

## Geochemistry and mineralogy of hardpan formation processes at the interface between sulphide-rich sludge and fly ash

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### ABSTRACT

The objective of this study is the mineralogical characterization of the neo-formed phases that precipitate at the interface between two residues with a chemically different nature: a pyritic sludge from the Iberian Pyrite Belt (SW Iberian Peninsula) and fly ash from the power plant of Los Barrios (Cádiz, S Spain). When both residues are deposited together, a hardpan is developed at the interface due to the precipitation of ferrihydrite, jarosite and aragonite. The development of a relatively rigid crust favours the isolation of the mining waste of weathering processes. The experiment was carried out in a non-saturated leaching column fills with pyritic sludge and two levels of fly ash intercalated with artificial irrigation (300 mL water each two or three weeks). As the hardpan formation process needs a relatively large time interval, a heating source (two infrared lamps) was placed on top of the column to accelerate the oxidation and precipitation processes.

### INTRODUCTION

The oxidative dissolution of sulphides results in the release of high concentrations of protons, metals and sulphate in to natural watercourses and groundwater, being this process known as Acid Mine Drainage (AMD) (Parker & Robertson, 1999). The production of AMD from sulphide-rich residues is one of the principle sources of pollution in the mining environment.

At the surroundings of mining districts, the mine tailings are composed of a high volume of inert sterile and small amounts of sulphides. From a hydrogeological point of view, the mine tailings are very porous and non-saturated environment, in which there exist a continuous renovation of atmospheric oxygen that favours the intense oxidation of sulphides and the production of AMD.

Some previous works propose the effectiveness of using sealants containing cement compounds and natural resins to isolate the mining waste of the weathering processes (Farah *et al.*, 1997). Both types of sealants form a cap whose main function is to protect the mining waste from the oxidation process, and therefore, retarding the generation of AMD.

On occasions isolation can be achieved in a natural way when two chemically different residues are deposited together. In this case, the process of self-isolation consists in the development of a rigid crust called hardpan at the interface between both residues (Ding *et al.*, 1998, 2002). This crust is originated by cementation of solid particles due to the precipitation of silica, iron oxyhydroxides, sulphates, etc. The precipitation of the neo-formed phases has a double function, on one hand, part of the contaminants transported in solution are retained, and on the other hand, the development of the crust o hardpan causes a resistance to water transport due to its low permeability. In addition, the advantage of the hardpan formation is that any mechanical damage of the rigid crust will be repaired automatically by means of these processes of precipitation (van der Sloot *et al.* 1995).

The aim of this work is to describe the mineralogy and the process of formation of a hardpan at the interface between sulphide-rich sludge and fly ash, a by-product of coal combustion.

### MATERIALS

A physical, chemical and mineralogical characterization has been realized with the materials used in this study. 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 sulphide 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 sulphides (71.6 % Pyrite) with a median grain-size of 25 µm, 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 is mainly constituted by spherical particles with a median grain size of 40 µm. Based on X-ray diffraction patterns, it is composed largely by a chalc-aluminosilicate glass phase (69.4%) together with mullite, quartz, porlandite and anhydrite (Querol *et al.*, 2001). It is characterized by high alkali content, and therefore has a high neutralizing potential (Table 1).

### Quartz sand

In the leaching experiments, a mixture of 10 wt.% pyritic sludge and 90 wt.% of an inert quartz sand was used. The sand material is composed by 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 sulphide-rich residue. The aim is to favour the processes of evaporation, oxygen renovation and sulphides oxidation, simulating the conditions that prevail in mine tailings.

