

# ACID NEUTRALIZATION AND METALS RETENTION IN SULFIDE-RICH MINING WASTES INDUCED BY THE ADDITION OF FLY ASH<sup>1</sup>

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**Abstract.** In mining environments with sulfide-rich wastes, the aqueous oxidation of pyrite and other metallic sulfides (arsenopyrite, chalcopyrite, sphalerite, galena, etc.) originates an acid drainage with high contents of sulfate and metals called Acid Mine Drainage (AMD). In this work, the oxidative dissolution of a sulfide-rich sludge sample (71.6% pyrite) from the Iberian Pyrite Belt (IPB), the generation of acid mine drainage (AMD), and the potential use of fly ash (a residue of coal combustion) to neutralize the acidity and reduce the metal content of the drainage, have been studied in column experiments.

Obtained results show that: (1) a non-saturated column experiment filled with pyrite-rich sludge with artificial irrigation leached an acid drainage (pH approx. 2) with high concentrations of sulfate, iron and heavy metals; (2) non-saturated columns filled with sulfide sludge and fly ash leached a drainage characterized by high pH values (pH  $\approx$  10), very low sulfate content, and lack of iron and other metals in solution; (3) inside columns with fly ash, the pyrite oxidative dissolution at high pH (as a consequence of the leaching of fly ash) favours metals precipitation (mainly iron), the coating of pyrite grains and the oxidation attenuation; (4) in addition to ferric hydroxide coating, the precipitation of other minerals in the interface between pyrite-rich sludge and fly ash developed a rigid crust, or hardpan, which isolates mining waste from the weathering processes.

Definitely, the addition of fly ash to a pyrite-rich sludge showed an improvement of the quality of the acid drainages and the development of mechanisms (iron coating and hardpan formation) that prevent the AMD production in a long term.

**Additional Key Words:** acid, metals, neutralization, sulfide-rich wastes, fly ash.

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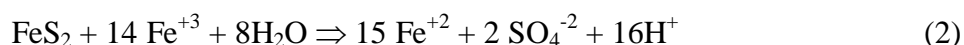
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## Introduction

The Iberian Pyrite Belt (IPB) is located in the Sud-Portuguese Zone of the Hesperic Range. It is one of the largest massive sulfide 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 exposure on the surface of a large amount of sulfides dispersed in mine tailings, tailings dam, open pits, etc.

Pyrite is the most abundant mineral in these polymetallic sulfide deposits. The oxidation of pyrite in an aqueous environment can be expressed by means of the following reactions (Singer and Stumm, 1970):



Oxidizing agents of pyrite are atmospheric  $\text{O}_2$  (Eq. 1) and  $\text{Fe}^{3+}$  (Eq. 2). The result of the oxidation process is a leachate containing high concentrations of protons, Fe and  $\text{SO}_4^{-2}$ . In addition other minor metallic sulfides exist in mining waste (i.e. chalcopyrite  $\text{CuFeS}_2$ , galena  $\text{PbS}$ , sphalerite  $\text{ZnS}$ , arsenopyrite  $\text{AsFeS}$ ) that when oxidized release other metals in solution (i.e. Cu, Pb, Zn, As). These extremely acid leachates containing high concentrations of sulfate, iron and other heavy metals are known as Acid Mine Drainage (AMD) (Parker and 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 mine tailings found in the areas surrounding the mining districts are generally composed of a great volume of inert sterile material that contains minor quantities of sulfides. From a hydrogeological point of view, mine tailings are considered as a highly porous and non-saturated environment, in which there exist a continuous renovation of atmospheric oxygen favouring the intense oxidation of sulfides and the subsequent production of large quantities of AMD.

The addition of limestone to sulfide rich 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 usually a high economic and environmental cost because limestone is a “resource” and not a “residue”.

Fly ash is an alkaline waste product derived from the combustion of coal in power plants. Although fly ash can be used as a construction material, high amounts of produced fly ash constitute a residue without application (Manz, 1997). At present there exist numerous investigations focused on the search of new applications for this residue. For example, the use of fly ash is an effective technique in metal retention processes in contaminated soils (Ayala et al., 1998; Brake et al., 2003; Dermatas and Meng, 2003). Other works propose the effectiveness of the use of fly ash to isolate the sulfide-rich waste from weathering processes (Farah et al., 1997).

