



# Dissolution kinetics of soil clays in sulfuric acid solutions: Ionic strength and temperature effects



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## ABSTRACT

Significant amounts of sulfuric acid ( $\text{H}_2\text{SO}_4$ ) rich saline water can be produced by the oxidation of sulfide minerals contained in inland acid sulfate soils (IASS). In the absence of carbonate minerals, the dissolution of phyllosilicate minerals is one of very few processes that can provide long-term acid neutralisation. It is therefore important to understand the acid dissolution behavior of naturally occurring clay minerals from IASS under saline–acidic solutions. The objective of this study was to investigate the dissolution of a natural clay-rich sample under saline–acidic conditions (pH 1–4; ionic strengths = 0.01 and 0.25 M; 25 °C) and over a range of temperatures (25–45 °C; pH 1 and pH 4). The clay-rich sample referred to as Bottle Bend clay (BB clay) used was from an IASS (Bottle Bend lagoon) in south-western New South Wales (Australia) and contained smectite (40%), illite (27%), kaolinite (26%) and quartz (6%). Acid dissolution of the BB clay was initially rapid, as indicated by the fast release of cations (Si, Al, K, Fe, Mg). Relatively higher Al (pH 4) and K (pH 2–4) release was obtained from BB clay dissolution in higher ionic strength solutions compared to the lower ionic strength solutions. The steady state dissolution rate (as determined from Si, Al and Fe release rates;  $R_{\text{Si}}$ ,  $R_{\text{Al}}$ ,  $R_{\text{Fe}}$ ) increased with decreasing solution pH and increasing temperature. For example, the highest  $\log R_{\text{Si}}$  value was obtained at pH 1 and 45 °C ( $-9.07 \text{ mol g}^{-1} \text{ s}^{-1}$ ), while the lowest  $\log R_{\text{Si}}$  value was obtained at pH 4 and 25 °C ( $-11.20 \text{ mol g}^{-1} \text{ s}^{-1}$ ). A comparison of these results with pure mineral dissolution rates from the literature suggests that the BB clay dissolved at a much faster rate compared to the pure mineral samples. Apparent activation energies calculated for the clay sample varied over the range  $76.6 \text{ kJ mol}^{-1}$  (pH 1) to  $37.7 \text{ kJ mol}^{-1}$  (pH 4) which compare very well with the activation energy values for acidic dissolution of monomineralic samples e.g. montmorillonite from previous studies. The acid neutralisation capacity (ANC) of the clay sample was calculated from the release of all structural cations except Si (i.e. Al, Fe, K, Mg). According to these calculations an ANC of 1.11 kg  $\text{H}_2\text{SO}_4$ /tonne clay/day was provided by clay dissolution at pH 1 ( $I = 0.25 \text{ M}$ , 25 °C) compared to an ANC of 0.21 kg  $\text{H}_2\text{SO}_4$ /tonne clay/day at pH 4 ( $I = 0.25 \text{ M}$ , 25 °C). The highest ANC of 6.91 kg  $\text{H}_2\text{SO}_4$ /tonne clay/day was provided by clay dissolution at pH 1 and at 45 °C ( $I = 0.25 \text{ M}$ ), which is more than three times higher than the ANC provided under the similar solution conditions at 25 °C. In wetlands with little solid phase buffering available apart from clay minerals, it is imperative to consider the potential ANC provided by the dissolution of abundantly occurring phyllosilicate minerals in devising rehabilitation schemes.

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## 1. Introduction

Iron sulfide rich sediments are referred to as acid sulfate soils (ASS) due to their potential to release sulfuric acid upon exposure

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to the atmosphere (Fitzpatrick et al., 1996). Minerals in the soil matrix can provide 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 the resultant ecological impact.

The presence of large quantities of sulfidic sediments in inland wetlands of Murray Darling Basin (MDB) have been reported

previously (Fitzpatrick et al., 1996). The accumulation of sulfidic materials in these wetlands is proposed 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 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). It is also known that some of these identified wetlands have acidified in the recent past in response to natural or human-induced drying events (Bibi et al., 2011a; Glover et al., 2011). In wetland sediments with little or no carbonate mineral content, the acid dissolution (or chemical weathering) of phyllosilicate minerals is probably the only significant acid neutralisation pathway (Whitworth et al., 2014). The reaction of saline-acidic solutions with phyllosilicates is therefore of considerable interest in understanding the acid neutralisation process in inland acid sulfate soils (IASS). Considerable efforts have been devoted to study the dissolution mechanisms of individual phyllosilicates under laboratory conditions (Amram and Ganor, 2005; Bibi et al., 2011c; 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). Only limited research has been done on the acid dissolution of natural clay samples or phyllosilicates isolated from soils (Jurjovec et al., 2002; Salmon and Malmstrom, 2006; Shaw and Hendry, 2009), particularly with a focus on comparing the neutralisation potential of different mineral groups such as carbonates, oxide minerals and phyllosilicates. To our knowledge there is no published research on the dissolution of natural soil clays such as those encountered in IASS under highly-saline and acidic conditions.

