The use of alkaline residues for the inhibition of acid mine drainage processes in sulphide-rich mining wastes

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ABSTRACT
Oxidative dissolution of pyrite and others metallic sulphides (chalcopyrite, sphalerite, galena, etc.) originate an extremely acid drainage enriched with high concentrations of sulphate, iron and other heavy metals called Acid Mine Drainage (AMD). In this work, the oxidative dissolution of a pyrite-rich sludge from the Iberian Pyrite Belt in the non-saturated zone, the generation of AMD, and the potential use of fly ash (residue of coal combustion) to neutralize the acidity and reduce the high metal content of the drainage, have been studied in column experiments. A column experiment fills with pyrite-rich sludge with artificial irrigation (100 mL water week^{-1}) leached an acid drainage (pH approx. 2) with high concentrations of sulphate, iron and metals. However, drainages of non-saturated columns fill with pyrite-rich sludge and fly ash were characterized by high pH (pH approx. 10), very low sulphate content and the lack of iron and other metals in solution.

INTRODUCTION
The Iberian Pyrite Belt (IPB) is located in the Sud-Portuguese Zone of the Hesperic Range. It is one of the largest massive sulphide provinces in the world and is characterized by the presence of a high number of deposits. The intense mining activity in the IPB, which is dated back to the Third Millennium BC, has caused the exposition in the surface of a large amount of sulphides dispersed in mine tailings, tailings dam, open pits, etc.
Pyrite is the most abundant mineral in these polymetallic sulphide deposits. The oxidation of pyrite in an aqueous environment can be expressed by means of the following reactions (Singer & Stumm, 1970):

$$FeS_2 + 7/2O_2 + H_2O \Rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+ \qquad (1)$$
$$FeS_2 + 14Fe^{3+} + 8H_2O \Rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+ \qquad (2)$$
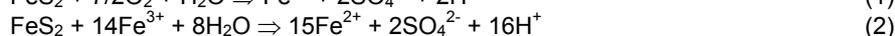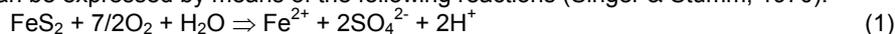
Oxidizing agents of pyrite are atmospheric O_2 (Eq. 1) and Fe^{3+} (Eq. 2). The result of the oxidation process is a leachate containing high concentrations of protons, iron and sulphate. In addition other minor metallic sulphides exist in mining waste (i.e. chalcopyrite $CuFeS_2$, galena PbS, sphalerite ZnS, arsenopyrite $AsFeS$) that when oxidized release other metals in solution (i.e. Cu, Pb, Zn, As). These extremely acid leachates containing high concentrations of sulphate, iron and other heavy metals are known as Acid Mine Drainage (AMD) (Parker & Robertson, 1999). The production of AMD is the main pollution process of natural watercourses in mining environments of the IPB (Olias et al., 2004).
The addition of limestone to sulphidic wastes is the most commonly employed technique to prevent acid production (Nicholson et al., 1988, 1990; Mylona et al., 2000; and others). However the use of limestone implies a high economic and environmental cost, because limestone is a "resource" and not a "residue". In this work the main objectives have been: (1) to simulate oxidation conditions prevailing in sulphur-rich mining waste by means of non-saturated column experiments; (2) to demonstrate the efficiency of acid neutralization and metal retention process in AMD by the addition of fly ash (a residue of coal combustion) to pyrite-rich residues.

MATERIALS AND METHODS

Characterization of samples
The materials used in the column experiments are pyritic sludge and fly ash. The pyrite-rich sludge was collected from the tailings dam at Cueva de la Mora, situated in Huelva, Spain (central part of the Iberian Pyrite Belt). This residue comprises dominantly of pyrite (71.6 %) and other metallic sulphides as chalcopyrite (0.2 %), galena (0.9 %), arsenopyrite (0.2 %) and sphalerite (0.2 %). It has a high acid generation potential and is the material responsible for producing AMD.
Fly ash is a waste product derived from the combustion of coal, and the material used in this study is from the Los Barrios power plant (Cádiz, Spain). Fly ash is comprised of a glass phase (69.4 %), mullite (20.8 %), quartz (4.5 %), porlandite (4.1 %) and anhydrite (4.3 %) (Querol et al., 2001) and is characterized by high alkali concentration (5.3 % CaO), and therefore has a high neutralizing potential.

