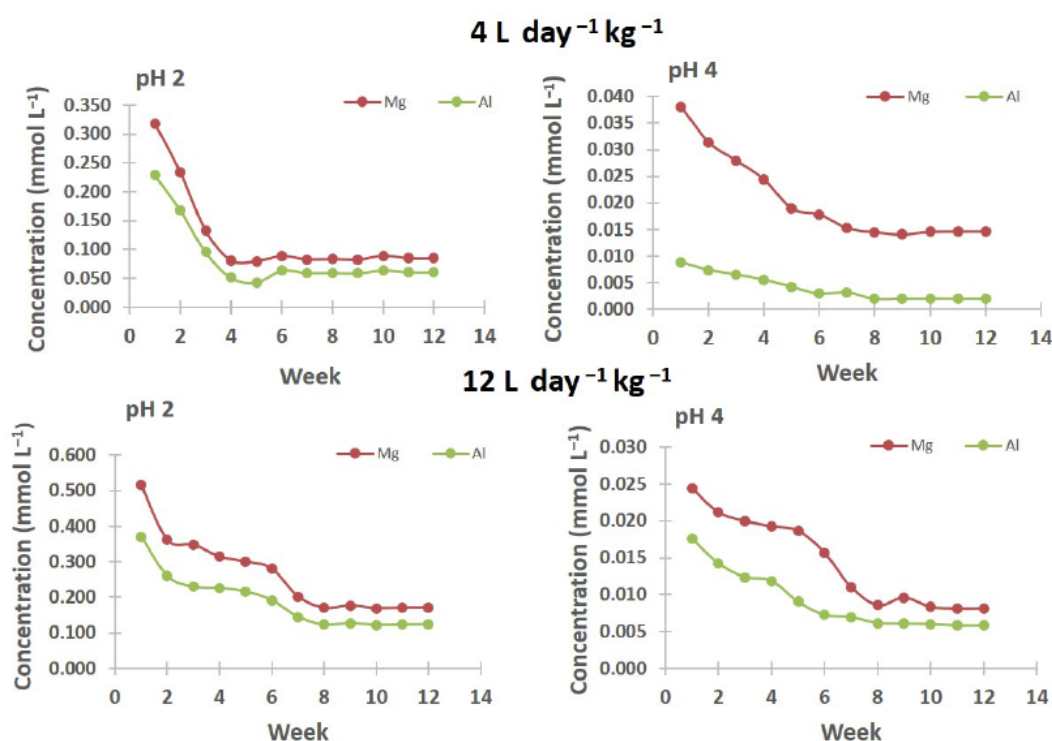


Figure 2: The concentration of major cation concentrations for chlorite dissolution at pH 2 and 4 and at 4 and 12 L day⁻¹ kg⁻¹ flow rates.

3.2.1. Chlorite Dissolution

Figure 2 shows the evolution trends of various cations released from chlorite dissolution as a function of time. At pH 2, the dissolution of chlorite reached steady-state after 6 weeks at 4 L day⁻¹ kg⁻¹ and after 8 weeks at 12 L day⁻¹ kg⁻¹. At pH 4, chlorite dissolution reached steady-state after 8 weeks, irrespective of the flow rate. The concentrations of Mg and Al released from chlorite dissolution at pH 2 were one order of magnitude greater than at pH 4 after dissolution for 1 week at both flow rates and decreased over time at the

two pH, suggesting that the initial (non-steady state) chlorite dissolution can provide greater ANRnc.

After 5 weeks of dissolution at pH 2 and 4 L day⁻¹ kg⁻¹, the molar ratio of Mg:Al (1.4:1) in the leachate was identical to that (1.4:1) in the bulk chlorite, indicative of stoichiometric dissolution. However, the concentration of Al ($\approx 2.0 \times 10^{-3}$ M) at pH 4 and 4 L day⁻¹ kg⁻¹ was one order of magnitude lower than that of Mg ($\approx 1.4 \times 10^{-2}$ M), suggesting incongruent dissolution. This is possibly due to precipitation of Al phases. When the flow rate increased from 4 to 12 L day⁻¹ kg⁻¹, the concentration of

Mg ($\approx 7.6 \times 10^{-3}$ M) was slightly greater than that of Al ($\approx 5.8 \times 10^{-3}$ M) after 8 weeks of dissolution at pH 4. The Mg:Al ratio (1.2) is close to that for dissolution at pH 2 after 8 weeks (Mg:Al=1.4), suggesting near-congruent dissolution. Incongruent dissolution typically releases cations from silicate mineral structures and generates residual secondary and possibly tertiary phases that are more stable under geochemical conditions [16]. Factors that determine whether dissolution is congruent or incongruent include mineral structure, composition and external environmental conditions such as pH, equilibrium conditions, temperature, redox conditions and the presence of “foreign” ions [17].

The surface morphology of chlorite before and after dissolution for 11 weeks at pH 2 and pH 4 and at 4 L day⁻¹ kg⁻¹ (Figure 3a–f). Small variations in the chlorite surface morphology were observed, with etch pits (Figure 3e, f) becoming apparent after acid attack and grain edges becoming less well-defined, particularly at pH 2.

3.2.2. Olivine Dissolution

The dissolution of olivine at pH 2 and pH 4 and at 4 and 12 L day⁻¹ kg⁻¹ flow rates reached steady-state almost from the beginning of experiments (Figure 4). The release of Mg at pH 2 is at least one order of

magnitude faster than at pH 4, regardless of the flow rate. This is consistent with findings reported in Olsen and Rimstidt [18] who found that the rate of dissolution of forsterite (the Mg-rich end-member of olivine) increased with decreasing pH. Figure 4 shows that the concentration of Ca released was greatest in the first week and dramatically decreased to almost zero at 2 or 4 weeks. Olivine dissolves faster than other three silicates under the same conditions due to the breaking of strong Si-O-Si bonds of the orthosilicate structure. Previous studies have shown that in the initial stages of forsterite dissolution at low pH, Mg is released more rapidly than Si [19, 20]. The high molar ratio of Mg/Ca (>100) for olivine dissolution at both pH 2 and 4 and at the flow rates of 4 and 12 L day⁻¹ kg⁻¹, indicates that olivine dissolution is non-stoichiometric (Mg/Ca = 36:1 in the bulk) under the conditions investigated herein. In Olsen's work [21], incongruent dissolution of forsterite was observed and confirmed by XPS which showed a greater Si/Mg ratio on the acid-leached surface than on the unreacted surface. Although olivine dissolution occurred at pH 2 and 4 over 11 weeks based on observation of cations released (Figure 4), SEM analysis found no apparent changes in surface morphology after dissolution at pH 2 and 4 (Figure 5a–f).

