Weathering of sulphide minerals at circum-neutral-pH in semi-arid/arid environments: influence of water content

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Abstract
Despite its importance to mine-sites in inland Australia, little is known about the rate of pyrite oxidation at circum-neutral-pH where dry conditions are the norm. In semi-arid and arid environments, oxidation of sulphide minerals (e.g. pyrite) is influenced by the supply of water which often occurs as sporadic, intense rainfall events. In this research, columns containing mixtures of pyrite dominated sulphide, limesand and quartz-sand had their water saturation contents maintained at 0.1 %, 25 %, 70 % and 95 %, and were aged at 20°C for periods ranging up to 12 weeks. After different ageing times, selected columns were removed, and the mineral mixtures extracted with deionised water to determine the amount of sulphate produced. Sulphate production peaked at the intermediate water contents. Reduced sulphate production near saturation reflects the well known limiting oxygen diffusion rate in porous media at high water contents. Reduced sulphate production at the dry-end of the moisture range is believed to reflect conditions (e.g. critical water film thickness to allow oxidation and/or inhibition by high reaction product concentrations) at reaction sites on pyrite-grain surfaces that stifle oxidation, despite oxygen supply being non-limiting in the air-filled pores. The findings of this study have important environmental implications for the management of pyritic mine-wastes in semi-arid/arid settings.

Introduction
When exposed to the atmosphere, iron-sulphur minerals (e.g. pyrite) typically oxidise and generate acidity (Nordstrom 1982). The overall oxidation of pyrite may be described by the following reaction:

$$FeS_{2(s)} + 15/4O_{2(g)} + 7/2H_2O_{(l)} \rightarrow 2SO_4^{2-}{}_{(aq)} + Fe(OH)_{3(s)} + 4H^+{}_{(aq)} \quad (1)$$

Reaction (1) implies that both oxygen and water are required for pyrite oxidation to proceed to completion. In the case of waste-rock weathering at mine-sites, the pH regime is determined by the pH-buffering properties of the groundmass minerals (e.g. carbonates and silicates). Where carbonate minerals are present, reaction (1) will occur at circum-neutral-pH for as long as the carbonates remain to neutralise the acid produced through pyrite oxidation.

Since oxidation takes place at reaction sites on the pyrite-grain surface, the rate of reaction (1) is sensitive to the formation of solid "secondary-oxidation" products (e.g. ferrihyrite-type phases) that act as a physical barrier to reactants (e.g. O_2). The formation of solid "secondary-oxidation" products at circum-neutral-pH has been shown many times in earlier research on pyrite oxidation (Moses and Herman 1991; Nicholson *et al.* 1988; Nicholson *et al.* 1990). The formation of alteration rims should be favored at low water contents where thin films of porewater become saturated with solutes derived from pyrite oxidation.

Materials at or near water saturation exhibit reduced oxygen fluxes owing to low solubility of oxygen in water (8.6 g/m^3 at 20°C) and the rather low oxygen diffusivity of ~2x10^{-9} m^2/s in water relative to 1.78x10^{-5} m^2/s in air (Nicholson *et al*. 1989; Simms *et al.* 2000). Thus, oxygen influences on pyrite oxidation depend on the amount of existing pore-water and gas within the pore spaces. Guevremont *et al.* (1998a and 1998b) and Rosso *et al.* (1999) have examined the influence of coadsorbed water and oxygen on the oxidation of FeS_2. They observed that oxygen alone has no effect on non-defect sites of FeS_2 and is less effective at oxidizing mono-sulphide defects than water. In contrast, the exposure of water + oxygen gas mixture resulted in oxidation of both mono- and disulphide species. Oxygen from water and not free O_2 is incorporated into the resulting sulphate formed from oxidative dissolution of pyrite (Henderson 2002).

Oxidation of sulphides will therefore occur at varying rates and produce different products, depending on water content (Borek 1994; Watzlaf 1992). Recent studies (Jeon *et al.* 2003; and Moses and Herman 1991) suggest that Fe^{3+} is the preferred sulphide oxidant at circumneutral pH, but that during dry phases of wet-dry cycles, pyrite surfaces may be armoured against oxidation by various amorphous or poorly crystalline Fe^{3+} oxides, hydroxides or oxy(hydroxy)sulphate minerals (Jambor *et al.* 2002; Nordstrom 1982).

