The role of iron coating in the oxidative dissolution of a pyrite-rich sludge

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ABSTRACT

The oxidative dissolution kinetics of a pyrite-rich sludge at alkaline pH is investigated using flow-through and saturated column experiments and addition of a fly-ash material. Preliminary results show that: (1) at pH 9 in a non-stirred flow-through experiment the sludge dissolution is practically nil as a result of a Fe-mineral coating on the pyritic grains; (2) In a stirred flow-through experiment, such a coating is not observed for 600 h, and based on the sulphate concentration at the steady state, the sludge dissolution rate is 6.05×10^{-11} mol m^{-2} s^{-1}; (3) A leaching experiment with a fly-ash column and neutral pH eluent showed a high neutralization capacity of this material, yielding a leachate pH of approx.10; (4) In a saturated column, consisting of an initial thick layer of fly-ash material and a layer of pyritic sludge, attenuation of the pyrite-rich sludge oxidation is observed at pH approx. 10 due to Fe-mineral coating on the pyrite grains (e.g., pyrite encapsulation); (5) In a saturated column experiment solely filled with the pyritic sludge, oxidation occurred favourably at pH approx. 3.6.

INTRODUCTION

In superficial conditions the oxidation of pyrite and other metallic sulphurs in mining districts produces an extremely acidic effluent containing high concentrations of sulphate, iron and other heavy metals known as Acid Mine Drainage (AMD).

The addition of alkaline substances is a commonly used technique to prevent acid production generated during the weathering of sulphide-rich sludges. The oxidative dissolution of pyrite at alkaline pH favours the precipitation of iron held in solution, producing the attenuation of the oxidation process due to: (1) decrease in the concentration of ferric iron, the main oxidizing agent of pyrite in mining environments (Singer & Stumm, 1970); and (2) the precipitation of ferric iron to form a ferric hydroxide coating on the pyritic grains (i.e. microencapsulation; Evangelou, 1995).

In this work, we show the efficiency of using fly-ash (an alkaline waste produced during the combustion of coal) in the attenuation processes of the oxidation of a pyritic sludge. Fly ash is an important waste product of thermal power plants and its use to treat AMD may represent an application of this study, because a waste product could be used to neutralize another waste product.

CHARACTERIZATION OF MATERIALS

In the experiments carried out in this study, two materials with a chemically different nature were utilized: a pyritic sludge from the Cueva de la Mora tailings dams (Iberian Pyrite Belt, SW Iberian Peninsula), and fly ash from the Los Barrios power plant (Cádiz, S Spain).

The pyritic sludge is a potentially acid producing residue containing pyrite (71.6 %) as the main phase along with minor amounts of other metallic sulphides (chalcopyrite 0.2 %, galena 0.9 %, sphalerite 0.2 %, and arsenopyrite 0.2 %). The median grain size is 25 μm and the BET-determined initial surface area is 1.44 ± 0.035 m^2 g^{-1}, using 5-point N_2 adsorption isotherms.

The fly ash on the other hand is a potentially acid neutralizing residue. Based on X-ray diffraction patterns it is composed of mullite (20.8 %), quartz (4.5 %), portlandite (4.1 %) anhydrite (4.3 %) and a chalco-aluminosilicate glass phase (66.4 %) (Querol *et al*., 2001). The median grain size is 40 μm and the specific surface area is 0.63 ± 0.022 m^2 g^{-1}.

EXPERIMENTAL SETTING

Three types of experiments were carried out, (a) a fly ash leaching test, (b) flow-through experiments and (c) saturated columns (Fig. 1). The experimental procedure consisted of passing water from a reservoir (input solution) through the material of a reactor or a column (according to the experiment) with a flow-rate of 0.050 ± 0.005 mL min^{-1}. The flow-rate was controlled using a peristaltic pump and the output solutions were collected every 24 h after passing through a 0.45 μM Millipore Durapore filter. The pH was measured in a by-pass completely isolated of the atmospheric conditions to avoid the effects of $CO_2(g)$ dissolution on the pH outputs (mainly at alkaline pH) (Fig. 1).

In output solutions, the total concentrations of Al, As, Ba, Ca, Cu, Fe, K, Mg, Na, Pb, S, Si and Zn were analyzed by means of Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES). In addition, when the experiments finished, the mineralogical characterization of reacted materials was performed using a scanning electron microscopy equipped with an energy dispersive system (SEM-EDS) of microanalysis.