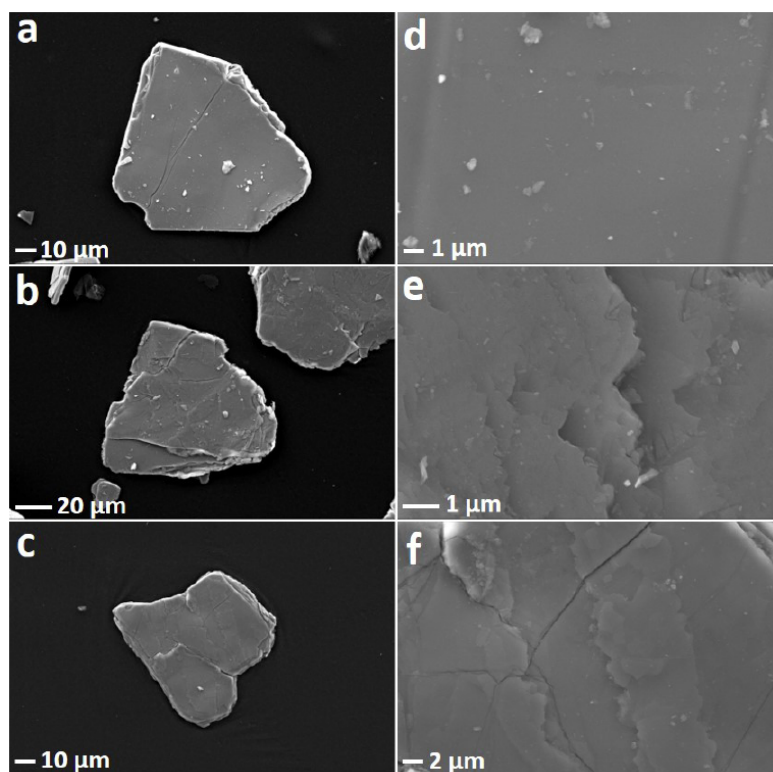


Figure 3: SEM images of chlorite: (a) fresh sample, (b) and (c) chlorite dissolved at pH 2 and pH 4 respectively at 4 L day⁻¹ kg⁻¹ for 11 weeks, and (d)–(f) are the corresponding enlarged SEM images of (a)–(c).

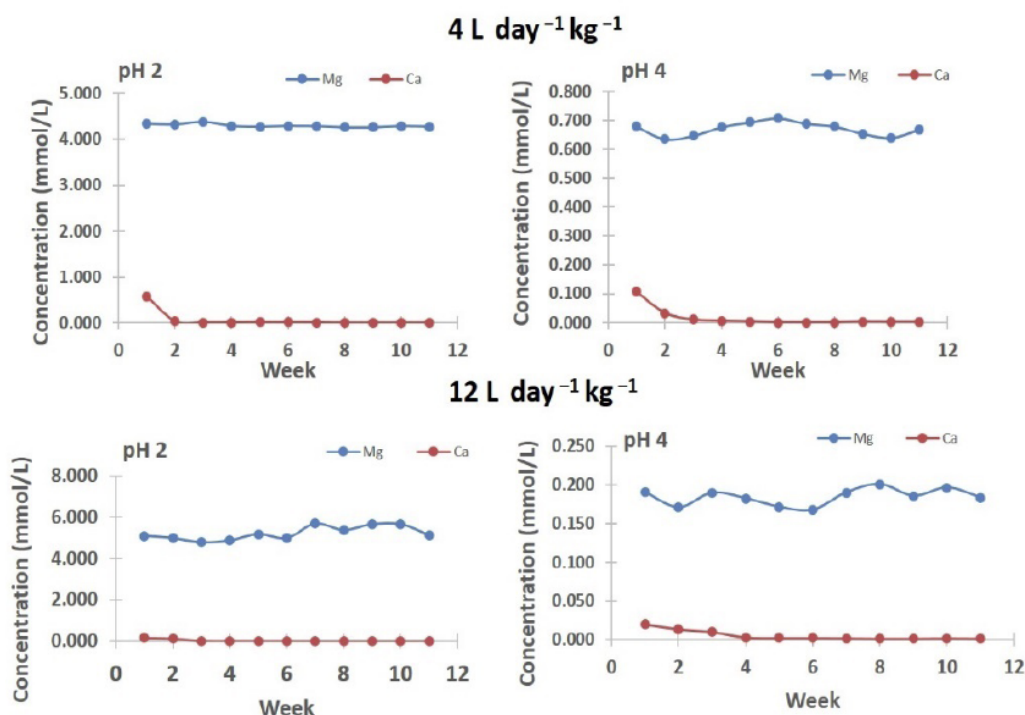


Figure 4: The concentration of major cations from the dissolution of olivine at pH 2 and 4 and at 4 and 12 L day⁻¹ kg⁻¹ flow rates as a function of time.

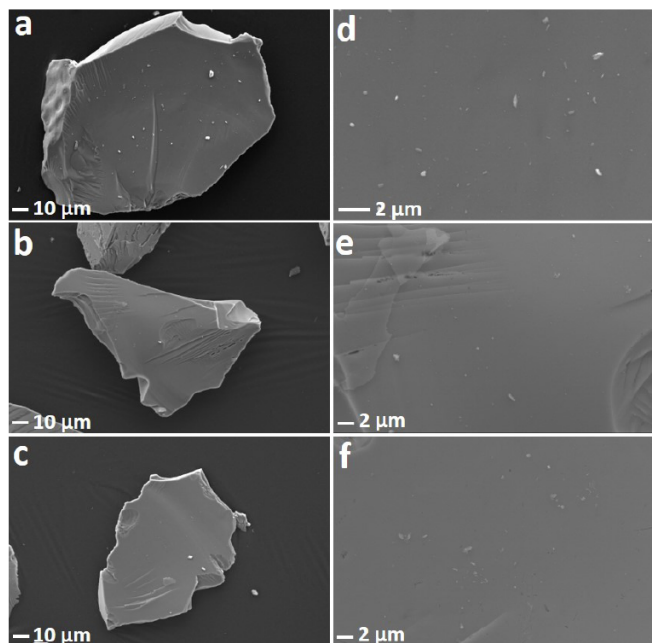


Figure 5: SEM images of olivine: (a) fresh sample, (b) and (c) olivine dissolved at pH 2 and pH 4 respectively at 4 L day⁻¹ kg⁻¹ for 11 weeks, and (d)–(f) are the corresponding enlarged SEM images of (a)–(c).