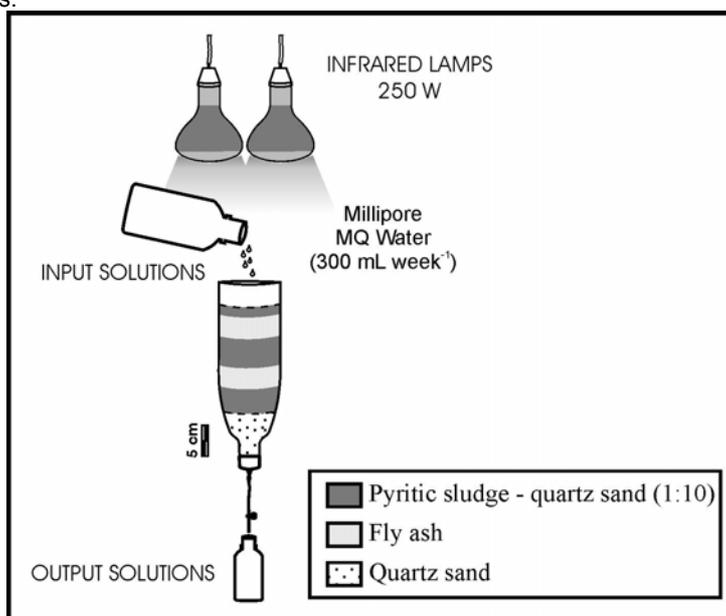
**Table 1: Chemical and mineralogical composition of the pyritic sludge and fly ash**

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

### METHODS

The characterization of both residues evidences that they are chemically different. The pyritic sludge is a potentially acid producing residue, whereas fly ash is potentially acid neutralizing residue. In order to simulate the self-sealing process of the pyritic sludge, a non-saturated column of 30 cm in length and 10 cm in diameter filled with the mixture of quartz sand and pyritic sludge, and with two levels of intercalated fly ash was constructed. A layer of quartz sand was placed at the bottom of the column in order to favour the drainage (Fig. 1).

The diffusion coefficient of oxygen in air is five orders of magnitude higher than in water. In addition, the oxygen concentration in air can be higher than in water. For this reason, two infrared lamps were placed on top of the column to increase the surface temperature (to approx. 50°C) and to accelerate the evaporation, oxidation and precipitation processes.



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

The column was watered 14 times with 0.3 L Millipore MQ water (18.2 MΩ) over a period of approximately 15 weeks. Conductivity and pH were determined immediately after sample collection. The concentration of sulphate and cations was obtained using inductively coupled plasma emission spectroscopy (ICP-OES) analysis. When the

experiment was finished the reacted materials were observed under a JEOL JSM-5410 scanning electron microscope (SEM) with an energy dispersive spectroscopy (EDS). The mineralogy of some selected samples was also studied with a powder X-ray diffractometer (XRD) using  $\text{K}\alpha\text{Cu}$  radiation.

## RESULTS AND DISCUSSION

### Temporal evolution in pH and conductivity

Due to the presence of fly ash, the acid leachates generated by oxidation of the pyritic sludge became neutralised. The pH and conductivity values of the leachates after 45 days averaged 8 and 1.5 mS/cm respectively (Fig. 2). The low conductivities are correlated clearly with the low concentrations of sulphate and metals in solution.

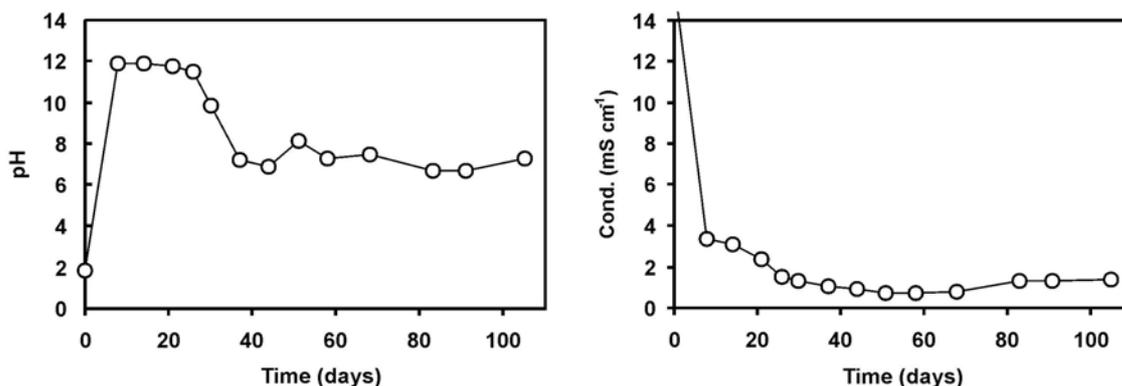


Figure 2: variation in pH and conductivity as a function of time in the non-saturated column experiment  
Temporal evolution in the sulphate and metals concentrations

The leachates are characterized by low sulphate concentrations ( $1.10 \times 10^{-2} \text{ mol L}^{-1}$ ) and iron concentrations below the detection limit of the ICP-OES used (Fig. 3). Zinc, lead, arsenic and copper concentrations are relatively low, and often are also below the detection limit.