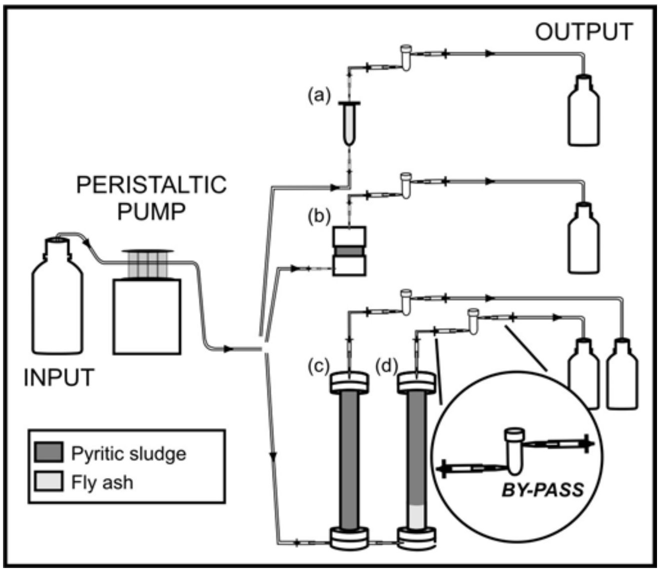

Figure 1: Scheme showing the experimental design

Fly ash leaching test

This experiment consisted of a 5 cm^3 saturated column volume filled with fly ash (ca. 7.5 g) that was crossed by a continuous upward Millipore MQ water flow (18.2 MΩ) (Fig. 1a).

Flow-through experiments

The leaching of fly ash generates solutions with high pH values (approx. 10) (Querol *et al.*, 2001). Therefore if the saturated column were filled with a mixture of fly ash and pyritic sludge, the oxidative dissolution of pyrite would occur at alkaline pH. The dissolution kinetics of the pyrite-rich sludge at alkaline pH was studied with flow-through experiments (Fig. 1b).

The experiments were carried out in a 40 cm^3 methacrylate reactor volume using 1g of pyritic sludge. To simulate the pyritic sludge oxidation at alkaline pH the input solution was prepared at pH 9 using Millipore MQ water and analytical-grade $Na_2B_4O_7 \cdot 10H_2O$ and HCl reagents (Merck). Two experiment types were realized: non-stirred and magnet-stirred flow-through experiments.

Saturated column experiments

The saturated column experiments are: (i) a saturated column of 2.5 cm in diameter and 18 cm in length filled with a mixture of 10 wt.% sludge and 90 wt.% of an inert quartz sand (Fig. 1c) and (ii) a saturated column of 2.5 cm in diameter and 24 cm in length filled with a lower 6 cm thick layer of fly-ash material and topped up with a mixture of pyritic sludge and quartz sand (Fig. 1d). In both experiments the input solution was Millipore MQ water (18.2 MΩ) circulating through the columns from the base upward.

CALCULATIONS

In the flow-through experiments, the reaction rate *R* (mol m^{-2} s-^{1}) is calculated when concentrations in the output solution reach the steady state, according to the equation 1 (Nagy *et al.*, 1991):

$$R = \frac{q}{A_{min} \cdot v_i} (C_{i,out} - C_{i,inp}) \qquad (1)$$

where *q* is the flow rate (m^3 s^{-1}), $C_{i,out}$ is the concentration of the element *i* (mol m^{-3}) in the output solution at the steady state, $C_{i,inp}$ is the concentration of the element *i* (mol m^{-3}) in the input solution, v_i is the stoichiometric coefficient of the element *i*, and A_{min} is the total surface area of the mineral (m^2).

The pyritic sludge comprises dominantly pyrite (71.6 %). Therefore, the sludge dissolution rate is very similar to the pyrite dissolution rate proposed by Domènech *et al.* (2002) using the pyritic sludge from the Aznalcóllar Mine (Iberian Pyritic Belt). The sludge dissolution rate was calculated based on the releasing of aqueous sulphate at the steady state.

RESULTS AND DISCUSSION

Fly ash leaching test

Leachates generated by the fly ash leaching experiment are characterized by an alkaline pH (ca. 10) with relatively high concentrations of Ca, Si, Al and S with respect to the rest of the elements analysed (0.33 mmol L^{-1}, 0.13 mmol L^{-1}, 0.04 mmol L^{-1} and 0.03 mmol L^{-1} respectively at steady state) (Fig. 2).