The aim of this study was to investigate the dissolution behavior of a natural polymineralic clay sample under conditions of high salinity and high ( $\text{SO}_4^{2-}$  based) acidity, mimicking the composition of IASS. The specific objective of this research was to measure the dissolution rates of natural clay in acidic solutions ( $\text{SO}_4^{2-}$  based) over the pH range 1–4 and at two ionic strengths (0.01 and 0.25 M), and in doing this, determine the capacity of these clays to buffer acidity generated through oxidation of sulfide minerals contained in IASS.

## 2. Materials and methods

### 2.1. Clay sample

The clay sample used in this study was separated from a soil core collected from an inland wetland, (Bottle Bend (BB) lagoon) located adjacent to the Murray River in the south-west of New South Wales, Australia. The sediments at the BB wetland contain a sulfidic sediment layer between a clay layer below and an overlying oxidized (sulfuric) layer (Fig. A1). The depths of different layers in the partially submerged soil core collected from the wetland were: sulfuric layer – 5 cm, sulfidic layer – 20 cm and 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 drought over the 2002–2010 period resulted in lowering of the water table and the development of highly saline conditions. The exposure of these sulfidic materials which were subsequently oxidized to produce highly acidic conditions (pH ~ 2) in conjunction with very high salinity (EC up to 216,000  $\mu\text{S}/\text{cm}$ ).

### 2.2. Sample pre-treatment and characterization

The dissolution experiments presented in this study were performed using the clay-sized fraction (<2  $\mu\text{m}$ ) separated from BB sediments. The clay fraction was isolated by a sedimentation-resuspension procedure and saturated with Na, following the methodology described previously (Bibi et al., 2011c). A small amount of the separated clay fraction was saturated with Ca by repeated shaking with  $\text{CaCl}_2$  solutions of decreasing concentration (0.1 and 0.01 M  $\text{CaCl}_2$ ) followed by repeated washing 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 laboratory analyses and characterization. The Na-saturated clay was used in all dissolution experiments reported in this work; while the Ca-saturated clay sample was used only for random powder X-ray diffraction (XRD) and clay mineral quantification.

The specific surface area (SSA) of the Na-saturated clay sample was determined using a Quantachrome™ Autosorb-1 surface area analyser, after outgassing at 110 °C. The SSA of the clay sample was determined to be 104.5  $\text{m}^2 \text{g}^{-1}$  by the five-point  $\text{N}_2$  adsorption method (Braunauer et al., 1938).

### 2.3. Chemical composition determination

Table 1 shows the chemical composition of the Na-saturated clay sample as determined by X-ray fluorescence (XRF) spectroscopy (Norris and Hutton, 1977). The detection limits of XRF for  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{MgO}$ ,  $\text{CaO}$ ,  $\text{K}_2\text{O}$ , and  $\text{Na}_2\text{O}$  analyses were 61.5, 25.6, 27.7, 11.7, 59.7, 12.4, 9.7, and 164.2  $\text{mg kg}^{-1}$ , respectively, and the accuracy of XRF results was better than 1 wt.%. Iron(II) content was determined by the 1,10-phenanthroline colorimetric method (Amonette and Templeton, 1998). The atomic ratios calculated from the chemical composition (XRF data) of the Na-saturated clay are presented in Table 2.

### 2.4. X-ray diffraction analysis

The mineralogy of the Na-saturated clay fraction of the BB sample was determined by X-ray diffraction (XRD) analysis of both basally and randomly oriented samples (GBC MMA:  $\text{Cu K}\alpha$  radiation,  $\lambda = 1.5406 \text{ \AA}$ , operating conditions of 35 kV and 28.5 mA).

Randomly oriented XRD pattern of the clay powder was collected from 4° to 75°  $2\theta$  at a step size of 0.02°  $2\theta$  and a scan speed of 1.0°  $2\theta \text{ min}^{-1}$ . For the identification of phyllosilicates, basally oriented clay samples were analyzed after standard pre-treatments, i.e. Mg-saturated and air-dried, Mg-saturated and ethylene glycol solvated, K-saturated and air-dried, K-saturated and heated at

**Table 1**  
Bulk chemical composition (XRF) of Na-saturated Bottle Bend (BB) clay fraction.

Oxide	wt.%
$\text{SiO}_2$	49.17
$\text{Al}_2\text{O}_3$	23.75
$\text{TiO}_2$	0.91
$\text{Fe}_2\text{O}_3$	7.13
$\text{FeO}$	1.16
$\text{MnO}$	0.02
$\text{MgO}$	1.08
$\text{CaO}$	0.03
$\text{Na}_2\text{O}$	0.71
$\text{K}_2\text{O}$	2.27
$\text{P}_2\text{O}_5$	0.07
LOI	14.25
Total	100.55

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