3.2.3. K-feldspar Dissolution

The dissolution profiles of cations for K-feldspar at pH 2 and 4 and at the two flow rates are shown in

Figure 6. It appears that a near steady-state dissolution occurred after six weeks under all conditions examined. At pH 2, the concentration of cations at 4 L day⁻¹ kg⁻¹ was about 3 times greater than at 12 L day⁻¹ kg⁻¹, but the concentration of cations released at pH 4 was similar, irrespective of the flow rate. At pH 4, almost no Al³⁺ (effluent pH≈4.2) was detectable by solution ICP-MS, probably due to Al precipitation (or preferential dissolution of other cations). Prior to steady-state dissolution, the concentration of cations released from K-feldspar dissolution at pH 2 followed the sequence of Al > K > Na. After dissolution at pH 2 for 6 weeks, the molar ratio of K/Na was ≈3.5 at 4 L day⁻¹ kg⁻¹ and ≈4 at 12 L day⁻¹ kg⁻¹, close to that in the bulk K-feldspar (≈4), suggesting near congruent dissolution. At pH 4, the K:Na ratio for steady-state dissolution was calculated to be ≈3.2 at 12 L day⁻¹ kg⁻¹ (after 5 weeks) and 3.8 at 4 L day⁻¹ kg⁻¹ (after 4 weeks), also suggesting possible congruent dissolution. Figure 7a–f compares the SEM surface morphology of K-feldspar particles before and after dissolution at pH 2 and pH 4. K-feldspar surfaces after leaching at pH 2 and 4 for 11 weeks were porous and had obvious etch pits (particularly at pH 2), showing evidences of acid attack (Figure 7e,f).

3.2.4. Biotite Dissolution

The dissolution of biotite reached steady-state after 4 weeks at both pH 2 and 4 and at the 4 L kg⁻¹ day⁻¹

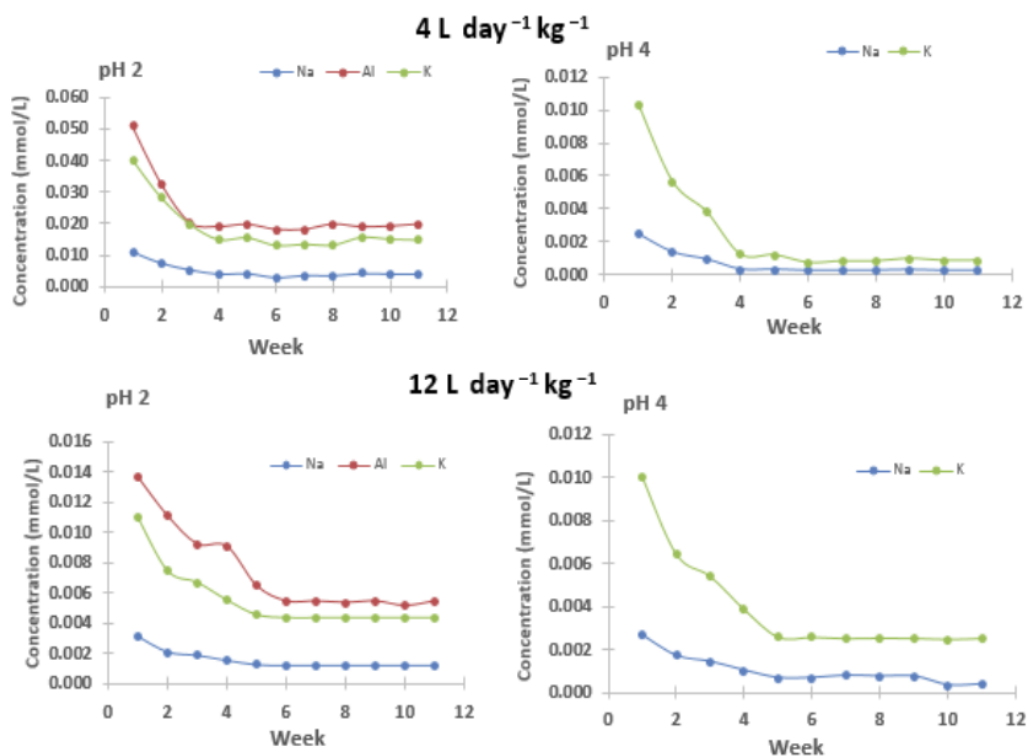


Figure 6: The concentration of major cations released from the dissolution of K-feldspar at pH 2 and 4 and at 4 and 12 L day⁻¹ kg⁻¹ flow rate as a function of time.

flow rate. In comparison, steady state was achieved after 7 weeks for dissolution at both pH and at 12 L kg⁻¹ day⁻¹ (Figure 8). At pH 2, the concentration of cations released followed the order of Mg > K > Al > Na under non-steady state conditions (before 4 and 7 weeks at 4 and 12 L kg⁻¹ day⁻¹ flow rates, respectively). The concentration of cations released at 4 L day⁻¹ kg⁻¹ was found to be greater than at 12 L day⁻¹ kg⁻¹ under otherwise identical conditions. Previous studies have reported early fast release of cations from interlayers of some 2:1 (tetrahedral : octahedral layers = 2:1) phyllosilicate minerals, and attributed the rapid release of cations to cation exchange reactions, primarily exchange of H⁺ from solution for cations in the interlayers [22, 23]. During the steady-state dissolution of biotite at pH 2, the Mg:K molar ratio was ≈12:1 at 4 L kg⁻¹ day⁻¹ and 2:1 at 12 L kg⁻¹ day⁻¹, significantly different from the Mg:K molar ratio of the bulk biotite (≈3:1), suggesting incongruent dissolution. Similarly, the Mg:K molar ratio during the steady state dissolution of biotite at pH 4 was ≈1 at 12 L day⁻¹ kg⁻¹ and 0.4 at 4 L day⁻¹ kg⁻¹, suggesting incongruent dissolution. Acker and Bricker [24] studied biotite dissolution in the pH range 3–7, using fluidized-bed reactors and flow through columns, and also found that biotite dissolved incongruently under the pH conditions examined.