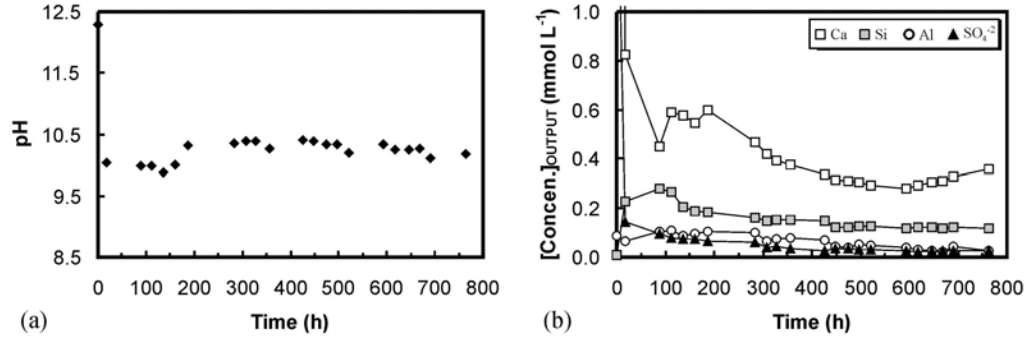

Figure 2: Variation in the (a) pH and in the (b) output concentrations of Ca, Si, Al and SO_4^{-2} as a function of time in the fly ash leaching test

Flow-through experiments

In the non-stirred flow-through experiment at pH 9 the concentration of sulphate at the steady state is below the detection limit, and therefore the sludge dissolution is practically nil (Fig. 3a). During the pyrite oxidation process at alkaline pH the released iron precipitates as Fe oxyhydroxides (most probably ferrihydrite) on the pyritic grains (Fig. 4). Fe-phases coatings on pyrite surface prevent further contact between oxidizing agents and the pyrite, and the oxidation process halts at this time.

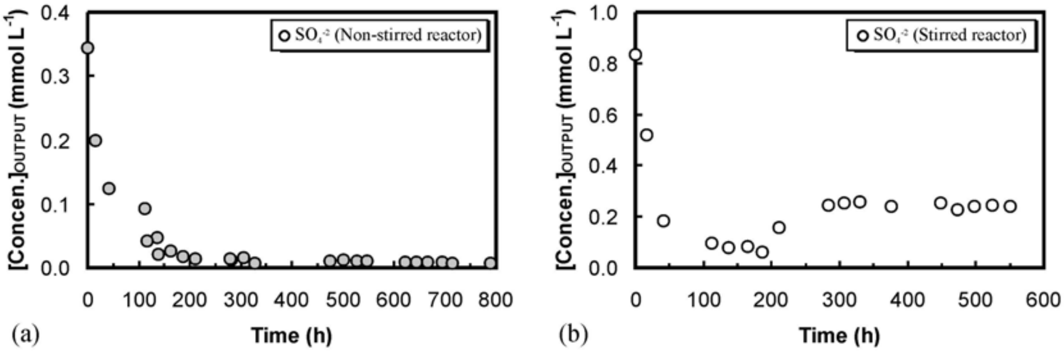

Figure 3: Variation in the output concentrations of SO_4^{-2} in the (a) non-stirred flow-through experiment and in the (b) stirred flow-through experiment

In the magnet-stirred flow-through experiment at pH 9, according to Eq. 1 the concentration of sulphate at the steady state is approximately 0.25×10^{-3} mmol L^{-1} and the sludge dissolution rate is 6.05×10^{-11} mol m^{-2} s^{-1} (Fig. 3b). The iron and other metals also precipitate as Fe oxyhydroxides. Nevertheless, the complete stirring of the solution inside the reactor favours that these precipitates become separated from the pyrite surface and the oxidation process does not slow.