Experimental setting
The experimental design consisted in a column of 20 cm in length and 8 cm in diameter. A total of four columns were constructed (see Fig. 1). Columns were watered once a week with 100 mL of Millipore MQ water (18.2 MΩ). The duration of the experiment was 30 weeks.
At the surroundings of mining districts in the IPB, the mine tailings are composed of a high volume of inert sterile and small amounts of sulphides. In the leaching experiments, a mixture of 10 wt.% pyritic sludge and 90 wt.% of a inert quartz sand was used. The quartz sand has been used to increase the porosity and permeability of the

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sulphide-rich residue. The aim is to favour the processes of evaporation, oxygen renovation and sulphide oxidation, simulating the conditions that prevail in mine tailings.
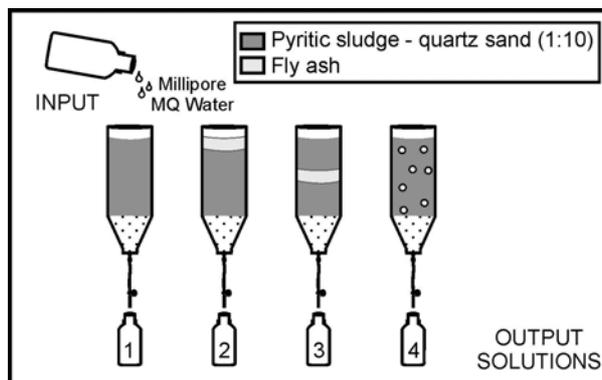

Figure 1: Scheme showing the experimental design of non-saturated columns

The column 1 is a control column packed only with a mixture of 10 wt.% pyrite sludge and 90 wt.% of inert quartz sand. The rest of columns were filled with a mixture of pyrite sludge, quartz sand and fly ash (Table 1). The leachates were collected, filtered and analyzed (pH, conductivity and concentration of sulphate and cations).

	DESCRIPTION	PS+QS (1:10) (g)	PS (g)	FA (g)	% PS+QS (1:10)
1.	Filled with pyrite-rich sludge and quartz sand (1:10)	872	79	-	100
2.	Filled with pyrite-rich sludge and quartz sand (1:10) and a top layer of fly ash (20%)	721	65	121	≈ 80
3.	Filled with pyrite-rich sludge and quartz sand (1:10) and a middle layer of fly ash (20%)	723	66	126	≈ 80
4.	Filled with a homogeneous mixture of pyrite-rich sludge and quartz sand (1:10) and fly ash (8%).	794	68	53	≈ 92

Table 1: Description of the four non-saturated columns (PS: Pyrite Sludge; QS: Quart Sand; FA: Fly Ash)

Conductivity, pH and concentration of sulphate and cations were determined in the leachates. The concentrations of sulphate and cations were analyzed by means of Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES). In addition, when the experiment finished, the reacted materials were observed under a JEOL JSM-5410 scanning electron microscope (SEM) with an energy dispersive spectroscopy (EDS).

RESULTS

Temporal evolution of pH and conductivity

Leachates of column 1 (pyritic sludge) present low pH values during all the experiment (approx 2), and high conductivity values (from 2 to 4 mS cm^{-1}) (Fig. 2). In contrast, the leachates generated by columns 2, 3 and 4 (pyritic sludge and fly ash) present an alkaline pH (approx. 9, 10 and 7.5 respectively). It is precisely in these columns where the lowest conductivities are reached, being even of 300 µS cm^{-1} in columns 2 and 4 (Fig. 2).
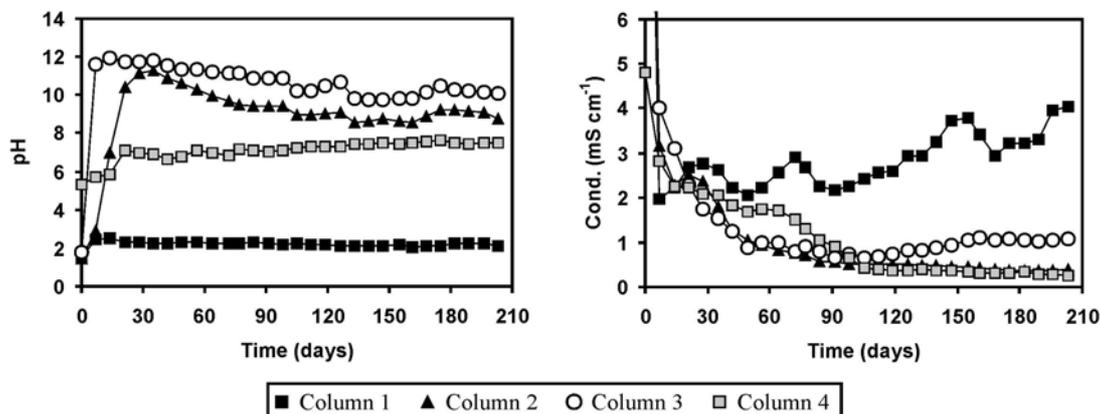