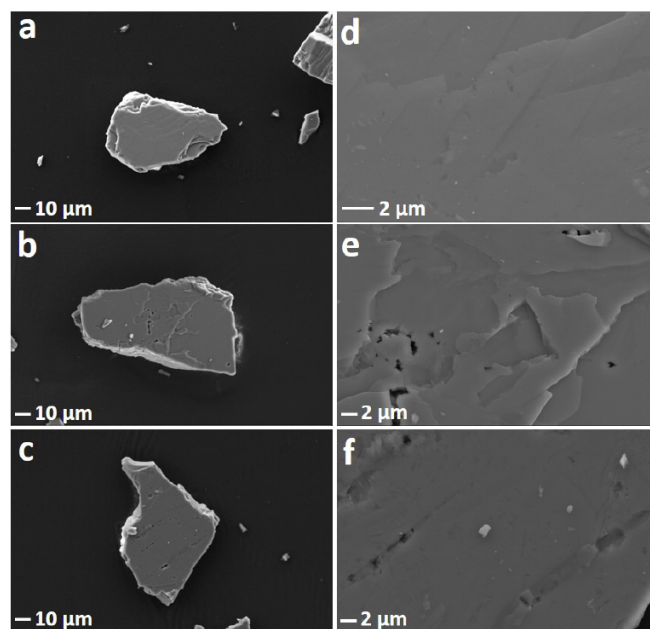


Figure 7: SEM images of K-feldspar: (a) fresh sample, (b) and (c) K-feldspar dissolved at pH 2 and pH 4 respectively at 4 L day⁻¹ kg⁻¹ for 11 weeks, and (d)–(f) are the corresponding enlarged SEM images of (a)–(c).

Figure 9a–f shows the SEM images of biotite particles before and after dissolution at pH 2 and pH 4. It is clear that the basal surface of the fresh biotite was relatively smooth (Figure 9a,d). After dissolution at pH

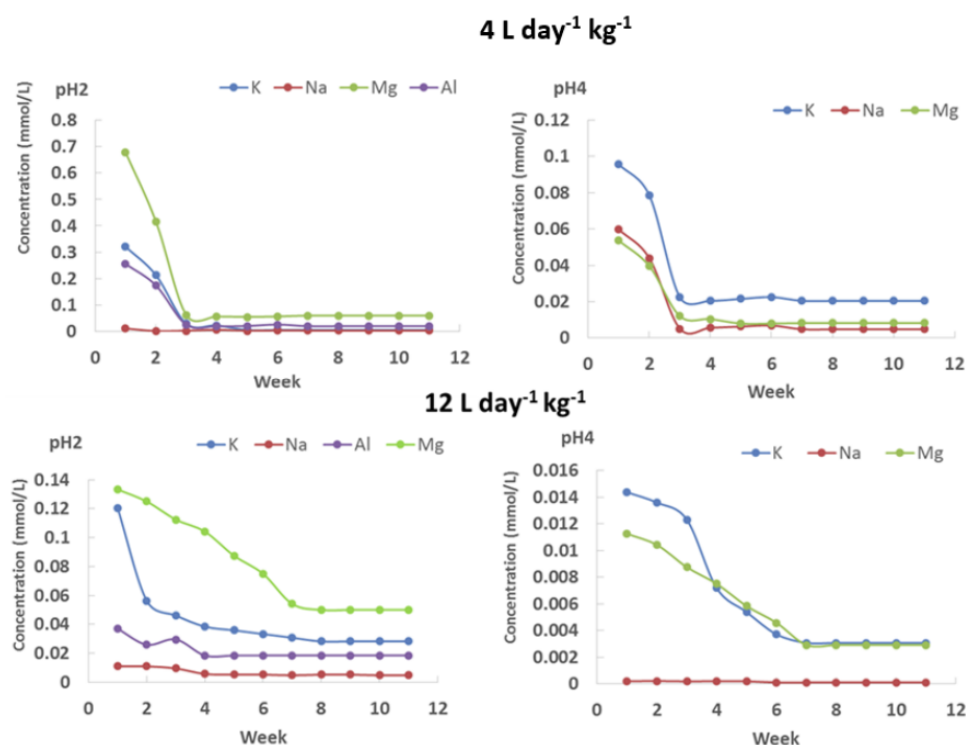


Figure 8: Major cation concentrations for biotite dissolution at pH 2 and 4 and at 4 and 12 L day⁻¹ kg⁻¹ flow rates as a function of time.

2 for 11 weeks, biotite surface appeared to be similar to the fresh surface (Figure 9b,e). In comparison, biotite surface became rougher with probably secondary surface precipitates after dissolution at pH 4 for 11 weeks (Figure 9c,f).

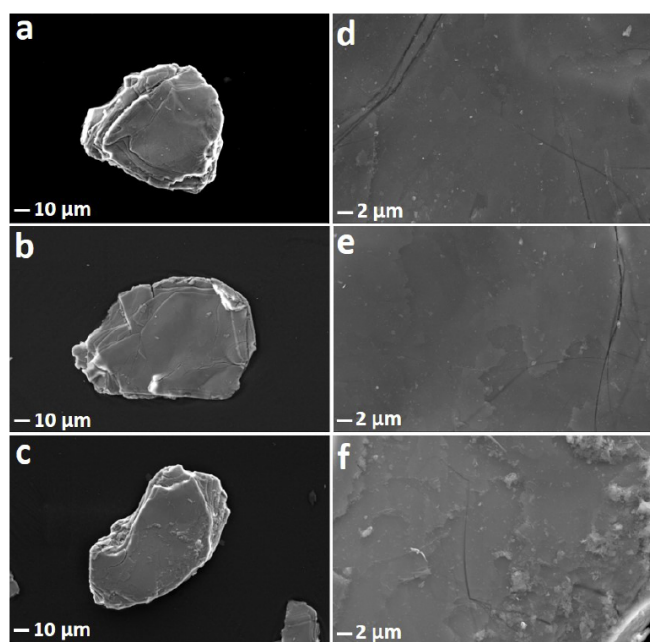


Figure 9: SEM images of biotite: (a) fresh sample, (b) and (c) biotite dissolved at pH 2 and pH 4 respectively at 4 L day⁻¹ kg⁻¹ for 11 weeks, and (d)–(f) are the corresponding enlarged SEM images of (a)–(c).

