

## Factors affecting the transformation of a pyritic tailing: scaled-up column tests

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### Abstract

Two different methods for predicting the quality of the water draining from a pyritic tailing are compared; for this, a static test (ABA test) and a kinetic test in large columns were chosen. The different results obtained in the two experimental set-ups show the necessity of being careful in selecting both the adequate predictive method and the conclusions and extrapolations derived from them.

The tailing chosen for the weathering tests (previously tested in shake flasks and in small weathering columns) was a pyritic residue produced in a flotation plant of complex polymetallic sulphides (Huelva, Spain). The ABA test was a modification of the conventional ABA test reported in bibliography. The modification consisted in the soft conditions employed in the digestion phase. For column tests, two identical methacrylate columns (150 cm high and 15 cm diameter) were used to study the chemical and microbiological processes controlling the leaching of pyrite.

The results obtained in the two tests were very different. The static test predicted a strong potential acidity for the tailing. On the contrary, pH value in the effluents draining from the columns reached values of only 5 units, being the concentration of metals (<600 mg/L) and sulphate ions (<17,000 mg/L) very small and far from the values of a typical acid mine drainage.

In consequence, the static test may oversize the potential acidity of the tailing; whereas large columns may be saturated in water, displacing the oxygen and inhibiting the microbial activity necessary to catalyse mineral oxidation.

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**Keywords:** Pyritic tailing; Scaled-up column model; Predictive weathering tests

### 1. Introduction

Nowadays environmental management is based on a preference for prediction and prevention of a problem over corrective actions once a problem has arisen. There is therefore growing interest in the improvement of contamination prediction tests, and in particular any topic related to the prevention of acid rock drainages affecting mining activities.

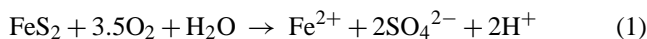
Residues from mining and metallurgical plants, once dumped, remain exposed to changing environmental conditions. The phenomenon known as weathering refers to the ac-

tion of water, oxygen, microorganisms, temperature, etc. on these residues and their subsequent transformations. It is important to predict the evolution of such residues in response to all those environmental factors in order to institute measures to prevent the negative consequences of their transformation.

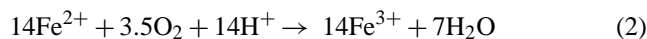
There are three determinant factors in the transformation of a pyritic residue to produce an acidic drainage: (1) chemical oxidation; (2) the role of microorganisms in such oxidation; and (3) the final disposal conditions of the residue. Obviously, the oxidation rate of the residue is directly related to how easily the oxidant reaches the solid and hence to the fluid (water) flow and the rock characteristics [1]. Typical oxidants are oxygen and ferric iron. The concentration of oxygen in groundwater is very small compared to the large amounts of

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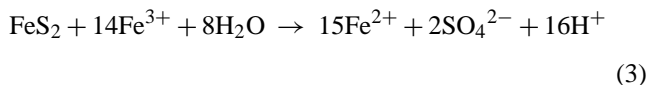
oxygen required in the overall reaction:



Thus, the dominant pathway for pyrite dissolution involves oxidation of ferrous iron by oxygen:



followed by reduction of ferric iron by sulphide:



The oxidation of ferrous iron is controlled by indigenous microbes and is thus limited by the availability of nutrients [2]. The actual role of bacteria in the bioleaching process has not been completely resolved; albeit recent findings suggests that the oxidation of sulphide minerals occurs mainly via the chemical attack by ferric iron and/or acid, which are generated by bacteria [3].

On the other hand, there are several important factors such as temperature, pH, availability of nutrients, sulphide minerals, O<sub>2</sub> and CO<sub>2</sub>, solid ratio, metal toxicity, etc., that affect the growth of bacteria and hence the dissolution process [4].

Basically, assessment of the contaminant potential of a residue consists of the following steps [5–7]: (1) comparison with situations in similar or nearby areas; (2) design of a programme to collect representative samples of the waste; (3) static tests; (4) kinetic tests using samples identified as potentially acid generating; and (5) modelling.

Static tests are simple and fast, but they are not used to predict the quality of waste drainage over a long period. For this reason, static tests must be considered as qualitative prediction methods.

One example of a widely used static test, described by the US Environmental Protection Agency (EPA) under Method 1312, is the acid–base account test (ABA test). The ABA test [5,8–10] is based on a comparison between the maximum potential acidity that a sample can produce, obtained from the total S content of such sample, and its neutralization potential, determined from the attack on the sample in the presence of a known concentration of acid.

On the other hand, kinetic tests are used to confirm the predictions of static tests, to determine the rate of acid generation, sulphide oxidation and neutralization, and to assess the efficiency of control/treatment techniques. This information is critical because in some cases the rate of acid generation can be insignificant, or only significant in short-lived extreme circumstances, so that costly long-term techniques are not necessary to prevent environmental problems. In addition, data from kinetic tests can be used to design very specific acid generation prevention techniques and to address each concrete situation while optimising the cost of drainage treatment.