Despite its importance to environmental management throughout the mining provinces of inland Australia, little is known of the nature and rate of mine-waste weathering where dry conditions are the norm, and seldom interrupted by wet spells. This investigation, under the hypothesis that in semiarid arid environments weathering of sulphide minerals and solute transport are strongly influenced by water content, has been undertaken to primarily provide an indication of the kinetics of pyrite oxidation at circum-neutral-pH. For this a reference mineral mixture (pyrite + calcitic sand + quartz sand), was incubated in a series of columns. Water contents in columns were set at a range of values, with oxidation rates inferred from sulphate production.

Methods

Preparation of pyrite mixtures

Well formed octahedral pyrite crystals (originally from Perú) were ground to a mean grain size of 108 µm (90 – 125 µm). To remove finer particles, samples were rinsed with deionised water until the supernatant was clear. Samples then were dried in a desiccator and resieved. To remove potential ferric hydroxide precipitates, samples were rinsed using a 6N HCl solution, rinsed thoroughly using deionised water and reagent-grade acetone, and dried in a desiccator under vacuum.

Quartz sand (99.5% SiO_2) with grain sizes in the range 150 to 250 µm was used as an inert matrix. To remove potential organic particles sand samples were washed with 10% peroxide and rinsed-dried-rinsed-dried with deionised water.

A calcitic sand (from Lancelin, Western Australia) was used to equilibrate the system at a circumneutral pH. This material contains magnesian calcite as the major carbonate and aragonite in minor but significant proportions. Neutralizing values were between 88 – 89% based on titration with HCl (Whitten 2002). To remove potential organic particles in sieved (150 to 250 µm) calcitic sand, the sample was washed three times with freshly prepared sodium hypochlorite solution (pH 9.5) followed by rinsing with 2 percent sodium carbonate-sodium bicarbonate solution adjusted to pH 9.5. Rinsed calcitic sand samples were dried at 105°C overnight.

After pre-treatment bulk composite-samples were uniformly mixed in the proportions 5% pyrite, 5% calcitic sand and 95% quartz sand. Equal weights of this mixture were packed into 30mm height × 30mm diameter columns, ensuring that the packing process did not result in separation of the mixture. The final mean dry bulk density in columns was 1.60 gcm^{-3}.

Water content

Columns at 25%, 70% and 95% saturation were placed into a perspex chamber designed to maintain a 100 % humidity environment. Samples at 0.1% saturation were placed in a desiccator to minimise absorption of water.

Sample solutions for analysis of sulphate were extracted at the end of each reaction time (Table 1). A number of columns belonging to each group were removed from the chambers and weighed. The column contents were placed into 120 mL capacity vials with 50 mL degassed deionised water. These were placed in an end-over-end shaker for about 18 hours and centrifuged for 15 minutes at 3500 rpm. The pH and electrical conductivity (EC) of supernatants were determined immediately, and a portion of extract was frozen pending analysis for sulphate by ion chromotography.

Table 1. Experimental design showing number of replicates as a function of relative saturation and reaction time.

Water regime in column	*Reaction times*				
	3.5 days	1 week	3 weeks	6 weeks	12 weeks
Group A: (95 % saturation)	3	3	3	3	3
Group B: (70% saturation)	3	3	3	3	3
Group C: (25% saturation)	3	3	3	3	3
Group D: Air dried (0.1% saturation)	2	3	3	3	2
Total columns	11	12	12	12	11

Table 2. Summary of physical parameters of columns containing a mixture of: sand (95%; mean 200 µm), pyrite (5%; mean 108 µm) and calcitic sand (5%; mean 200 µm). (Particle density of mixtures: mean 2.69 g cm^{-3}, median 2.69 g cm^{-3}, and std. dev. 0.02 g cm^{-3}).

