

PRELIMINARY RATES OF SULFIDE OXIDATION UNDER CIRCUM-NEUTRAL AND ACIDIC CONDITIONS: LOVEDAY BASIN, LOWER MURRAY FLOODPLAINS, SOUTH AUSTRALIA

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INTRODUCTION

The Loveday Basin is an evaporative disposal basin that has received saline groundwater and irrigation discharge for the last 30 years. Continual evaporation has concentrated sulfur which, combined with a permanent water cover, has led to the formation of sulfidic material, which can potentially be harmful to the environment (LAMONTAGNE et al., 2004). The basin also has high carbonate concentrations with sufficient buffering capacity to neutralise the potential acidity from pyrite oxidation, giving the basin a bulk neutral pH. The process of oxidation at circum-neutral pH is currently poorly understood and suggested mechanisms ranging from abiotic O₂ and Fe^(II) oxidation to biotic oxidation in acidic micro-environments (BIERENS DE HAAN et al., 1994; MIELKE et al., 2003; MOSES and HERMAN, 1991; NORDSTROM and SOUTHAM, 1997). The following describes some preliminary results from laboratory experiments aimed at determining the processes, rates and microbial control of sulfide oxidation at neutral and low pH in the Loveday Basin.

METHODS

Sediments from the Loveday Basin were analysed for mineral composition and bulk chemistry by X-ray diffraction, X-ray fluorescence and scanning electron microscopy, whilst the sulfur fractions were determined by LECO, chromium-reducible-sulfur and acid-volatile-sulfur. Sulfide-rich sediments and sulfidic materials were oxidised in batch experiments with 10 g of wet sample to 150 ml of Milli-Q water. Sediment slurries were kept aerated by continual mixing on an orbital-shaker at 2000 rpm with water samples taken for physiochemical parameters and analysed for cations via Inductively Coupled Plasma –Atomic Emission Spectroscopy.

RESULTS AND DISCUSSION

SULFIDE-RICH SEDIMENTS AND SULFIDIC MATERIAL

Partial draining of the Loveday Basin has produced three distinct surface zones: ‘wet’ sediments; ‘dry’ sediments; and ‘wet-dry’ sediments that undergo intermittent wetting and drying. The different water regimes of these three zones have produced distinct sediment textures and distinct distributions of sulfides and carbonate (Table 1; WALLACE et al., 2006). The basin sediments/soils, as a whole, have sufficient carbonate neutralising capacity to counter the potential acidity from sulfide oxidation and, for the most part, where sulfides are most concentrated so is carbonate. In some areas sediments have a higher ratio of sulfides to carbonate, typically from 10-40 cm depth in the wet-dry zone, forming localised acidic horizons (i.e. sulfuric materials) with jarosite mottles.

Table 1: Carbonate and sulfide concentrations for the three distinct zones of the Loveday Basin.

	Wet Zone	Wet-Dry Zone	Dry Zone
Description	Permanently saturated clays with little evidence of oxidation	Prominent pedal structures with reduced and oxidised features	Dry oxidised flocculated sediments with relict pedal structures
CaCO ₃ % w/w	2 – 13	> 0.05 – 3	> 0.05
FeS ₂ % w/w	0.3 – 1.2	> 0.002 – 1.2	> 0.002 – 0.04
pH	7 – 8	3 – 7	6 – 7

Sediments / sub-soils were selected to represent the buffered and un-buffered conditions in the field. ‘Buffered’ samples contain 5 % w/w of CaCO_3 (0.1 mmol/g potential buffering capacity), providing excess alkalinity to neutralise the potential acidity from the 1 % w/w FeS_2 (0.03 mmol/g potential acidity). ‘Un-buffered’ samples contain less than 0.05 % w/w CaCO_3 (> 0.001 mmol/g potential buffering capacity) for the 1 % w/w of FeS_2 (0.03 mmol/g potential acidity) giving the sediments net potential acidity. As sulfur was used as a proxy for sulfide oxidation, samples were chosen where sulfides made up greater than 80 % of the total sulfur to that ensure sulfide oxidation could be differentiated from gypsum dissolution.

ACIDIC VS NEUTRAL OXIDATION

At the start of the experiment, one day after addition of Milli-Q water, an initial pulse of Na, K, and S ions are released for all sediments (Figure 1) due to the rapid dissolution of the soluble chloride and sulfate salts present in the sediments. In the buffered sediments the pH remains neutral and the concentrations of dissolved ions remain relatively constant, after the initial pulse, throughout the experiment (Figure 2). In the un-buffered experiment the oxidation of pyrite lowers pH from pH 7 to pH 2 (Figure 1). Associated with the decrease in pH is a release of ions (K, Na, S and Fe) between 7 and 14 days (Figure 1).