There are two basic models of kinetics tests: shake flasks and columns. This second solution is attractive in that it serves

at once to monitor evolution of the quality of the water that a particular waste leaves as a consequence of weathering and to identify the minor temporal variations taking place in the course of acid water generation.

There are many possible ways to design weathering experiments using the column model. There are no established rules for their implementation because they are often planned to deal with the particular characteristics of the residue and to gather a specific kind of information. However, in the experimentation described in the literature, certain column sizes and certain ways of treating the solid residue are more frequently used [11–14]. The British Columbia Acid Mine Drainage Task Force has published a detailed guide that describes both the different prediction methods of acid rock drainage and the different control techniques [15]. Also, the US Bureau of Mines (Pittsburgh, USA) has worked on a research line that addresses the factors affecting the dissolution and migration of dissolved heavy metals from mining wastes.

The correct design of a column (also known as a lysimeter) is essential to assure valid and applicable results. An inappropriate design can overestimate the contaminant capacity of a waste, or it can mask some important factors, thus preventing a correct appreciation of the problem. The data obtained through these bioreactors can be used to determine what steps are necessary to foresee or to correct the environmental problem, and to calculate the costs associated with such steps.

Additionally, Foucher et al. [16] have demonstrated how important an appropriate design is in determining the bacterial population associated with a waste and the activity of that population.

The last step of the weathering study of a residue considers different methods of prevention and/or treatment. To this end, once it has been demonstrated that the chosen model suitably reproduces the behaviour of the system, it is used to test such methods [17].

Two predictive tests (a static ABA test and a kinetic test in large column) have carried out to determine factors affecting the transformation of a pyritic tailing under weathering conditions. The effectiveness of the two methods as predictive test has also studied.

## 2. Materials and methods

### 2.1. The system

The pulp sample used for the experiments was taken from the exit of the flotation plant of a mining company situated in the Iberian Pyritic Belt (Huelva, Spain). The residues are sent to a pond for liquid–solid separation through a 3 km open-air gravity channel. In the pond, the solids settle to the bottom, giving rise to two different zones in terms of the oxygen gradient: an anaerobic zone at the bottom of the pond and an aerobic zone occupied by surface solids and waters. For additional details of the system characteristics, see [18].

## 2.2. Chemical and mineralogical analysis

### 2.2.1. Solid samples

The solids contained in the pulp samples were characterised by X-ray diffraction (Philips X'Pert-MPD) and granulometric analysis. In this last case, the Coulter counter method based in the electrical resistance of the medium was used (Microtac FRA). Chemical composition was determined after acid digestion of the samples; subsequent analysis of metals in solution was performed by atomic absorption spectrophotometry (AAS) (Perkin-Elmer 1100B). Sulphur content was determined using an automatic analyser from Leco.

### 2.2.2. Liquid samples

pH evolution was monitored using a Crison 2001 electrode. Sulphate was analysed by a photocolimeter (Metrohm 662), which determines the turbidity of barium sulphate precipitates formed by reaction of sulphate ion with barium chloride [19]. Metals contained in the liquid samples were monitored by AAS.  $\text{Fe}^{2+}$  was determined by photocolometry using *o*-phenanthroline as colorimetric reagent in acetic medium [19,20] and the same Metrohm 662 photocolimeter.

## 2.3. Microbiology

The pulp used for the weathering tests was characterised microbiologically. The following culture mediums were used to isolate microorganisms:

### 2.3.1. Aerobic

- *Chemolithotrophs*: 9 K medium at pH 3 [21] ( $(\text{NH}_4)_2\text{SO}_4$ , 3 g/L; KCl, 0.1 g/L;  $\text{K}_2\text{HPO}_4 \cdot 3\text{H}_2\text{O}$ , 0.618 g/L;  $\text{MgSO}_4$ , 0.5 g/L;  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ , 0.013 g/L) containing one of the following compounds as energy source: ferrous iron (33 g/L), tetrathionate (5 g/L), thiosulphate (5 g/L) or elemental sulphur (spatula tip).
- *Heterotrophs (bacteria, yeasts and fungi)*: (1) medium A: 9 K medium at pH 3 with 10 g/L glucose, 5 g/L yeast extract and 15 g/L agar; (2) medium I: 9 K medium at pH 3 with 0.5 g/L bactotrypton; 1 g/L malt extract; 10 g/L glucose; and 15 g/L agar.

### 2.3.2. Anaerobic

Postgate C medium ( $\text{KH}_2\text{PO}_4$ , 0.5 g/L;  $\text{NH}_4\text{Cl}$ , 1.0 g/L;  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ , 0.06 g/L, sodium lactate (70%), 3.5 g/L; yeast extract, 1.0 g/L;  $\text{CaSO}_4$ , 1.0 g/L;  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ , 0.01 g/L;  $\text{Na}_2\text{SO}_4$ , 4.5 g/L;  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ , 0.06 g/L; sodium citrate, 0.3 g/L) was used (ASTM D 4412-84). The same medium but with sodium molybdate was also used for the control.

The samples were inoculated in a solid medium to isolate microorganisms.