Initial dry conditions of columns mixture						
	Gravimetric water content (gg^{-1})		Volumetric water content, θ, (cm^{3}cm^{-3})		Sample bulk density, ρ, (gcm^{-3})	
	Mean	Std. Dev.	Mean	Std. Dev.	Mean	Std. Dev.
	0.006	0.000	0.010	0.001	1.677	0.106
Final conditions of columns mixture at selected saturations (i.e. after ageing period)						
Relative saturation (%)	Gravimetric water content (gg^{-1})		Volumetric water content (cm^{3}cm^{-3})		Sample bulk density (gcm^{-3})	
	Mean	Std. Dev.	Mean	Std. Dev.	Mean	Std. Dev.
0.10	0.0004	0.0004	0.001	0.001	1.586	0.116
25.3	0.064	0.009	0.106	0.015	1.647	0.106
70.5	0.189	0.017	0.299	0.028	1.576	0.032
94.2	0.236	0.008	0.380	0.013	1.602	0.029

Determination of total sulphur, sulphate and pyrite mineralogy

Pyrite samples were analysed for S by pyrolysis using a LECO tube furnace and quartz dilution. Sulphate-S (SO_4^{2-}) from pyrite was determined gravimetrically following extraction with sodium carbonate. XRD analysis of pyrite samples was performed using an automated Philips XRD system using Cu K-α radiation. Sulphate from extracted solutions was determined by ion chromatography; blanks and sample duplicates were analyzed with each batch of samples. Pyrite contained a mean 53.7% of total sulphur and 1% of sulphur as SO_4^{2-}. XRD analysis showed the sample is pyrite dominated with traces of halite and barite.

Results

Water content of columns

The physical properties of mixtures are presented in Table 2. This shows that θ did not vary significantly at each relative saturation value. The weight of samples remained constant during ageing period with weight changes having a mean of 0.06g, with a standard deviation of 0.35g.

pH and Electrical conductivity

From a total of 58 readings, the initial pH mean was 8.66 ± 0.4. After each ageing period mean pH slightly decreased down to 8.6 ± 0.9. Initial electrical conductivity presented a mean of 0.74 ± 0.17 mS/cm and after ageing period readings presented a mean of 0.22 ± 0.1 mS/cm.

Sulphate concentration of extracted solutions

Water-extractable sulphate is taken to largely represent the amount of sulphate produced via pyrite oxidation during the various ageing-periods. Figure 1 show that SO_4^{2-} production varied in relation to the degree of saturation and ageing time. In samples with 95% saturation, sulphate production ranged from an initial mean of 1.8 mg SO_4^{2-}/kg sample up to a mean of 301 mg SO_4^{2-}/kg sample after 12 weeks of reaction. In contrast, in samples at air-dried conditions sulphate production ranged from an initial mean of 2.4 mg SO_4^{2-}/kg sample up to a mean of 24.8 mg SO_4^{2-}/kg sample at 12 weeks. In samples with intermediate degrees of saturation, namely 70% and 25%, sulphate production increased substantially during the experiment. At 70% saturation sulphate production increased from an initial mean of 2.9 mg SO_4^{2-}/kg sample, up to a mean of 485.8 mg SO_4^{2-}/kg sample. At 25% saturation, sulphate production

increased from an initial mean of 8.5 mg SO_4^{2-}/kg sample up to a mean of 1179 mg SO_4^{2-}/kg sample for the 12 weeks oxidation.

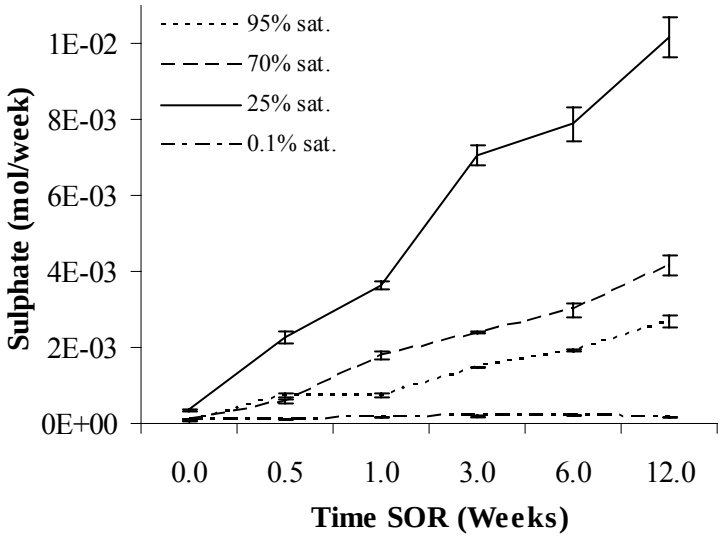

Figure 1. Sulphate concentrations in function to sulphide ageing-periods.