3.2.5. Effluent pH

Effluent pH was measured throughout each dissolution cell test. At pH 2 and at 4 and 12 L day⁻¹ kg⁻¹ flow rates, the effluent pH remained largely constant at pH 2 for dissolution of all samples throughout the entire dissolution processes, independent of the flow rate.

At pH 4 and 12 L day⁻¹ kg⁻¹, the effluent pH of olivine dissolution increased rapidly to approximate pH 6.5 in the first week and dropped to about pH 4.6 at week 4 and then remained almost constant for the remaining period of time, while the effluent pH for dissolution of all other silicates under the same conditions fluctuated between 4.1 and 4.5 over 11 weeks.

At pH 4 and 4 L day⁻¹ kg⁻¹, the effluent pH for olivine dissolution increased rapidly to ≈pH 8 in the first week, declined to ≈pH 7 at week 4 and then stabilised around this near-neutral pH until the end of experiment (Figure 10). Under the same conditions, chlorite dissolution resulted in an increase in pH from 4 to 7.5 in the first week, followed by a remarkable decrease in effluent pH to 4.4 at week 8. Similarly, the effluent pH for biotite dissolution initially reached ≈7 in the first two weeks, decreased to pH 5 at week 5 and then remained almost constant. For dissolution of K-feldspar at pH 4 and 4 L

$\text{day}^{-1} \text{kg}^{-1}$, the effluent pH increased to $\approx \text{pH } 6$ in the first week, decreased markedly to $\text{pH } 4.1$ at week 4 and stayed constant around 4.1 thereafter. The results here clearly showed that the dissolution of olivine (in the NSS and SS dissolution regimes), chlorite (NSS regime only) and biotite (NSS regime only) at $\text{pH } 4$ and $4 \text{ L day}^{-1} \text{kg}^{-1}$ significantly increased the pH to neutral (or slightly alkaline), suggesting that they can potentially contribute to acid neutralisation. Our results are in good agreement with those reported in earlier studies [16, 25] that the dissolution of some silicate minerals can buffer pH to e.g. $\text{pH } 6$ under certain conditions.

The results above indicate that the dissolution of olivine and chlorite can only buffer pH from about 4.5 to 7 at the slow flow rate (i.e. $4 \text{ L day}^{-1} \text{kg}^{-1}$) in this work, suggesting the importance of the duration of contact between minerals and solution. The longer the interaction between the acidic solution and the neutralising silicates, the greater the opportunity for a proton exchange reaction and acid buffering/neutralisation to take place. An increase in the flow rate will reduce the degree of these reactions/interactions, therefore resulting in lower effluent pH.

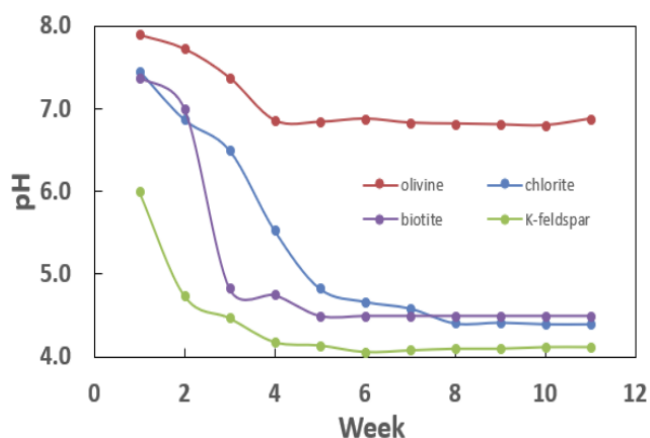


Figure 10: Variations of effluent pH for dissolution of silicates at $\text{pH } 4$ and at the $4 \text{ L day}^{-1} \text{kg}^{-1}$ flow rate.

3.2.6. Non-Steady State Dissolution (Fast Initial Dissolution) and Steady State Dissolution

The initial rapid silicate dissolution observed in this study may be attributed to disrupted surfaces of mineral samples formed during crushing and grinding and the fast dissolution of high-energy surface sites [26–29]. For example, a rapid initial dissolution of biotite with fast releases of Mg, Al, Si and Fe was also observed previously [29], followed by time-independent steady state dissolution rates after 10–14 days. Brandt *et al.* [30] also reported a rapid dissolution of chlorite

during the first 50 h of experiments conducted at $\text{pH } 2$ – 5 using dilute $\text{HCl}/\text{NaClO}_4$ solutions.