The main aims of this study have been: (1) to simulate oxidation conditions prevailing in mine tailings by means of a non-saturated column experiment filled with a homogeneous mixture of small proportions of a sulfide-rich residue and inert quart sand; and (2) to demonstrate the efficiency of acid neutralization and metal retention processes in AMD by the addition of alkaline substances (fly ash) to sulfide-rich residues in non-saturated column experiments.

## Materials and methods

### Characterization of samples

A physical, chemical and mineralogical characterization has been performed on the pyritic sludge and the fly ash, in order to understand the geochemical behavior of these materials under leaching conditions. Grain size distribution was conducted employing a laser diffraction size analyser and the chemical and mineralogical compositions were determined by X-ray fluorescence (XRF) and X-ray diffraction (XRD) respectively (Table 1).

Pyritic sludge. A sulfide rich sludge sample from the Cueva de la Mora tailings dam (Iberian Pyrite Belt, SW Iberian Peninsula) was used as the mining waste that is trying to be isolated in this study. This residue is comprised mainly of sulfides (71.6 % Pyrite) with a median grain-size of 25  $\mu\text{m}$ , and with a high acid generation potential (Table 1).

Fly ash. A material with a chemically different nature from the pyritic sludge was utilized in the process of self-isolation. Fly ash, a residue of coal combustion from the power plant of Los Barrios (Cádiz, S Spain), was the suitable material. It mainly consists of spherical particles with a median grain size of 40  $\mu\text{m}$ . Based on X-ray diffraction patterns, it is composed largely of a chalco-aluminosilicate glass phase (69.4%) together with mullite, quartz, portandite and anhydrite (Querol et al., 2001). It is characterized by high alkali content, and therefore has a high neutralizing potential (Table 1).

Table 1. Chemical and mineralogical composition of the pyritic sludge and fly ash

| PYRITIC SLUDGE                     |       |              |      | FLY ASH                            |       |             |      |
|------------------------------------|-------|--------------|------|------------------------------------|-------|-------------|------|
| Comp.                              | %     | Mineral.     | %    | Comp.                              | %     | Mineral.    | %    |
| <b>SO<sub>3</sub></b>              | 49.84 | Pyrite       | 71.6 | <b>SiO<sub>2</sub></b>             | 41.27 | Mullite     | 20.8 |
| <b>Fe<sub>2</sub>O<sub>3</sub></b> | 30.54 | Chalcopyrite | 0.2  | <b>Al<sub>2</sub>O<sub>3</sub></b> | 27.53 | Quartz      | 4.5  |
| <b>SiO<sub>2</sub></b>             | 8.61  | Galena       | 0.9  | <b>CO<sub>2</sub></b>              | 16.40 | Lime        | 4.1  |
| <b>BaO</b>                         | 8.02  | Sphalerite   | 0.2  | <b>CaO</b>                         | 5.30  | Anhydrite   | 1.3  |
| <b>Al<sub>2</sub>O<sub>3</sub></b> | 1.42  | Arsenopyrite | 0.2  | <b>Fe<sub>2</sub>O<sub>3</sub></b> | 3.28  | Glass phase | 69.4 |
| <b>K<sub>2</sub>O</b>              | 0.22  | Barite       | 9.9  | <b>TiO<sub>2</sub></b>             | 1.41  |             |      |
| <b>CaO</b>                         | 0.04  | Quartz       | 7    | <b>P<sub>2</sub>O<sub>5</sub></b>  | 1.31  |             |      |
| <b>Pb</b>                          | 0.76  | Feldspar     | 5.8  | <b>MgO</b>                         | 1.31  |             |      |
| <b>Zn</b>                          | 0.13  | Muscovite    | 4.3  | <b>K<sub>2</sub>O</b>              | 0.82  |             |      |
| <b>As</b>                          | 0.10  |              |      | <b>SO<sub>3</sub></b>              | 0.54  |             |      |
| <b>Cu</b>                          | 0.08  |              |      | <b>Na<sub>2</sub>O</b>             | 0.33  |             |      |
|                                    |       |              |      | <b>MnO</b>                         | 0.04  |             |      |

Quartz sand. In the leaching experiments, a mixture of 10 wt.% pyritic sludge and 90 wt.% of a inert quartz sand was used. The sand material is composed of quartz grains (approx. 99%) with a median grain size of 0.31 mm. The function of this material is to increase the porosity and

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

### Experimental setting

The experimental design consisted of a column 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.

Column 1 is a control column packed only with the 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 2). The leachates were collected immediately after watering, filtered and analyzed (pH, conductivity and concentration of sulfate and cations).