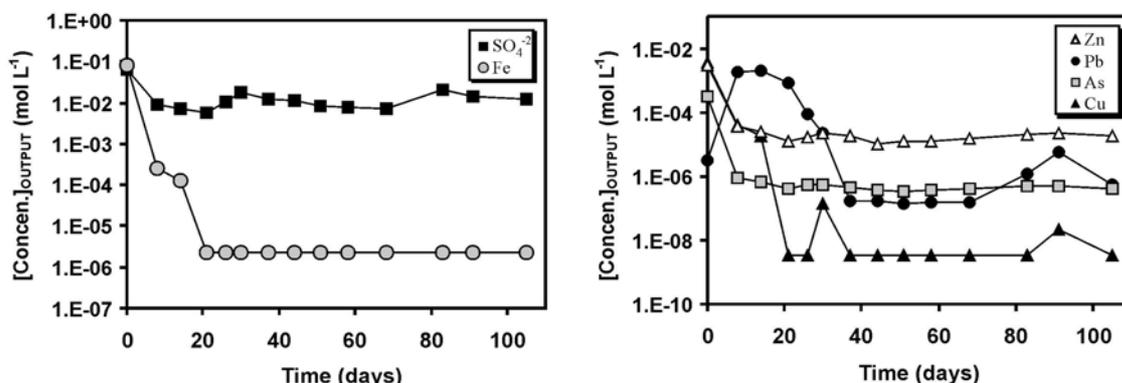


Figure 3: Variation in the sulphate, iron and other metals as a function of time in the non-saturated column experiment

### Mineralogical characterization of the column experiment

When the experiment was finished, two neo-formed levels were observed inside the column, one at the upper contact between the pyritic sludge and the top layer of fly ash, and the other in the lower contact with the underlying layer of fly ash. The upper neo-formed level was better developed, forming even a relatively hard crust or hardpan. The neo-formed phases that constitute this level are: ferrihydrite, jarosite and aragonite.

In Figure 4, a scheme of the formation process of the upper neo-formed level is shown. During the leaching experiment, the pyritic sludge leached acid drainage containing high concentrations of sulphate and metals. In contrast the fly ash leaches alkaline solutions containing high concentrations of alkali elements. At the interface between both residues, acid drainages are neutralized and metal retention process by precipitation of neo-formed phases occurs.