Net sulphate produced after 12 weeks of pyrite oxidation, calculated from the difference between the final and the initial production of SO_4^{2-}, is presented in Figure 2. This shows that the highest amounts of SO_4^{2-} relate to the intermediate saturations of samples, 25% and 70%, and the lower production relates to the extreme saturations, i.e. air-dried conditions (0.1%) and 95%.

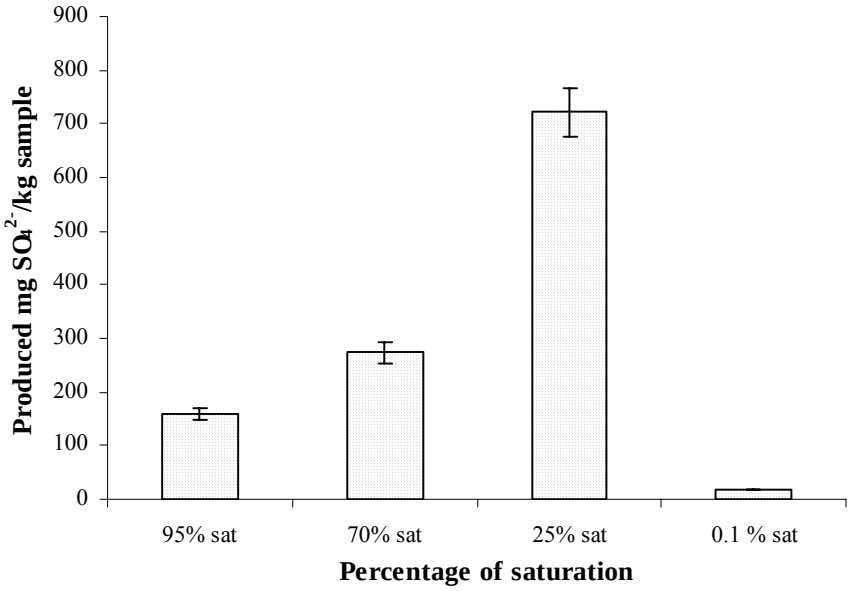

Figure 2. Net produced sulphate after 12 weeks of pyrite oxidation in relation to relative saturation.

When sulphide oxidation rates (SOR) are compared in relation to time (days), the rate of sulphate production substantially declines (Figure 3).

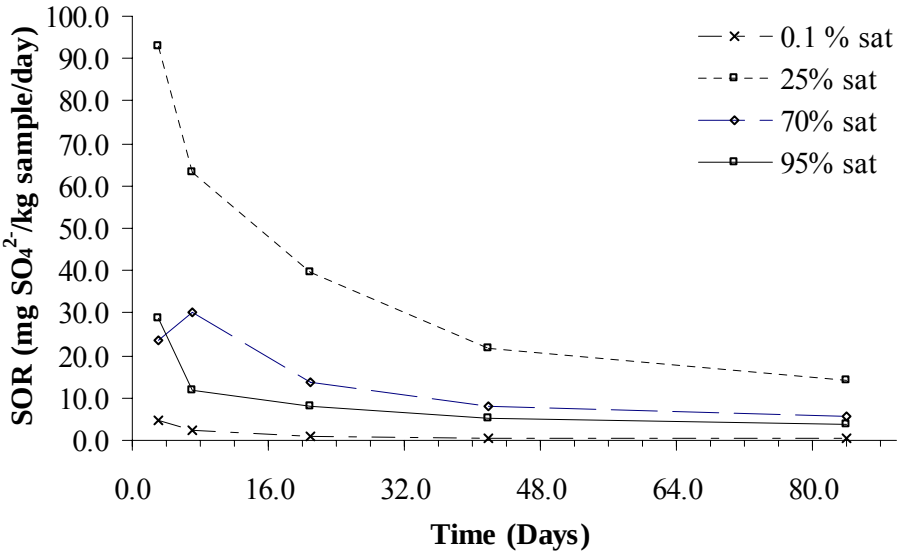

Figure 3. Rates of suphide oxidation as a function of time.