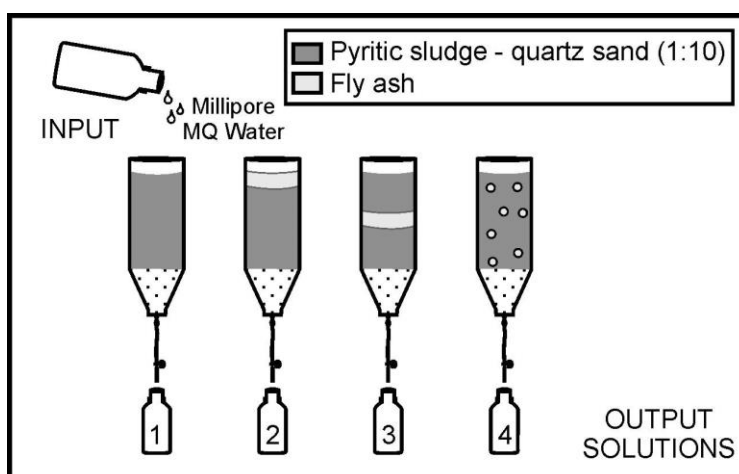


Figure 1. Scheme showing the experimental design of non-saturated columns.

Conductivity, pH and concentration of sulfate and cations were determined in the leachates. The concentrations of  $\text{SO}_4^{-2}$  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).

Table 2. Description of the four non-saturated columns (% PS+QS percentage of the mixture between Pyrite Sludge and Quartz Sand).

| DESCRIPTION   | % PS+QS<br>(1:10) |
|---|-------------------|
| 1. Filled with pyrite-rich sludge and quartz sand (1:10)  | 100               |
| 2. Filled with pyrite-rich sludge and quartz sand (1:10) and a top layer of fly ash (20%)           | ≈ 80              |
| 3. Filled with pyrite-rich sludge and quartz sand (1:10) and a middle layer of fly ash (20%)        | ≈ 80              |
| 4. Filled with a homogeneous mixture of pyrite-rich sludge and quartz sand (1:10) and fly ash (8%). | ≈ 92              |

### Results

### Temporal evolution of pH and conductivity

Leachates from column 1 (pyritic sludge) presents low pH values during all of the experiment (approx 2), and high conductivity values (from 2 to 4 mS cm<sup>-1</sup>) (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, as low as 300 μS cm<sup>-1</sup> in columns 2 and 4 (Fig. 2).

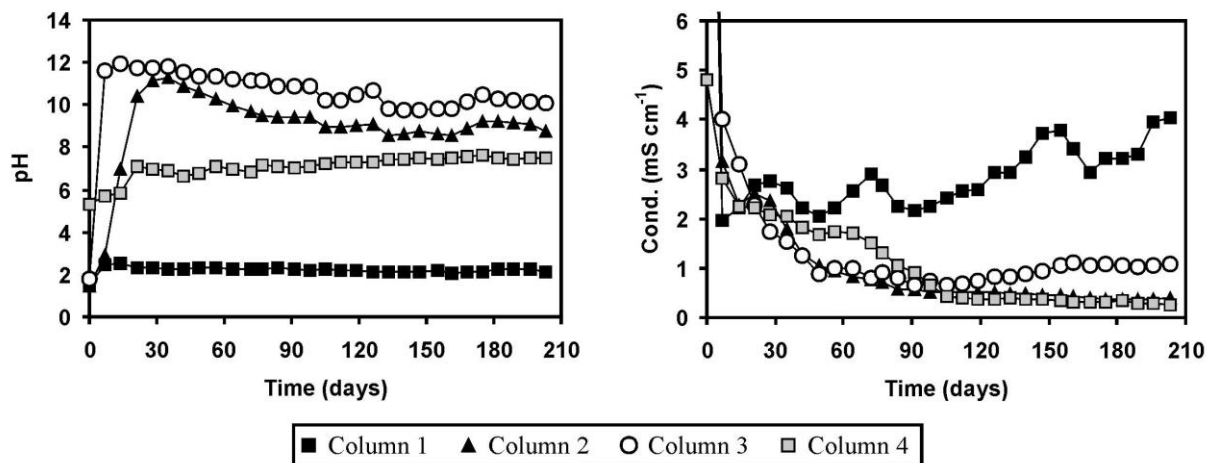


Figure 2. Variation in the pH and the conductivity as a function of time in the non-saturated column experiments.