Figure 2: Variation in the pH and the conductivity as a function of time in the non-saturated column experiments

Temporal evolution in the sulphate and iron concentrations
In column 1, the sulphate and iron concentrations in the leachates show a similar evolution to the conductivity (Fig. 3). The sulphate and iron concentrations averaged 1×10^{-2} and 0.8×10^{-2} mol L^{-1}, respectively.
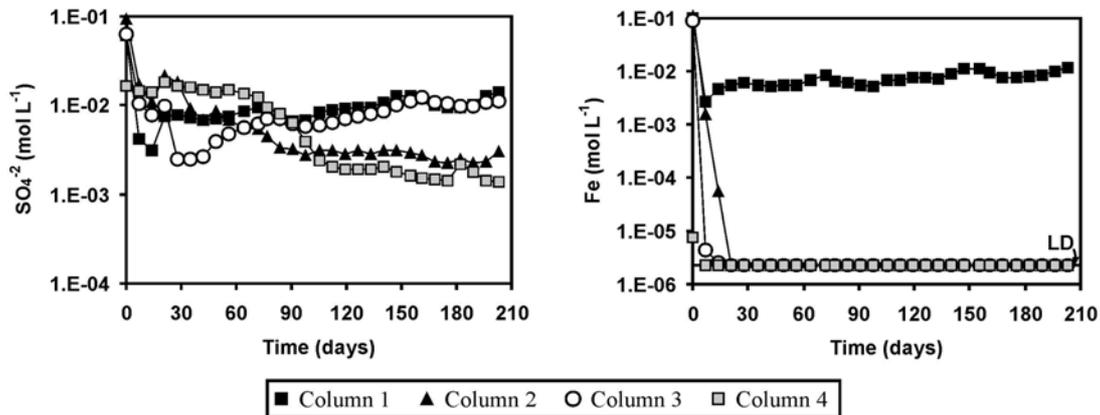

Figure 3: Variation in output concentrations of SO_4^{-2} and Fe as a function of time in the non-saturated column experiments

However, sulphate and iron concentrations in the leachates of columns 2 and 4 present a temporal evolution very different from that of the column 1. In spite of the fact that the leachates reach high sulphate concentrations at the onset of the experiment, values decrease gradually until a steady state is attained after 100 days approximately. At the steady state, sulphate concentrations are about 2.8×10^{-3} mol L^{-1} and 2.5×10^{-3} mol L^{-1} in columns 2 and 4, respectively. On the other hand, the behaviour of iron in the leachates of these columns is very significant, excepting the first leachate, the rest of them do not contain iron in solution (Fig. 3).
In column 3, the leachates present a lack of iron in solution, as in column 2 and 4. However, the sulphate concentrations are much higher than in column 2 although not as high as in column 1 (approx 0.8×10^{-2} mol L^{-1} at the steady state).

Temporal evolution in the copper, lead, zinc and arsenic concentrations
The average concentrations of copper, lead, zinc and arsenic in the leachates of column 1 are 1.4×10^{-5}, 1.4×10^{-4}, 3×10^{-6} and 2.5×10^{-5} mol L^{-1} respectively (Fig. 4). In contrast, just like the behaviour of iron, the concentrations of these metals are much lower in the leachates of columns with fly ash. For example, the average concentrations of copper, lead, zinc and arsenic in the leachates of column 4 are 2.5×10^{-7}, 3.8×10^{-8}, 1×10^{-6}, 1.2×10^{-7} mol L^{-1} respectively (Fig. 4).

