OXIDATIVE DISSOLUTION AT BASIC pH OF A PYRITE-RICH SLUDGE DOPED WITH FLY ASH[1]

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Abstract. A study of sulfur-rich sludge (71.6% pyrite) dissolution at alkaline conditions (pH ca.9) was investigated using non-stirred and stirred flow-through experiments at room temperature (26 $\pm$ 1.2ºC) and O_2 partial pressure of 0.20 atm. The dissolution rate of pyrite-rich sludge was calculated based on the S release (aqueous SO_4^{-2}) at the steady-state. Results show that: (1) in the non-stirred reactor the sludge dissolution is practically nil as a result of a Fe-mineral coating on the pyritic grains; (2) In the stirred reactor, such a coating is not observed for 600 h, and the sludge dissolution rate is 6.05×10^{-11} mol m^{-2} s^{-1}.

The dissolution kinetics at alkaline pH of the pyrite-rich sludge was also studied adding a fly-ash material (residue of coal combustion) to the mining waste using saturated column experiments. It is observed that: (1) A leaching experiment with a fly-ash column and neutral pH eluent enhanced the neutralization capacity of this material, yielding a leachate pH of approx.10; (2) 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 attained at pH approx.10 due to Fe-mineral coating on the pyrite grains (e.g., pyrite encapsulation); (3) In a saturated column experiment solely filled with the pyritic sludge, oxidation occurred favourably at pH approx.3.6.

Additional Key Words: oxidative, kinetics, pyrite, basic, pH.

Introduction

In superficial conditions the oxidation of pyrite and other metallic sulfides in mining districts produces an extremely acidic effluent containing high concentrations of sulfate (SO_4^{-2}), Fe 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 sulfide-rich residues (Nicholson et al., 1988, 1990; Mylona et al., 2000; and others). The oxidative dissolution of pyrite at alkaline pH favours the precipitation of Fe held in solution, producing the attenuation of the oxidation process due to: (1) decrease in the concentration of Fe^{+3} iron, the main oxidizing agent of pyrite in mining environments (Singer and Stumm, 1970); and (2) the precipitation of Fe^{+3} to form a $Fe(OH)_3$ coating on the pyritic grains. Fe-phases coatings on pyrite surface prevent further contact between oxidizing agents and the pyrite, and the oxidation process halts at this time. This process, described by Evangelou (1995), is known as pyrite microencapsulation process.

Some investigations have challenged the effectiveness of the carbonate minerals addition to prevent the mining waste oxidation (Evangelou and Huang, 1993; Evangelou et al., 1998; Hood, 1991; and others). These authors propose that in near neutral and alkaline environments, HCO_3^- and CO_2 react with pyrite surface and form some weak complexes which accelerate non-microbial pyrite oxidation rate. In addition, the use of limestone can imply a high economic and environmental cost, because limestone is a "resource" and not a "residue".

In this work, we show the efficiency of the pyrite microencapsulation and oxidation attenuation processes by the addition of fly ash to pyrite-rich residues. 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.

The main objectives of the present work are: (1) to study the pyrite oxidation process at acid media in a saturated column experiment fills with a pyrite-rich sludge; and (2) to make use of the strongly alkaline character of fly ash to neutralize the acidity and reduce the high metal content of the drainages resulting of pyrite oxidation process in a saturated column experiment fills with fly ash and a pyrite-rich sludge. In addition, in order to understand the behaviour of both wastes inside the saturated column filled with pyritic sludge and fly ash, other experiments were realized: (3) a fly ash leaching test was carried out to demonstrate the high neutralization capacity of this material; and (4) flow-through experiments at pH 9 were carried out to calculate oxidative dissolution rate of pyritic sludge in alkaline media (the media reached during the leaching of fly ash) and to study how the microencapsulation process affects on this dissolution rate.