### Temporal evolution of sulfate and iron concentrations

In column 1, the SO<sub>4</sub><sup>-2</sup> and Fe concentrations in the leachates show a similar evolution to the conductivity (Fig. 3). The SO<sub>4</sub><sup>-2</sup> and Fe concentrations averaged 1x10<sup>-2</sup> and 0.8x10<sup>-2</sup> mol L<sup>-1</sup>, respectively.

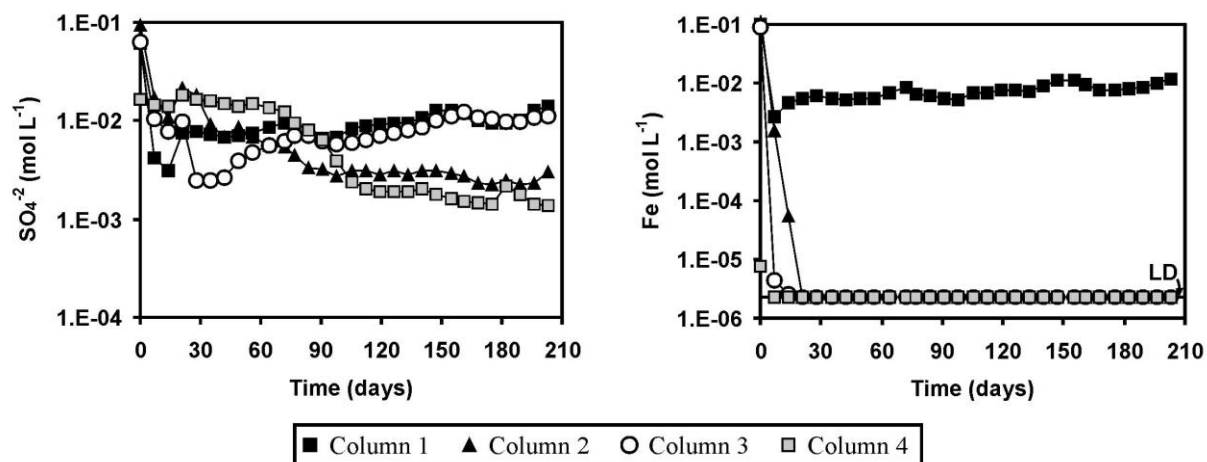


Figure 3. Variation in output concentrations of SO<sub>4</sub><sup>-2</sup> and Fe as a function of time in the non-saturated column experiments.

However, SO<sub>4</sub><sup>-2</sup> and Fe 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 SO<sub>4</sub><sup>-2</sup> concentrations at the onset of the experiment, values decrease gradually until a steady state is attained after approximately 100 days. At the steady state, SO<sub>4</sub><sup>-2</sup> concentrations are about 2.8x10<sup>-3</sup> mol L<sup>-1</sup> and 2.5x10<sup>-3</sup> mol L<sup>-1</sup> in columns 2 and 4, respectively. On the other hand, the

behaviour of Fe 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  $\text{SO}_4^{2-}$  concentrations are much higher than in column 2 although not as high as in column 1 (approx  $0.8 \times 10^{-2} \text{ mol L}^{-1}$  at the steady state).

#### Temporal evolution of Cu, Pb, Zn and As concentrations

The average concentrations of Cu, Pb, Zn and As in the leachates of column 1 are  $1.4 \times 10^{-5}$ ,  $1.4 \times 10^{-4}$ ,  $3 \times 10^{-6}$  and  $2.5 \times 10^{-5} \text{ mol L}^{-1}$  respectively (Fig. 4). In contrast, just like the behaviour of Fe, the concentrations of these metals are much lower in the leachates of columns with fly ash. For example, the average concentrations of Cu, Pb, Zn and As in the leachates of column 4 are  $2.5 \times 10^{-7}$ ,  $3.8 \times 10^{-8}$ ,  $1 \times 10^{-6}$ ,  $1.2 \times 10^{-7} \text{ mol L}^{-1}$  respectively (Fig. 4).