Discussion

Sulphide oxidation rates, as shown in Fig. 3, give a clear evidence for decreased reactivity of sulphide minerals as ageing time increased despite negligible pyrite dissolution. However it is also observed that the dissolution of pyrite directly relates to the degree of media saturation (Fig. 2). Oxidation of pyrite at near-saturated conditions is limited by the oxygen available by diffusive transport and, the kinetics of sulphide oxidation by O_2 is extremely slow at higher saturation conditions (Evangelou 1995; Holmes and Crundwell 2000; Rose and Cravotta 1998).

Sulphate production peaked at the intermediate water contents, i.e. at 25% and 70% saturation. Under such unsaturated conditions, the pores in solid media (especially large pores) are partially gas-filled and create interconnected channels through which oxygen can diffuse more rapidly. At the air-water interface, O_2 is dissolved with H_2O, and as a result there is a more aggressive oxidation of exposed sulphide surfaces (Rosso *et al.* 1999). Our results, especially at 25% saturation, show agreement with these prior aqueous-based observations on pyrite oxidation, with regard to the effects of H_2O and O_2 on pyrite oxidation.

The reduced production of sulphate at the dry-end of the moisture range (Fig. 2) has important environmental implications for the rate of acidification in semi-arid/arid settings where oxygen availability is most likely non-limiting. Within dry environments, water typically fills very small pores and occurs as films on particle surfaces. The mean nominal adsorbed water thickness (γ) in the 0.1% saturated mixtures is 3.1 x 10^{-6} cm (calculated by dividing the mixture's volumetric water content by the surface area):

$$\gamma = \frac{\theta r_s \rho_s}{3\rho_{bulk}} \tag{2}$$

where r_s (cm) the mean particle radius for a given particle size class, ρ_s (gcm^{-3}), the particle density, and ρ_{bulk}, the mixture's bulk density (gcm^{-3}). The mean particle radius for the mixture's particle-size class was calculated from:

$$r_s = \frac{d_{\max} + d_{\min}}{4} \tag{3}$$

where d_{max} and d_{min} are maximum and minimum effective particle diameter (cm) for the given size class.

Calculations based on the assumption that the oxidation of the pyrite can be defined according to the stoichiometric formula, Eq. (1), indicates that the mean 9.0 x 10^{-5} moles of SO_4^{2-} corresponds to 8.7 × 10^{-4} moles of water, and this represents a 10 fold excess of water in the system at 0.1% saturation. An apparent stoichiometric excess of water, however, may be misleading due to decreased water activity at high ionic strength or from interactions of water at particle surfaces. A water limitation effect can not therefore be discounted. Dold and Fontboté (2002) indicated that due to the lack of water in the hyperarid climate of the Atacama Desert (Chile), SOR decreased and the slow continuing oxidation of sulphide was attributed to fine-grained media in which, due to their higher water holding capacity, localized humid environments can be expected.

Conclusions

Water-extractable sulphate production, as measure of pyrite oxidation, was substantially decreased at very low water contents. This means that in semi-arid/arid settings, where oxygen availability is invariably non-limiting, water availability is the rate determining factor for sulphide oxidation. We also found that, under saturated conditions, in which there is limited availability of oxygen, sulphide will continuously oxidise but at low rates. Sulphate production at intermediate water contents reflect a continuous and more rapid sulphide oxidation reaction driven by the mixture of water and O_2. However, it is clear that the water content is the effective parameter controlling SOR. Contact time of water and the pyrite particle surfaces is as well a key component in comprehending SOR. Our results, give a clear indication that sulphide oxidation rate is not constant. Overall, the reactions of pyrite in relation to water content reflect the various environmental conditions under which sulphide can be oxidized.

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