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 sulfides (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, a column filled with pyritic sludge and another one filled with pyritic sludge and fly ash (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.
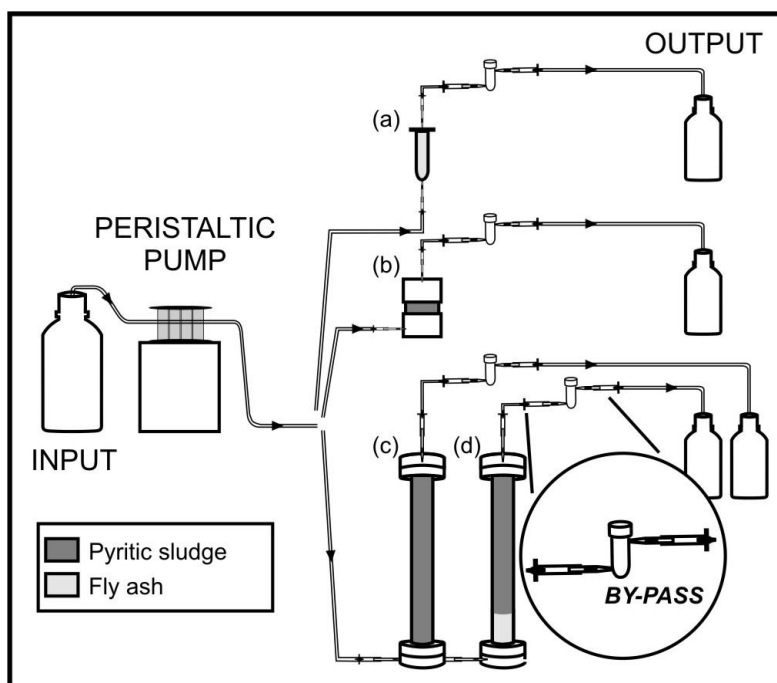

Figure 1. Scheme showing the experimental design.

<u>Fly ash leaching test</u>

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).

<u>Flow-through experiments</u>

The leaching of fly ash generates solutions with high pH values (approx.10) (Querol et al., 2001). Therefore, in the saturated column filled with a mixture of fly ash and pyritic sludge (see saturated column experiments), 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, 2).

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 (Fig. 2).
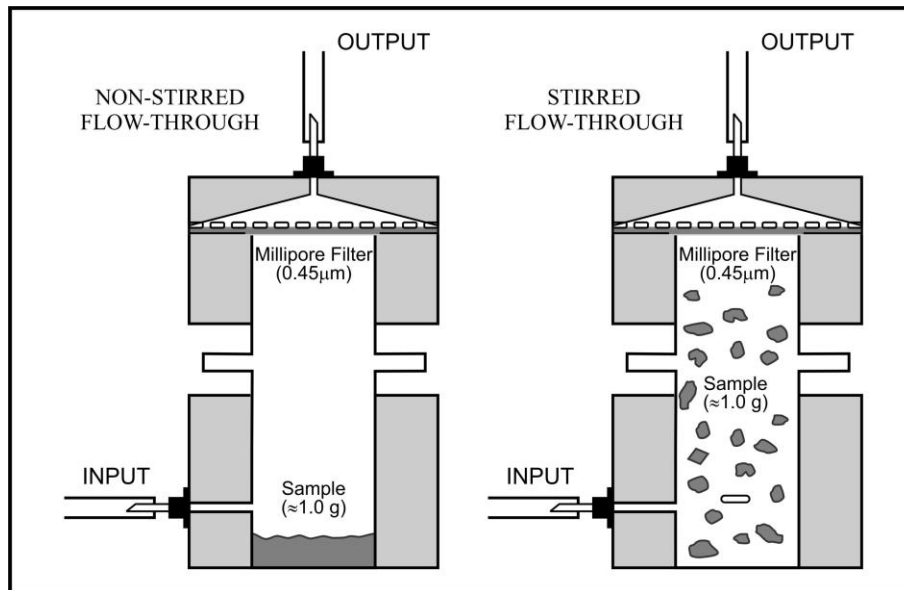

Figure 2. Experimental design of the reaction cells used in the non-stirred and stirred flow-through experiments.

<u>Saturated column experiments</u>

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.