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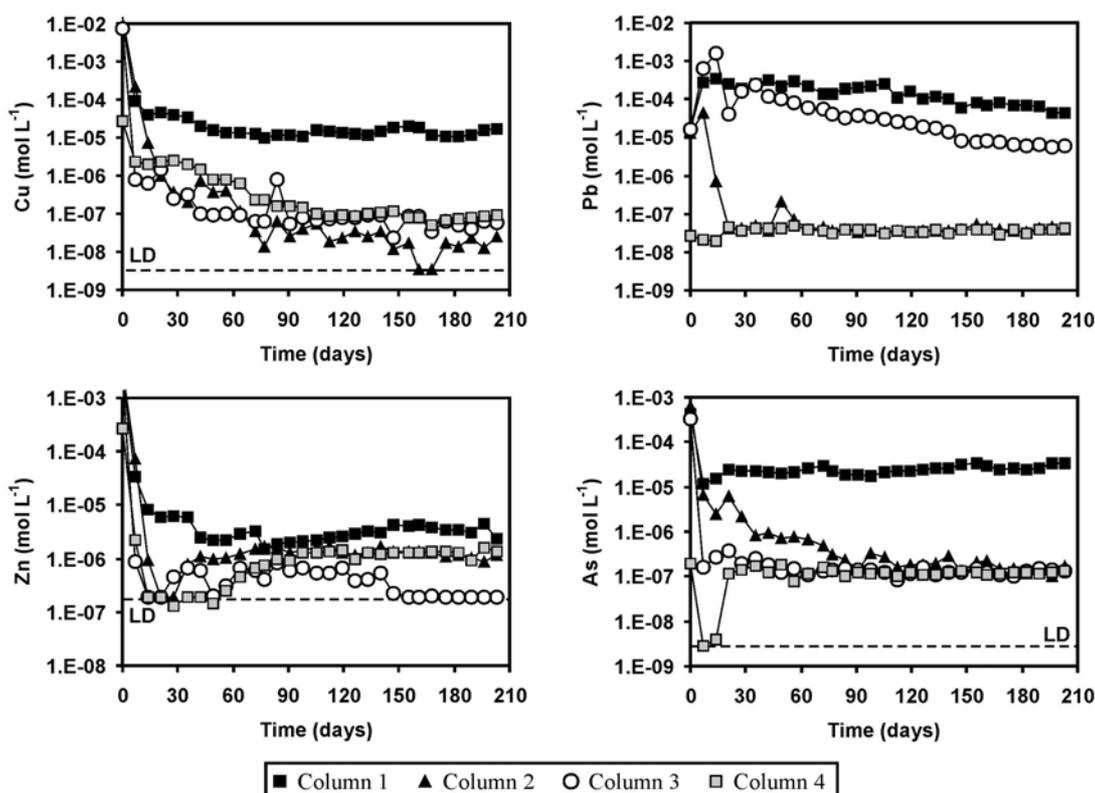
Figure 4: Variation in output concentrations of Cu, Pb, Zn and As as a function of time in the non-saturated column experiments (LD: detection limit)

DISCUSSION

In column 1, low pH values and high sulphate and iron concentrations in the leachates suggest that the oxidation of the pyritic sludge is favourably being produced inside the column, according to pyrite oxidation reactions (Eq. 1 and 2). The thermodynamic modelling of the leachates was realized using the equilibrium geochemical speciation/mass transfer model PHREEQC (Parkhust, 1995). The leaching solutions are supersaturated with respect to minerals of the jarosite group (Fig. 5). However, the precipitation of these minerals only retain a very low proportion of the pollution load, and the leachates transport in solution high sulphate, iron and metals concentration, typical of AMD.
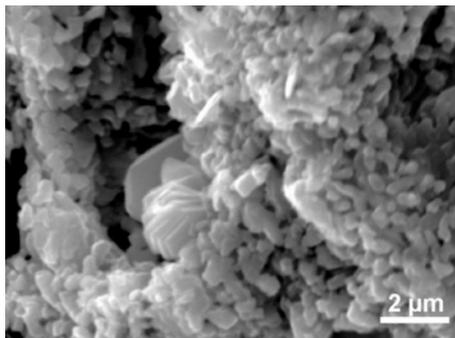

Figure 5: SEM Photographs of jarosite in the non-saturated column 1

However, in columns 2, 3 and 4, the leachates are characterized by high pH values, low sulphate concentration (except in the column 3) and a lack of iron in solution. Inside these columns, the pyrite oxidation process is being neutralized favourably due to the addition of fly ash. The process controlling acid neutralization and metal retention or immobilization in solution is the encapsulation of pyrite grains inside the column. The pyrite sludge is oxidized at alkaline pH due to the presence of fly ash. During pyrite oxidation process, S (aqueous sulphate) is released in solution whereas Fe precipitates immediately as ferrihydrite on pyritic grains (Parnell, 1983) (Fig. 6). Ferric hydroxide coatings prevent any contact between the pyrite and oxidizing agents and the oxidation process is stopped. Only a minor proportion of released S at the steady state comes from the pyrite oxidation (this process is being interrupted at the time), the rest of released S is derived from the leaching of the fly ash which also contains S in the glass phase.
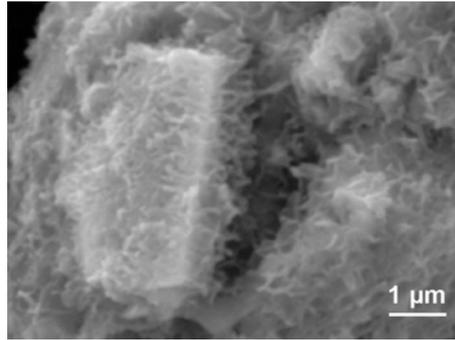
Figure 6: SEM Photograph of Fe-coating on pyrite grains (column 3)