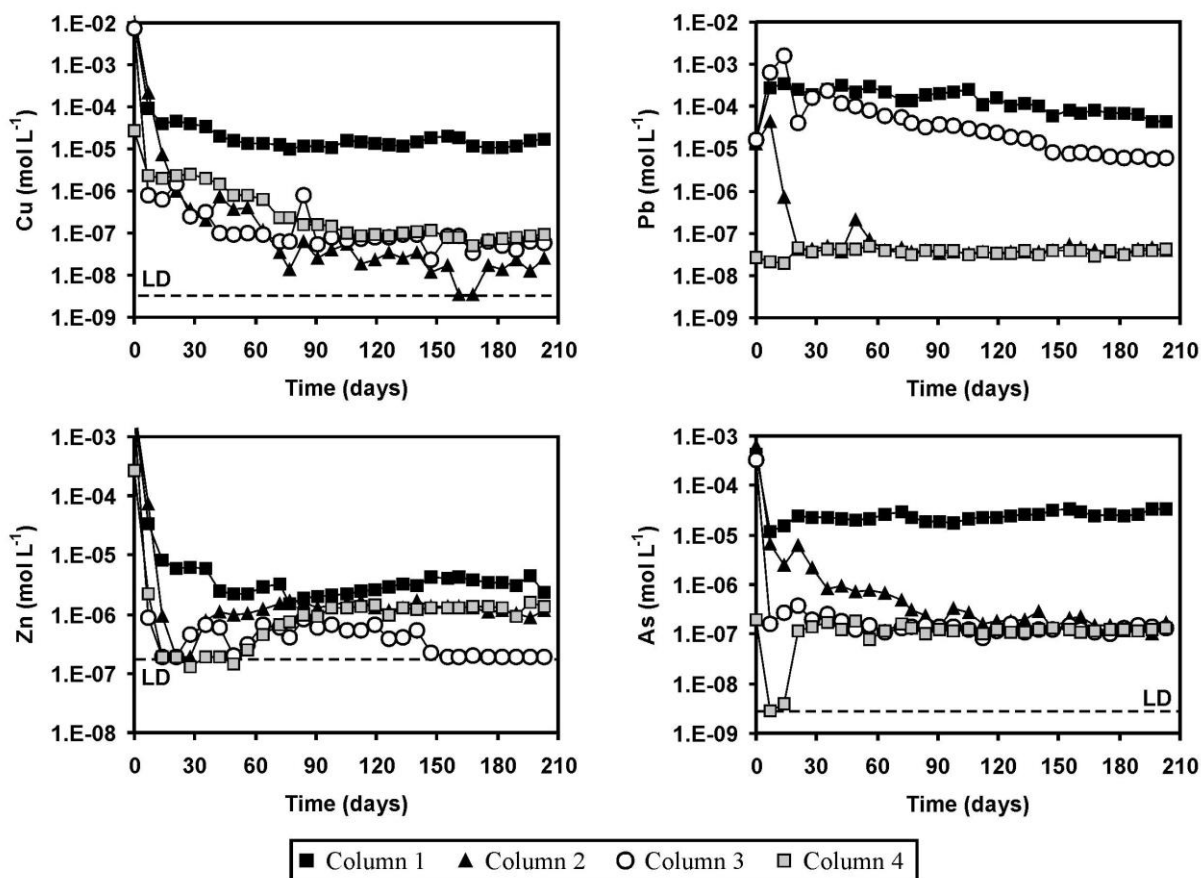


Figure 4. Variation in output concentrations of Cu, Pb, Zn and As as a function of time in the non-saturated column experiments (LD: detection limit).

#### Discussion

The physical, chemical and mineralogical characterization of the pyritic sludge evidences that this material is a potentially acid producing residue, mainly due to the high abundance of sulfides in the sample. Therefore, the geochemical behaviour under leaching conditions would be to produce acid waters. In fact, in column 1, the leachates present low pH values and high sulfate and iron concentrations. This suggests that the oxidation of the pyritic sludge occurs favourably inside the column, according to pyrite oxidation reactions (Eq. 1 and 2).

Thermodynamic modelling of the leachates was performed using the equilibrium geochemical speciation/mass transfer model PHREEQC (Parkhurst, 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 sulfate, iron and metals concentration, typical of AMD.

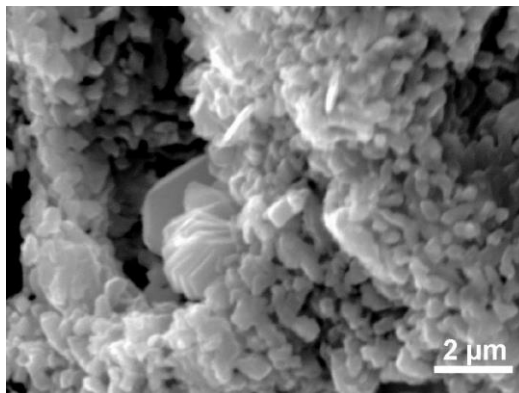


Figure 5. SEM Photographs of jarosite in the non-saturated column 1.