Inside saturated columns, stirring does not exist. Therefore, in order to simulate the conditions of pyrite oxidation in the column filled with fly ash and pyritic sludge, the non-stirred flow-through experiment at pH 9 was carried out.

In addition, the lack of stirring in the pyritic sludge also can favor that possible coatings on pyrite grains could be originated, that would not be originated under stirring conditions. Consequently, the dissolution rate of the pyritic sludge at pH 9 can be calculated with the stirred flow-through experiment; whereas with the non-stirred flow-through experiment, it is possible to calculate how this coating process has influence in the dissolution rate.

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):

$$R = \frac{q}{A_{min} \cdot v_i}(C_{i,out} - C_{i,inp})$$ (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 SO_4^{-2} 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. 3).

Flow-through experiments
In the non-stirred flow-through experiment at pH 9 the concentration of SO_4^{-2} at the steady state is below the detection limit, and therefore the sludge dissolution is practically nil (Fig. 4a). During the pyrite oxidation process at alkaline pH the released Fe precipitates as Fe oxyhydroxides (most probably ferrihydrite) on the pyritic grains (Fig. 5). Fe-phases coatings on pyrite surface prevent further contact between oxidizing agents and the pyrite, and the oxidation process halts at this time.
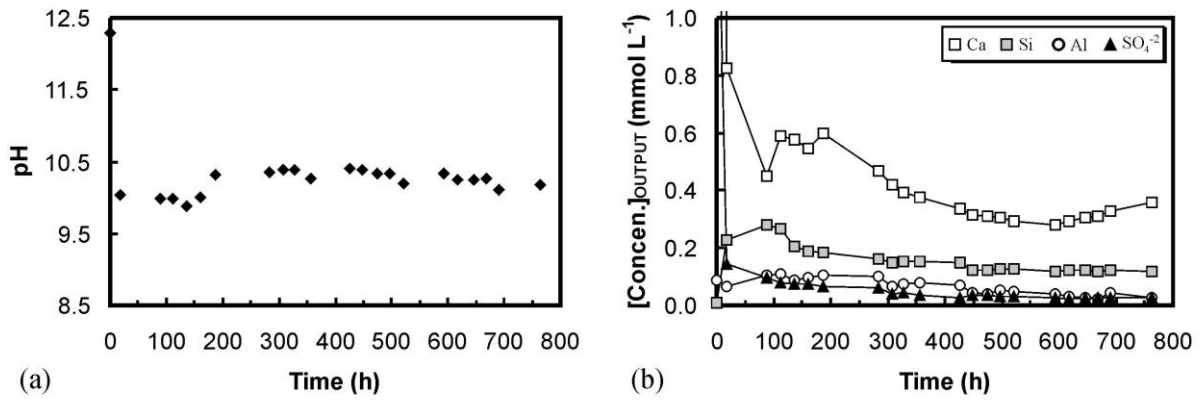
Figure 3. Variation in the (a) pH and in the (b) output concentrations of Ca, Si, Al and SO_4^{-2} as a function of time in the fly ash leaching test.
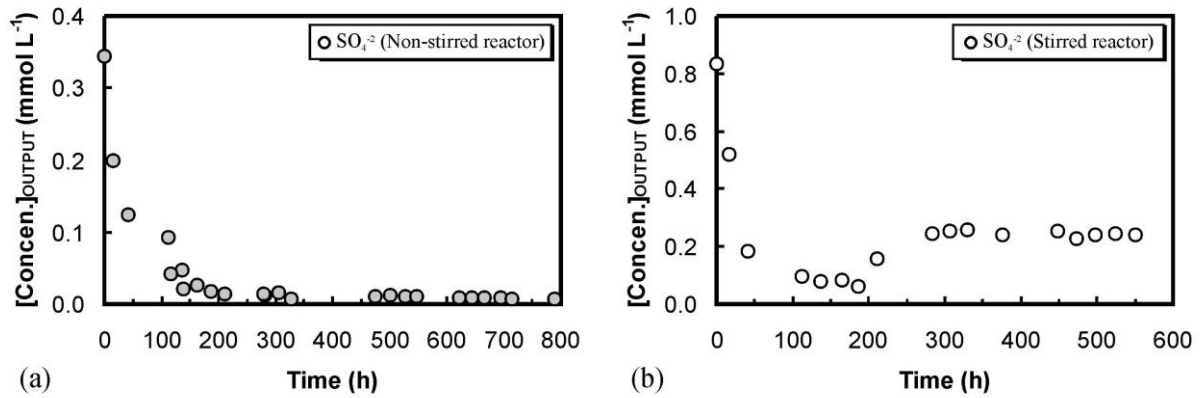