In column 3, there exist two levels of pyritic sludge, an upper level where the pyrite oxidation is produced at acid pH (just like in column 1) and a lower level, below the level of fly ash, where the pyrite oxidation is produced at alkaline pH (just like in column 2). The ferric hydroxide coatings on the pyritic surfaces are only produced in the lower level of pyrite-rich sludge. High concentrations of sulphate in the leachates are reached because the oxidation is not attenuated in the upper level of pyrite-rich sludge (although the iron precipitates when the leachates reach the layer of fly ash).

Copper, lead, zinc and arsenic concentrations in the leachates of column 1 are relatively much higher than the concentration of these metals in the leachates of the columns with fly ash. In fact, these metals co-precipitate and are adsorbed onto the ferrihydrite that is originated inside these columns (McGregor *et al.*, 1998).
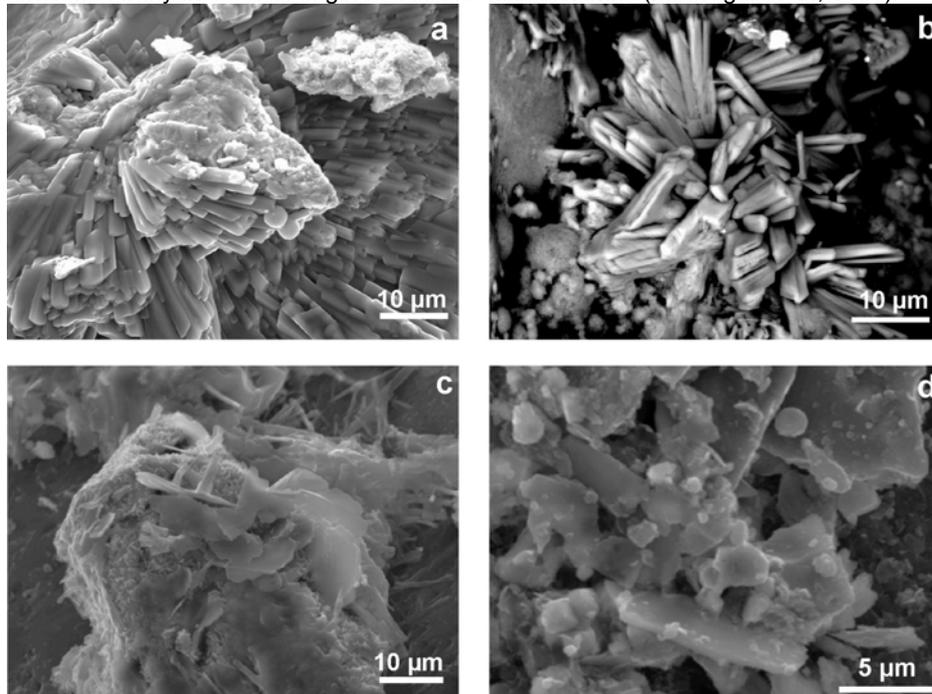

Figure 7: SEM Photographs of gypsum in columns 2 and 3 (a and b respectively) and jarosite in columns 2 and 3 (c and d respectively)

In columns 2 and 3 in addition to ferrihydrite, gypsum and jarosite precipitate at the interface between fly ash and pyritic sludge (Fig. 7). At the same time, a rigid crust or hardpan is developed, and the mining waste can be isolated from the weathering process.

CONCLUSIONS

Acid Mine Drainage (AMD) is one of the principle sources of pollution of natural watercourses and groundwater in the mining environment. In this study a laboratory experiment has been realized to characterize the production of AMD by means of a column experiment filled with a pyrite-rich sludge (71.6 % pyrite) sample from the Iberian Pyrite Belt. The addition of fly ash to this mining waste in column experiments has shown an improvement of the quality of the acid mine drainage generated by the oxidation of pyrite. During the oxidative dissolution of pyrite at basic pH, the released Fe precipitates as ferrihydrite on the pyrite surface. These ferric hydroxide coatings would be expected to significantly reduce the dissolution of pyrite.

ACKNOWLEDGEMENTS

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