In columns 2, 3 and 4, the pyritic sludge would be also the material responsible for producing AMD (as in column 1). However, the addition of fly ash favours the neutralization of the generated acidity, because fly ash has a high neutralizing potential, as it is deduced from its physical, chemical and mineralogical characterization. In fact, the leachates are characterized by high pH values, low  $\text{SO}_4^{2-}$  concentration (except in the column 3) and the lack of Fe 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  $\text{SO}_4^{2-}$ ) 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.

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  $\text{Fe}(\text{OH})_3$  coatings on the pyritic surfaces are only produced in the lower level of pyrite-rich sludge. High concentrations of  $\text{SO}_4^{2-}$  in the leachates are observed because the oxidation is not attenuated in the upper level of pyrite-rich sludge (although the Fe precipitates when the leachates reach the layer of fly ash).

The Cu, Pb, Zn and As 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).

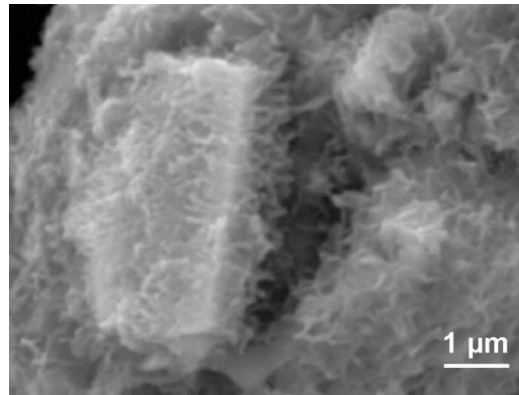


Figure 6. SEM Photograph of Fe-coating on pyrite grains (column 3).

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.

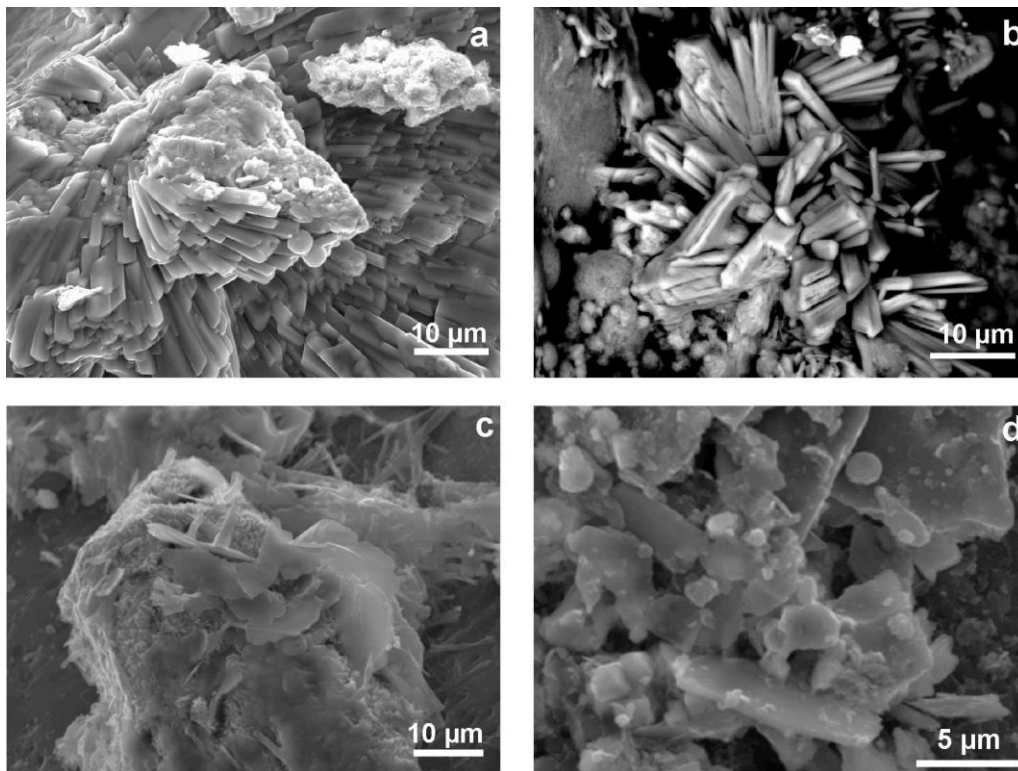


Figure 7. SEM Photographs of gypsum in columns 2 and 3 (a and b respectively) and jarosite in columns 2 and 3 (c and d respectively).

### 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 performed 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.

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