Figure 4. Variation in the output concentrations of SO_4^{-2} in the (a) non-stirred flow-through experiment and in the (b) stirred flow-through experiment.
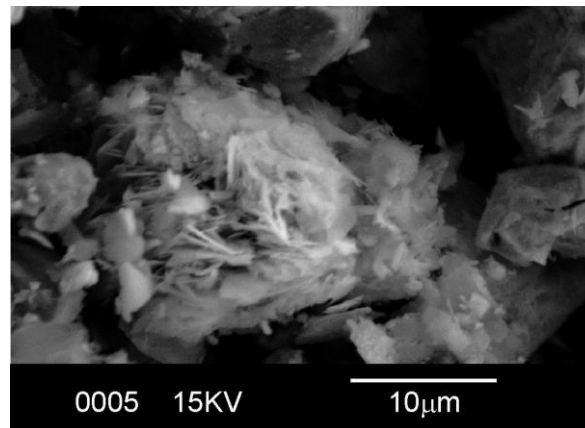

Figure 5. SEM image of Fe oxyhydroxides coating pyritic grains in the non-stirred flow through experiment.

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In the magnet-stirred flow-through experiment at pH 9, according to Eq. 1 the concentration of SO_4^{-2} 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. 4b). The Fe 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.

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 SO_4^{-2} and Fe 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 SO_4^{-2} and Fe concentrations are 0.140 and 0.039 mmol L^{-1} respectively at steady state (Fig. 6). The concentrations of SO_4^{-2} 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 Fe concentration in the leachates does not correspond with the maximum concentration of Fe that can be released during the oxidation process, because part of this Fe precipitates as ferrihydrite.
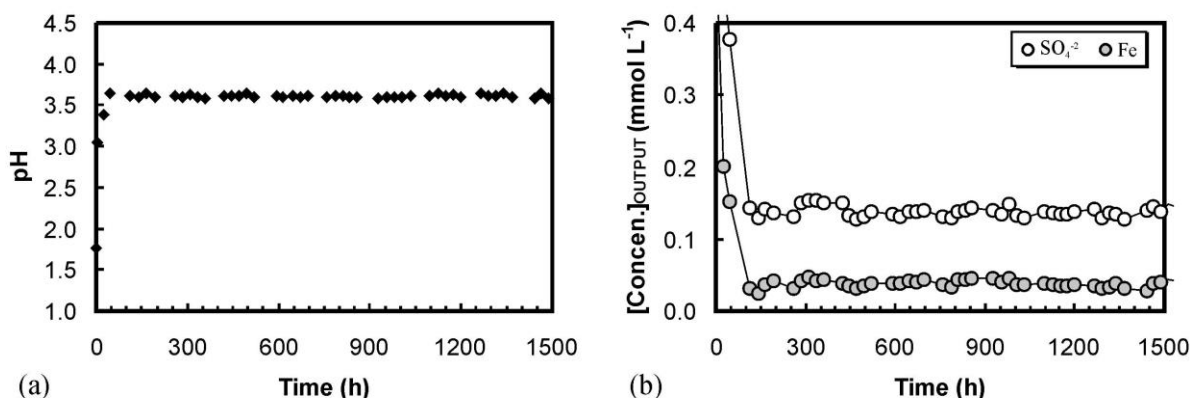

Figure 6. Variation in the (a) pH and in the (b) output concentrations of SO_4^{-2} and Fe as a function of time in the saturated column experiment fills with sulphide sludge.