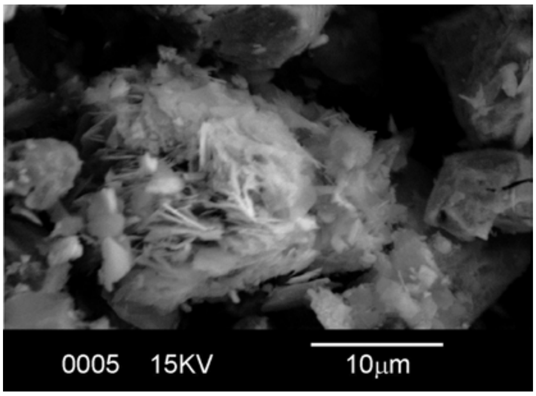

Figure 4: SEM image of Fe oxyhydroxides coating pyritic grains in the non-stirred flow through experiment

Saturated column experiments

Saturated column with pyritic sludge

In the saturated zone pyrite dissolution is limited by the concentration of aqueous oxygen, independently of pH. In the saturated column experiments where the input solution is at atmospheric oxygen pressure (0.250 mmol L^{-1} aqueous oxygen), according to the stoichiometry of the reaction, the maximum concentrations of sulphate and iron that can be released during the oxidation process are 0.143 mmol L^{-1} and 0.0714 mmol L^{-1}, respectively.

In the saturated column filled with the mixture of the pyritic sludge and quartz sand the average pH value is 3.7 and sulphate and iron concentrations are 0.140 and 0.039 mmol L^{-1} respectively at steady state (Fig. 5). The concentrations of sulphate and the pH in the leachates show that pyrite is dissolved favourably in a water-saturated porous medium where the dissolved oxygen in the input solution is totally consumed. However, the iron concentration in the leachates does not correspond with the maximum concentration of iron that can be released during the oxidation process, because part of this iron precipitates as ferrihydrite.

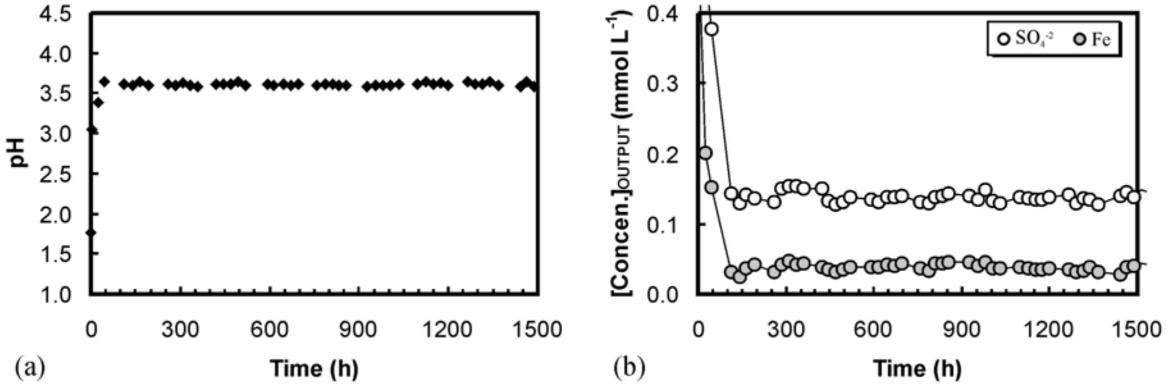

Figure 5: Variation in the (a) pH and in the (b) output concentrations of SO_4^{-2} and Fe as a function of time in the saturated column experiment fills with sulphide sludge

Saturated column with fly ash and pyritic sludge

Leachates generated by a saturated column filled with fly ash and a mixture of pyritic sludge and quartz sand are characterized by high values of pH, sulphate concentrations of approximately 0.113 mmol L^{-1} at the steady state, and deficiency in iron and other metals in solution (Fig. 6).

In this column the oxidative dissolution of the pyritic sludge is taking place at alkaline pH due to the presence of fly ash (see fly ash leaching test). According to the kinetics law of pyrite dissolution proposed by Williamson & Rimstidt (1994), being the concentration of dissolved oxygen in the recharge water the same in both saturated columns (0.250 mmol L^{-1}), the pyrite oxidation is faster at alkaline conditions, and therefore, should be faster in the column with fly ash. Nevertheless, as in this column the medium is also completely saturated in water, independently of pyrite dissolution rate, the maximum concentration of sulphate and iron that can be released during the oxidation process is limited by the concentration of dissolved oxygen in the input solution (sulphate and iron concentrations of 0.143 and 0.0714 mmol L^{-1} respectively).