Silicate minerals contain Si atoms, each of which is coordinated with four corner oxygen atoms in a regular tetrahedron. These silicate tetrahedra are bonded to cations, such as Na^+ , K^+ , Ca^{2+} , Mg^{2+} and Al^{3+} , which may easily be exchanged with other cations. In this study, early rapid dissolutions of the four silicate minerals were observed, with faster release of cations under non-steady state dissolution than under steady-state dissolution conditions. Under acidic conditions ($\text{pH } 2$ and 4), sufficient amounts of H^+ may be provided to replace those cations. The rapid release of cations from the interlayers of silicates investigated in this study are possibly due to ion exchange reactions. This conjecture is supported by Metz and Amram [23] who found that an early rapid leaching of Ca, Na and Mg from the interlayer sites of smectite (phyllosilicate) resulted in an increased depletion of protons in solution due to exchange reactions. Similarly, the initial rapid releases of K and Mg from the interlayer sites of vermiculite observed previously was also attributed to ion exchange with protons [22]. Note: smectite and vermiculite samples investigated previously and the biotite examined in this study are all phyllosilicates with the 2:1 tetrahedral and octahedral layered structures. In addition, the release of more cations at $\text{pH } 2$ than at $\text{pH } 4$ during the initial non-steady state dissolution of silicates in this study, suggests that H^+ promotes exchange reactions with some cations such as K^+ , Na^+ , Mg^{2+} and Ca^{2+} from interlayers. This is in good agreement with the proposal by Oelkers *et al.* [31] that H^+ is the dominant species involved in the exchange reaction during the dissolution of a ‘multi-oxide’ silicate minerals such as forsterite and albite in the absence of ions with similar charges and ionic radii. Chou and Wollast [32] studied the dissolution of albite at room temperature and suggested that the rapid exchange reactions between alkali ions and protons is the first step during the dissolution of fresh feldspar in aqueous solutions, resulting in the formation of hydrogen feldspar on the surface. Similar conclusions were made by Holdren and Speyer [33], based on investigation of the dissolution of a potassium-rich feldspar using a flow-through cell reactor.

3.3. ANRnc Calculation by the Dissolution Cell Method

Silicates can affect waste rock drainage pH and the associated behaviour of contaminants in the later stages of AMD formation, through their long-term neutralisation capacities from dissolution. The ANRnc

due to dissolution of silicates can be used for long term economically-sustainable AMD management, potentially providing an initial design target for emplacement and cover design by comparing two parameters, ANRnc and AGR. Miller *et al.* [7] have proposed a methodology for calculation of non-carbonate ANC from long-term kinetic leach column tests of both silicates and real waste minerals, requiring assessment of the thickness of the top cover and the degree of saturation needed to decrease residual low-level acid generation to a rate that can be matched by the ANRnc. Three different methods are commonly used for calculation of ANRnc of silicates: mineralogical composition-based, the dissolution cell, and the column leach methods. In this study, the ANRnc values of the silicate samples were calculated based on: (1) dissolution data from silicate dissolution cell tests for the initial and long-term dissolution stages (*i.e.* non-steady and steady states); and (2) silicate compositions and the pH-dependent dissolution rates from the database [34] (Section 3.4).

The ANRnc was calculated for all silicate samples, using the concentration of major cations released from dissolution (*e.g.* K, Na, Ca, Mg or Al) and Eq. 1, and converted to $\text{mg H}_2\text{SO}_4 \text{ kg}^{-1} \text{ week}^{-1}$.

$$\text{ANRnc} = \frac{[(\text{Na} + \text{K}) + ((\text{Mg} + \text{Ca}) \times 2) + (\text{Al} \times 3)] \times 49}{m/\text{SA}} \quad (1)$$

where Na, K, Mg, Ca and Al are concentrations in mmol; 2 and 3 are the ionic charges of Ca, Mg, and Al; 49 is the factor for conversion of mmol H^+ to $\text{mg H}_2\text{SO}_4$; m is the sample mass in kg; and SA is the BET surface area of the sample in $\text{m}^2 \text{ g}^{-1}$.

Tables 2 summarises the calculated ANRnc of the four silicates for the non-steady state and steady state dissolution stages under different pH and flow rate conditions. It was found that ANRnc values for the

steady state conditions were generally smaller than for the non-steady state conditions.

At pH 2 and $4 \text{ L kg}^{-1} \text{ day}^{-1}$, the ANRnc of olivine dissolution was calculated to be 16,989 and 16,399 $\text{mg H}_2\text{SO}_4 \text{ kg}^{-1} \text{ week}^{-1}$ for the non-steady state and steady-state conditions, respectively. In comparison, the non-steady state and steady-state ANRnc values for olivine dissolution at pH 4 under otherwise identical conditions were only 2,160 and 2,045 $\text{mg H}_2\text{SO}_4 \text{ kg}^{-1} \text{ week}^{-1}$, respectively. For chlorite dissolution at $4 \text{ L kg}^{-1} \text{ day}^{-1}$, ANRnc were 1,893 $\text{mg H}_2\text{SO}_4 \text{ kg}^{-1} \text{ week}^{-1}$ (non-steady state) and 972 $\text{mg H}_2\text{SO}_4 \text{ kg}^{-1} \text{ week}^{-1}$ (steady state) at pH 2 and 101 $\text{mg H}_2\text{SO}_4 \text{ kg}^{-1} \text{ week}^{-1}$ (non-steady state) and 64 $\text{mg H}_2\text{SO}_4 \text{ kg}^{-1} \text{ week}^{-1}$ (steady state) at pH 4. For K-feldspar dissolution at $4 \text{ L kg}^{-1} \text{ day}^{-1}$, the non-steady state and steady-state values of ANRnc were 176 and 94 $\text{mg H}_2\text{SO}_4 \text{ kg}^{-1} \text{ week}^{-1}$ respectively at pH 2, while the non-steady state and steady-state ANRnc were around 11 and 2 $\text{mg H}_2\text{SO}_4 \text{ kg}^{-1} \text{ week}^{-1}$ at pH 4. The non-steady state and steady-state ANRnc of biotite (Figure 7) were 3,089 and 405 $\text{mg H}_2\text{SO}_4 \text{ kg}^{-1} \text{ week}^{-1}$ respectively at pH 2, and 260 and 87 $\text{mg H}_2\text{SO}_4 \text{ kg}^{-1} \text{ week}^{-1}$ respectively at pH 4.