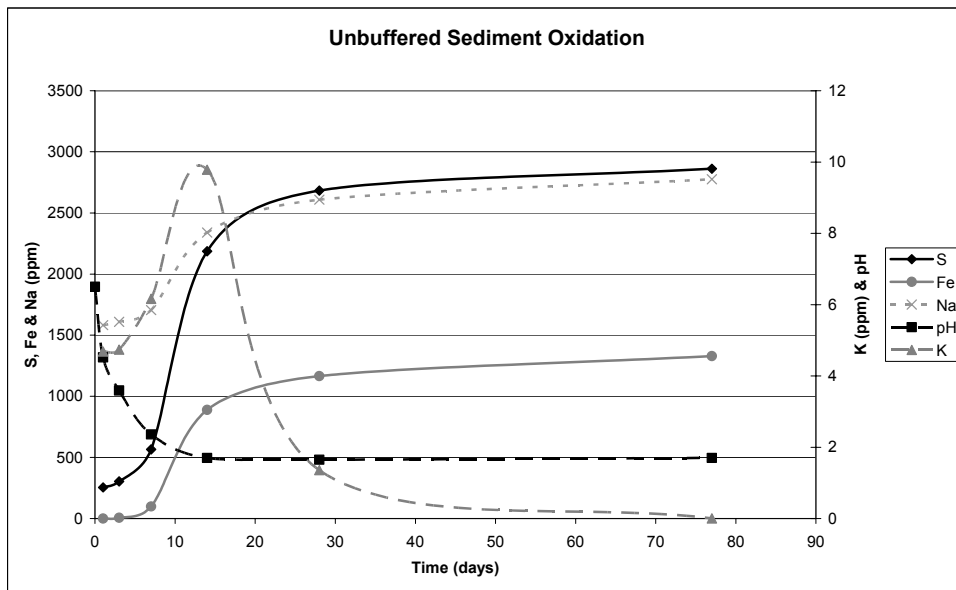


Figure 1: Element concentrations and pH over time for un-buffered oxidation of sulfidic sediments.

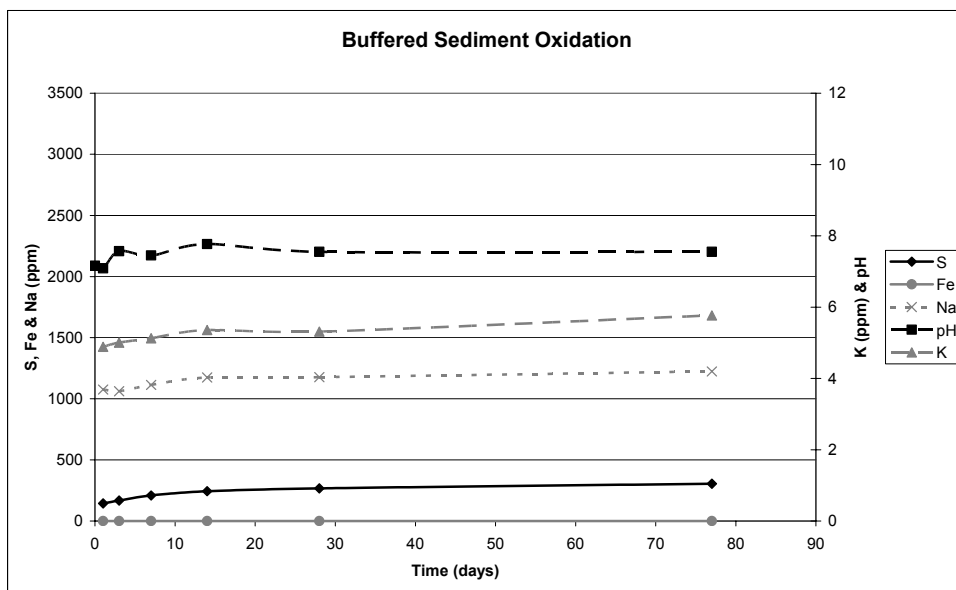


Figure 2: Element concentrations and pH over time for buffered oxidation of sulfidic sediments.

Pyrite oxidation in the un-buffered sediments rapidly releases sulfur and iron into solution between days 7 and 14. Using sulfur as a proxy, the rate of pyrite oxidation in the un-buffered sediments is $\sim 7.5 \times 10^{-5}$ (mol $\text{h}^{-1} \text{g}^{-1}$). The final concentrations of sulfur (minus the initial pulse of sulfate salts) in the un-buffered sediments show that >90 % the original pyrite in the sediments has been oxidised within one week. Over the same time period (days 7 to 14) the buffered sediments, assuming the increase in sulfur concentrations is due to pyrite oxidation, are oxidised at a rate of $\sim 1.6 \times 10^{-6}$ (mol $\text{h}^{-1} \text{g}^{-1}$), ~ 50 times slower than under acidic conditions. At this rate, it would take around one year to completely remove sulfides from the buffered sediments.

The increase in Na and K between day 7 and 14 in the un-buffered sediments is coincident with the drop in pH. This is most likely due to the displacement of exchangeable cations adsorbed to clay minerals. The one noticeable exception is the concentration of K which drops in the un-buffered solution, after day 14, as pH decreases below pH 3. The removal of K is due to the formation of the oxidation product jarosite [$\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$]. This is constant with pyrite oxidation in the field, where jarosite forms in un-buffered sediments and in micro-environments close to the pyrite surface, indicating that similar processes are occurring under field and laboratory conditions.

CONCLUSIONS

The rate of sulfide oxidation is greatly accelerated by acidic conditions produced in un-buffered sediments. Under acid conditions pyrite is completely removed from sediments within two weeks and jarosite is formed as an oxidation product. Under buffered conditions the oxidation of pyrite is considerably slower suggesting pyrite would take years to be removed from sediments. The consistency of laboratory experiments with field observations indicates that these experiments can be used to understand the process of sulfide oxidation in the field and help understand how sulfur is cycled in these systems.

FUTURE WORK

Future experiments will focus on the effect of carbonate concentrations on the oxidation of sulfides. In these experiments un-buffered sulfidic sediments will be oxidised with a range of carbonate concentrations. This will be used to determine how carbonate concentrations affects the rate of oxidation and the total amounts of solutes liberated under oxidising conditions. In addition, abiotic controls will be used to assess the role of bacteria in sulfide oxidation at neutral through to acidic pH.

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