However, when pyrite is oxidized at high pH values the iron and other metals precipitate as Fe oxyhydroxides (most probably ferrihydrite). As in the case of the non-stirred flow-through experiment at pH 9 Fe-minerals form a coating on pyritic grains (Fig. 7). The pyrite microencapsulation process prevents aqueous oxygen dissolving the pyritic grains and oxidation is halted.

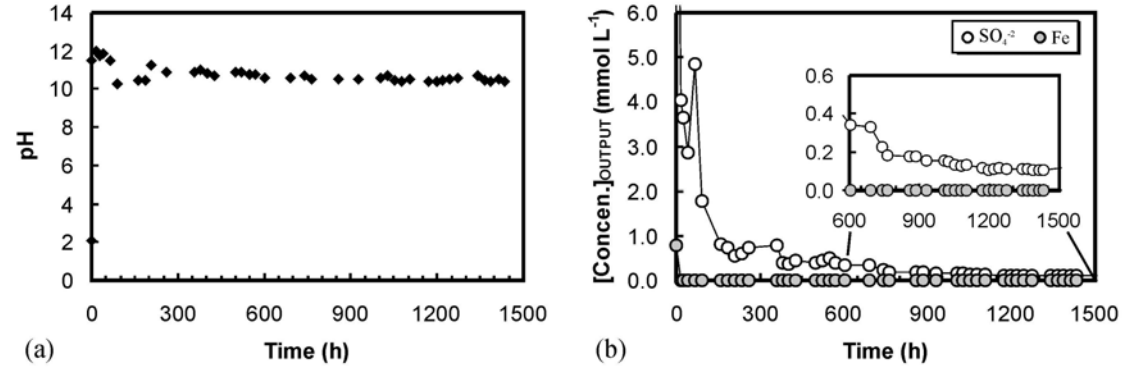

Figure 6: Variation in the (a) pH and in the (b) output concentrations of SO_4^{-2} and Fe as a function of time in the saturated column experiment fills with fly ash and sulphide sludge

The concentration of sulphate observed at the steady state appears to correspond with the maximum concentration of sulphate that pyrite can release in a saturated zone. Therefore despite the precipitation of Fe oxyhydroxides, the oxidation process seems to be produced favourably. However, the oxidation in fact most probably has been stopped completely, as the sulphate leached most probably comes from the initial thick layer of fly-ash that also contains sulphur in the glass phase (see fly ash leaching test).

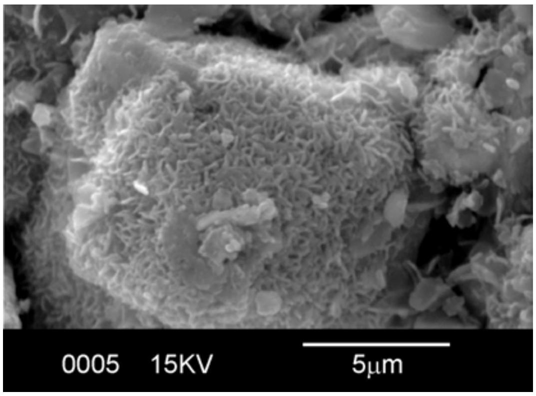

Figure 7: SEM image of Fe oxyhydroxides coating pyritic grains in the saturated column experiment fills with fly ash and pyritic sludge

CONCLUSIONS

The oxidation process of a pyritic sludge (pyrite; ca. 72 wt. %) in the saturated zone has been studied by means of leaching column experiments. In a saturated column fills with pyritic sludge and inert quart sand (1:10), the pyrite oxidation has taken place in acidic conditions (pH approx. 3.70). The sulphate concentrations and the pH in the leachates show that the pyrite oxidation is being produced favourably in a saturated medium where the dissolved oxygen in the input solution is totally consumed.

In another saturated column the pyrite oxidation has taken place at alkaline conditions (pH approx. 10.45), due to the addition of a potentially acid neutralizing residue: fly ash. In addition, in order to understand the behaviour of both wastes inside this column, a fly ash leaching test (leachates reach a pH>10) and two flow-through experiments at pH 9 were carried out to calculate oxidative dissolution rates of pyritic sludge in presence of the fly ash. The results show that the oxidation process of pyrite in this column is being neutralized favourably. The pyrite oxidation at alkaline pH favours the precipitation of the iron (and other metals), released during the oxidation process, on pyritic grains. At the time, a coating that prevent any contact between the pyrite and oxidizing agents is originated, and the oxidation process is attenuated.

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