At pH 2 and $12 \text{ L kg}^{-1} \text{ day}^{-1}$, the ANRnc of olivine dissolution was calculated to be 46,357 and 46,139 $\text{mg H}_2\text{SO}_4 \text{ kg}^{-1} \text{ week}^{-1}$ for non-steady state and steady state conditions respectively, but dramatically decreased to 2,560 and 2,434 $\text{mg H}_2\text{SO}_4 \text{ kg}^{-1} \text{ week}^{-1}$ at pH 4 and at the same flow rate. For chlorite dissolution at $12 \text{ L kg}^{-1} \text{ day}^{-1}$, ANRnc values were 4,080 $\text{mg H}_2\text{SO}_4 \text{ kg}^{-1} \text{ week}^{-1}$ (non-steady state) and 1,935 $\text{mg H}_2\text{SO}_4 \text{ kg}^{-1} \text{ week}^{-1}$ (steady-state) at pH 2, and 190 $\text{mg H}_2\text{SO}_4 \text{ kg}^{-1} \text{ week}^{-1}$ (non-steady state) and 102 $\text{mg H}_2\text{SO}_4 \text{ kg}^{-1} \text{ week}^{-1}$ (steady-state) at pH 4. For K-feldspar dissolution at $12 \text{ L kg}^{-1} \text{ day}^{-1}$, non-steady state and steady-state ANRnc were 211 and 118 $\text{mg H}_2\text{SO}_4 \text{ kg}^{-1} \text{ week}^{-1}$ respectively, while those at pH 4 were 50 (non-steady state) and 17

Table 2: Comparison of Calculated ANRnc ($\text{mg H}_2\text{SO}_4 \text{ kg}^{-1} \text{ week}^{-1}$) During the Non-Steady State and Steady State Dissolution Stages under Different Conditions

Silicate	$4 \text{ L kg}^{-1} \text{ day}^{-1}$				$12 \text{ L kg}^{-1} \text{ day}^{-1}$			
	pH 2		pH 4		pH 2		pH 4	
	N-SS	SS	N-SS	SS	N-SS	SS	N-SS	SS
Olivine	16,989	16,399	2,160	2,045	46,357	46,139	2,560	2,434
Chlorite	1,893	972	101	64	4,080	1,935	190	102
K-feldspar	176	94	11	2	211	118	50	17
Biotite	2,702	353	354	68	1,523	831	168	59

(N-SS: non-steady state; SS: steady state).

Table 3: Comparison of Surface area-Normalized Dissolution Rate Values Measured and Calculated from Literature ($\text{mol m}^{-2} \text{s}^{-1}$)

Silicate	Dissolution Rate (×10 ⁻¹¹ mol m ⁻² s ⁻¹)								Literature [*] (×10 ⁻¹¹ mol m ⁻² s ⁻¹)	
	4 L kg ⁻¹ day ⁻¹				12 L kg ⁻¹ day ⁻¹					
	pH 2		pH 4		pH 2		pH 4		pH 2 pH 4	
	N-SS	SS	N-SS	SS	N-SS	SS	N-SS	SS		
Olivine	104.2	100.6	13.3	12.5	284.4	283.1	15.7	14.9	3,765	340
Chlorite	4.2	2.2	0.2	0.1	9.2	3.9	0.6	0.2	1.7	0.2
K-feldspar	0.8	0.1	0.1	0.01	1.0	0.1	0.1	0.01	0.9	0.1
Biotite	7.0	1.4	0.9	0.2	4.0	2.2	0.4	0.2	8.1	0.3

* Kinetic dissolution rate from Palandri and Kharaka [35], Lowson *et al.* [36], Schweda and Kalinowski [37] and Bray *et al.* [38]; (N-SS: non-steady state; SS: steady state).

$\text{mg H}_2\text{SO}_4 \text{ kg}^{-1} \text{ week}^{-1}$ (steady state) respectively. The non-steady state and steady-state ANRnc of biotite dissolution were 1,850 and 1,146 $\text{mg H}_2\text{SO}_4 \text{ kg}^{-1} \text{ week}^{-1}$ at pH 2, and 130 and 45 $\text{mg H}_2\text{SO}_4 \text{ kg}^{-1} \text{ week}^{-1}$ at pH 4.

The results above indicate that the ANRnc of the four selected silicates at pH 2 were up to one order of magnitude higher than at pH 4 (Table 2) and that the faster flow rate resulted in greater ANRnc. Table 3 summarises the surface area-normalised dissolution rates (non-steady state and steady state) for different conditions in this study and the dissolution rates reported in the literature ($\text{mol m}^{-2} \text{s}^{-1}$). It is clear that the olivine dissolution rate is one order of magnitude less than those from the literature, but dissolution of other silicates is within the same order of magnitude as compared to published data. The dissolution rates of these four silicate minerals all decreased with increasing solution pH from 2 to 3.

In order to determine whether the ANRnc of these silicate minerals can match AGR, pyrite dissolution rate was calculated based on flow-through dissolution at pH 2 and 4 and at the flow rates of 4 and 12 L $\text{kg}^{-1} \text{ day}^{-1}$ (Table 4). At 4 L $\text{kg}^{-1} \text{ day}^{-1}$, AGR due to pyrite dissolution was 1,873 and 2,251 $\text{mg H}_2\text{SO}_4 \text{ kg}^{-1} \text{ day}^{-1}$ at pH 2 and 4, respectively. In contrast, at 12 L $\text{kg}^{-1} \text{ day}^{-1}$ pyrite AGR values were 2,260 and 3,429 $\text{mg H}_2\text{SO}_4 \text{ kg}^{-1} \text{ day}^{-1}$ at pH 2 and 4 respectively, greater than those at 4 L $\text{kg}^{-1} \text{ day}^{-1}$.

Table 4: AGR ($\text{mg H}_2\text{SO}_4 \text{ kg}^{-1} \text{ week}^{-1}$) Calculated Based on Pyrite Dissolution Data at pH 2 and 4 and at 4 and 12 L $\text{kg}^{-1} \text{ day}^{-1}$

Flow Rate (L $\text{kg}^{-1} \text{ day}^{-1}$)	pH 2	pH 4
4	1,873	2,251
12	2,260	3,429

Our results indicate that the non-steady state ANRnc (ANRnc-NSS) are greater than the steady-state ANRnc (ANRnc-SS). As the dissolution of olivine reached steady-state from the beginning of dissolution (0 or 2 weeks), the ANRnc-NSS and ANRnc-SS are almost identical. Compared with the pyrite AGR at pH 2, the ANRnc-NSS and ANRnc-SS of olivine dissolution is much greater, regardless of flow rate (Tables 2 vs. 4). For chlorite dissolution, it was found that only the ANRnc-NSS could match the pyrite AGR at pH 2 irrespective of the flow rate, while the ANRnc-SS of chlorite dissolution is smaller than the pyrite AGR under otherwise identical conditions (Tables 2 and 4). For biotite dissolution, the ANRnc-NSS (2,702 $\text{mg H}_2\text{SO}_4 \text{ kg}^{-1} \text{ week}^{-1}$; Table 2) is greater than pyrite AGR only at pH 2 and at 4 L $\text{kg}^{-1} \text{ day}^{-1}$ (Table 4). For K-feldspar dissolution, it appears that the ANRnc-NSS and -SS at pH 2 and pH 4, regardless of the flow rate, could not match the AGR of pyrite dissolution under the same conditions.