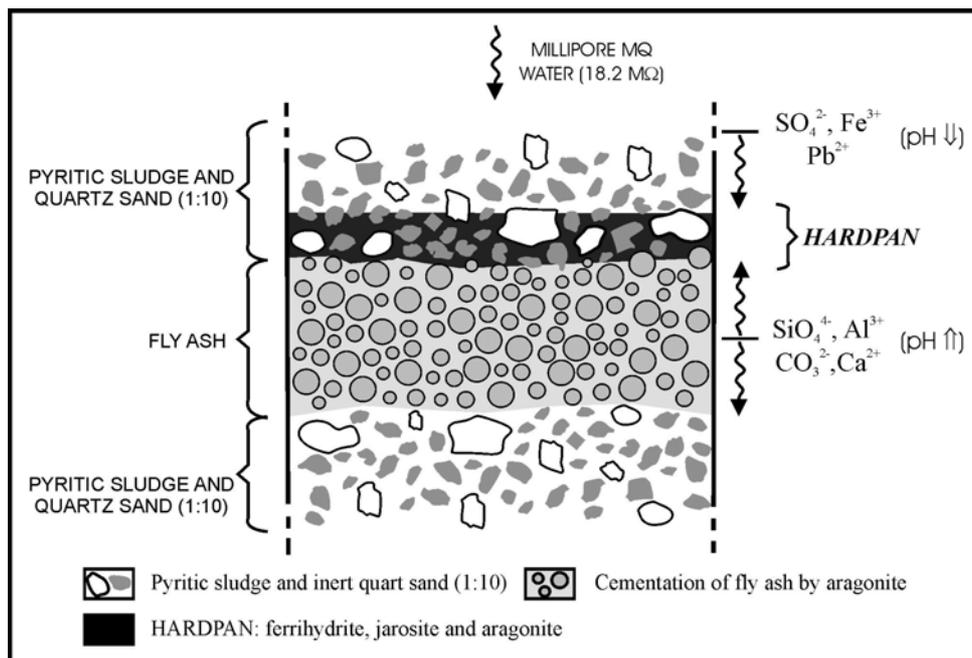


Figure 4: Scheme showing the formation process of the top hardpan

In the hardpan, ferrihydrite encapsulates the pyrite grains (Fig. 5a), jarosite coats the whole level (Fig. 5b) and aragonite cements all the mineral grains together (Fig. 5c). In this way, a relatively hard crust is developed, isolating one residue of the other. In the lower neo-formed level, these phases are less abundant and, therefore, this level presents a minor resistance.

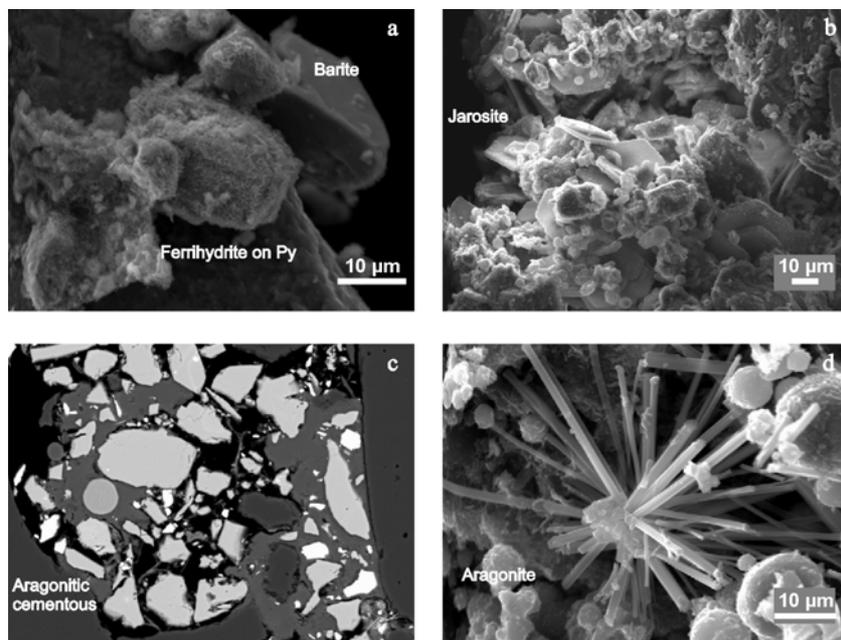


Figure 5: SEM Photographs. See text for explanation

The processes controlling the pollutant retention and immobilization in solution are: (1) the precipitation of the neo-formed phases; and mainly (2) the formation of ferrihydrite coating on the pyrite surface. During oxidation of pyrite, the Fe released precipitates immediately as ferrihydrite because of the alkaline pH (due to the presence of fly ash). These precipitates form a coating on the pyrite grains, and the oxidation process is slowed at this time (until it is annulled) (Pérez-López *et al.*, 2005).

The formation of a layer with low permeability prevents the contact between the pyritic sludge and the oxidizing agents, isolating the mining waste from the weathering process and retarding the production of AMD (McGregor & Blowes, 2002). This process is favoured by the self-cementation of the fly ash level due to the precipitation of aragonite (Fig. 5d).

## CONCLUSIONS

The oxidation of sulphides present in mining wastes is the principal source of Acid Mine Drainage. This drainage contains high concentrations of protons, sulphates and metals. When an acidity neutralizer residue (i.e. fly ash) is deposited on AMD producer residue (i.e. pyrite-rich sludge), the resultant leachates are characterized by alkaline pH values and low conductivity. In addition, the development of a hardpan at the interface between both residues has a double importance: (1) the neo-formed minerals of the hardpan retain part of the pollutant load (it explains the low values of conductivity) and (2) the isolation of the AMD generator residue is produced. The self-isolation process prevents the progress of further oxidation processes of the mining waste. This process is also favoured by the formation of a ferrihydrite coating on the pyrite grains.

## ACKNOWLEDGEMENTS

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