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, SO_4^{-2} concentrations of approximately 0.113 mmol L^{-1} at the steady state, and deficiency in Fe and other metals in solution (Fig. 7).

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 and Rimstidt (1994), being the concentration of dissolved O_2 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,

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independently of pyrite dissolution rate, the maximum concentration of SO_4^{-2} and Fe that can be released during the oxidation process is limited by the concentration of dissolved O_2 in the input solution (SO_4^{-2} and Fe concentrations of 0.143 and 0.0714 mmol L^{-1} ,respectively).
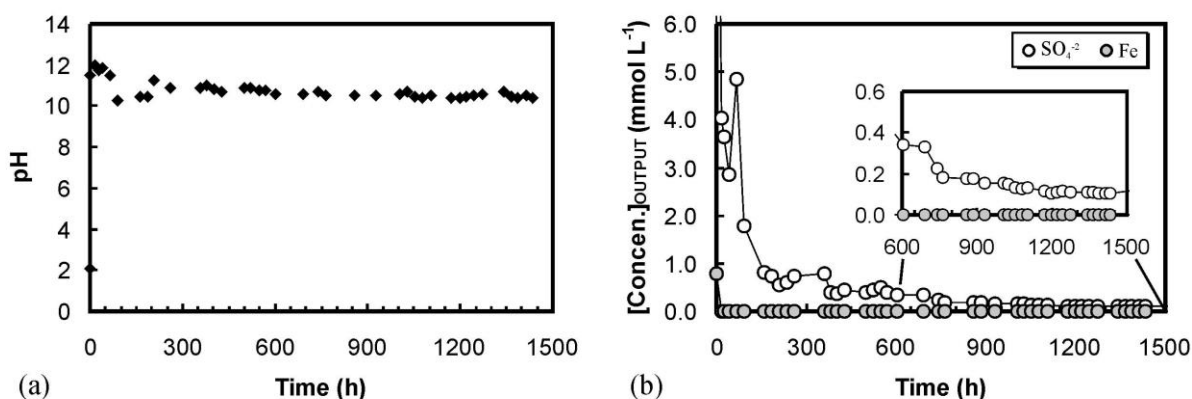

Figure 7. Variation in the (a) pH and in the (b) output concentrations of SO_4^{-2} and Fe as a function of time in the saturated column experiment fills with fly ash and sulfide sludge.

However, when pyrite is oxidized at high pH values the Fe 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. 8). The pyrite microencapsulation process prevents aqueous oxygen dissolving the pyritic grains and oxidation is halted.
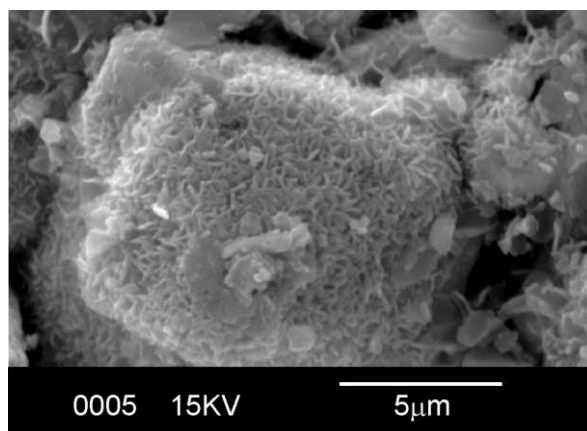

Figure 8. SEM image of Fe oxyhydroxides coating pyritic grains in the saturated column experiment fills with fly ash and pyritic sludge.

The concentration of SO_4^{-2} observed at the steady state appears to correspond with the maximum concentration of SO_4^{-2} 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 SO_4^{-2} leached

most probably comes from the initial thick layer of fly-ash that also contains S in the glass phase (see fly ash leaching test).

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 SO_4^{-2} concentrations and the pH in the leachates show that the pyrite oxidation is being produced favourably in a saturated medium where the dissolved O_2 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 Fe (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.

Acknowledgements

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