3.4. Calculation of ANRnc of Silicate Minerals using the Mineralogical Method

The ANRnc of a silicate mineral can also be calculated using quantitative mineralogical compositions and dissolution rates, as has been detailed in Smart *et al.* [6] and Miller *et al.* [7], which requires kinetic dissolution data from e.g. Palandri and Kharaka [35] and Lowson *et al.* [36]. According to Miller *et al.* [7], silicate mineralogical compositions can be used in conjunction with kinetic dissolution data for fast and simple estimation of maximum acid neutralisation capacity for the long-term ANRnc assessment of a silicate mineral. Therefore, the long-term ANRnc of the main silicate component of each silicate sample examined in this study was also calculated using the quantitative mineralogy and rate parameters from

Palandri and Kharaka [35] for a specific pH condition (Table 5). The minor impurity phases present in each silicate sample were not included in ANRnc calculations. In addition, the surface area of the major phase (olivine, chlorite, biotite and K-feldspar) in each silicate sample was assumed to be identical to that of the entire sample.

The mineralogy of these selected olivine, chlorite, biotite and K-feldspar samples were determined by QXRD analysis (Table 1), EPMA and bulk assay. ANRnc of silicate minerals were calculated and then compared with those measured from the dissolution cell tests.

Average ANRnc values calculated based on both the dissolution cell method (data from Table 2) and the mineralogical method are shown in Table 6. The ANRnc values of olivine dissolution measured using the dissolution cell tests were 16,624 (at 4 L kg⁻¹ day⁻¹) and 45,713 (at 12 L kg⁻¹ day⁻¹) at pH 2 and 2,610 (at 4 L kg⁻¹ day⁻¹) and 1,653 (at 12 L kg⁻¹ day⁻¹) at pH 4, in the same order of magnitude as compared to those calculated based on the mineralogical method. For all other silicate minerals, the ANRnc calculated using the two methods are also largely within the same order of magnitude. In summary, these results indicate that the long-term ANRnc can be predicted based on simple short-term dissolution cell tests. The advantage of

using the dissolution cell method is that it can provide both ANRnc-NSS and ANRnc-SS, while the mineralogical method only gives the 'average' ANRnc in the long term.

4. CONCLUSIONS

Flow-through dissolution tests of olivine, biotite, K-feldspar, chlorite and pyrite were carried out at pH 2 and 4 and at 4 and 12 L kg⁻¹ day⁻¹ to investigate both the initial non-steady state and long-term steady-state dissolution kinetics for calculation of ANRnc. The ANRnc of olivine dissolution (both non-steady state and steady state) calculated using the dissolution cell method can match the AGR from pyrite dissolution only under the conditions of pH 2 and the flow rate of 12 L day⁻¹ kg⁻¹. For both chlorite and biotite, ANRnc from non-steady dissolution can only match the AGR from pyrite dissolution under the conditions of pH 2 and 12 L day⁻¹ kg⁻¹. For K-feldspar, it appears that ANRnc cannot match the pyrite AGR under any conditions. The significant increases in effluent pH for the dissolution of olivine (non-steady state and steady state), chlorite (non-steady state only) and biotite (non-steady state only) at pH 4 suggest that these three minerals have greater potential for treatment of mildly acidic AMD wastewaters. Our results also suggest that the flow rate is critical in controlling the effluent pH. The kinetic data can provide an estimate of the possible

Table 5: Calculated ANRnc (mg H₂SO₄ kg⁻¹ week⁻¹) of each Silicate at pH 2 and pH 4 Based on the Main Component Only

Silicate	Formula ^a	Mass Fraction ^b	ANRnc pH 2	ANRnc pH 4
Olivine	(Ca _{0.05} Mg _{1.79} Fe _{0.16})SiO ₄	0.90	13,240	2,004
Chlorite	(Mg _{2.78} Fe _{2.22})Al ₂ Si ₃ O ₁₀ (OH) ₈	0.81	262	32
K-feldspar	(K _{0.79} Na _{0.21})AlSi ₃ O ₈	0.94	970	24
Biotite	K _{0.96} Na _{0.04} Mg _{2.72} Fe _{0.28} AlSi ₃ O ₁₀ (F,OH) ₂	0.93	3,351	203

^a Compositions determined by EPMA; ^b mass fraction obtained from QXRD analysis.

Table 6: Measured Average ANRnc (mg H₂SO₄ kg⁻¹ week⁻¹) at pH 2 and 4 from Dissolution Cell Tests vs. Calculated ANRnc

Silicate	pH 2			pH 4		
	4 L kg ⁻¹ day ⁻¹	12 L kg ⁻¹ day ⁻¹	Calculated	4 L kg ⁻¹ day ⁻¹	12 L kg ⁻¹ day ⁻¹	Calculated
Olivine	16,624	45,713	13,240	2,610	1,653	2,004
Chlorite	1,104	1,539	262	64	167	32
K-feldspar	139	123	970	30	47	24
Biotite	1,089	1,157	3,351	163	76	203

matching of AGR by ANR in real AMD wastes and an assessment of the amount of additional alkalinity required if ANRnc from silicate dissolution is lower than AGR.

The ANRnc measured based on the dissolution cell method and calculated using the mineralogy and published kinetic data are in the same order of magnitude, suggesting that both the short-term dissolution cell and the mineralogical methods are simple and reliable for estimating ANRnc. Results showed that despite their relatively small ANRnc values for steady-state conditions, silicates can provide substantial initial non-steady state neutralisation by ion exchange with protons. The results from this work may provide a sound, economic and environmental platform to help the mining industry develop simple and economically-sustainable methods to minimise AMD. The advantage of the dissolution cell method is that it can provide both non-steady state and steady-state ANRnc.

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