Enrichment cultures were also prepared in a different medium. For this purpose, 500 mL of pulp was filtered using a 0.22  $\mu\text{m}$  Millipore filter. The filter was washed with 10 mL of acid distilled water, from which aliquots of 100  $\mu\text{L}$  were

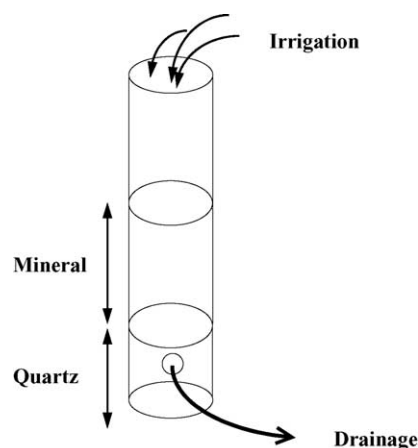


Fig. 1. Weathering column.

taken to inoculate 100 mL of the liquid mediums 9 K with Fe, 0 K (9 K medium without iron II) with S, and I. These cultures were kept in a shaker flask for at least 1 month with continuous shaking at 30 °C.

Enrichment cultures for the growth of anaerobic bacteria were also prepared in Postgate C medium at pH 7. The same medium was used at double concentration for liquid samples. In both cases, 10% inocula were used.

All cultures were kept at 30 °C.

Microorganism counts were performed using the more probable number (MPN) method [19,22,23].

## 2.4. Static test: ABA test

The potential acidity of the samples was determined by ABA test, although the test finally employed was a modification of the standard ABA test [8]. The novelty of this modification was that the digestion phase of the sample used soft conditions (orbital agitation at controlled temperature of 35 °C for 24 h instead of heating to boiling-point), thus avoiding overestimation of the sample neutralization potential. Samples were dried in air and ground to a homogenous size before testing (<50  $\mu\text{m}$ ).

## 2.5. Scaled-up column tests

Weathering tests were performed in two methacrylate columns. The columns (M1 and M2) were identical in height (150 cm) and in diameter (15 cm). The mineral was set as a slurry on a 20 cm bed of silica stones at the bottom of the column. Columns were watered through the upper part and drainages were collected by way of a pipe situated in the lower part (Fig. 1).

Each column was fed with pulp containing 30% solids in the weight indicated in Table 1. The characteristics of the pulps used in each column were similar but not identical, as they came from two different samplings conducted in the waste pond. Pulp P1 was used in column M1 and pulp P2 in column M2. The final heights of the beds in the columns once

the solids had settled were 65 and 50 cm, respectively. The columns were heated at approximately 30 °C (28–33 °C) in a thermostatically controlled metal basin with turbine-powered air recycling.

The tests were started by placing the pulp in the columns and leaving it for long enough to ensure an efficient and appropriate distribution of the liquid and solid phases inside the system. Weathering of the solid residue in the columns consisted of two steps. In the first step, which lasted 16 weeks and was only tested in column M1 using pulp P1, the column was continuously watered by a peristaltic pump whose flow was modified as required by the percolation conditions of the system. When the column was stabilised, the optimum observed percolation flow was 2 mL h<sup>-1</sup> (48 mL day<sup>-1</sup>) with a watering flow of 45 mL day<sup>-1</sup> adjusted to add 15 mL every 8 h. In these conditions the solid was wet but there was no water on top of the pulp surface.

The second step consisted in subjecting the pulp to dry and wet cycles. In this case both columns (M1 with pulp P1 and M2 with pulp P2) were used. Each column was dosed with 2 L of distilled water per cycle. After watering, water remained in contact with the solid residue for 48 h; then the columns were drained and kept dry for the next 12 days. The second step lasted 20 weeks.

A modified version of this second step was also used, in which the dry cycles were longer. These new cycles lasted approximately 45 days, with the same watering volume (2 L) and humidity time (48 h) in both columns.

The total duration of the tests was 36 weeks.

Table 1 summarises the characteristics of the columns used in this work.

## 2.6. Control of the experiments

The weathering tests were controlled by analysing different variables relating to column drainage. The chemical variables were: pH; Eh; and iron, copper, zinc and sulphate concentration in solution. All analyses were based on the total volume of the drainages once the column had ceased to drain more liquid.

## 3. Results and discussion

### 3.1. Characterisation of tailings

The characteristics of the two pulp samples are summarised in Tables 2–5. In both cases the solid chemical composition (obtained by means of X-ray diffraction and con-

Table 2  
Chemical composition of the solids contained in pulps P1 and P2

Pulp	Cu (%)	Pb (%)	Zn (%)	Fe (%)	S (%)	Ag (g/t)	Sb (g/t)
P1	0.5	2	2	38	37	45	970
P2	0.2	1.3	1.4	36	38	25	448

firmed by the results of elemental chemical composition) is that of a pyrite ore (Table 2) with an average particle size of 22.9 µm for pulp P1 and of 41.9 µm for pulp P2. The chemical composition of the water associated with the pulps is similar (Table 3), with pH values up to 7.0 and very low concentration of heavy metals and sulphates. Table 4 shows the microorganism counts of each sample before experimentation. The presence of lithoautotroph bacteria was confirmed by the amber colour of the flask solution, by the precipitation of jarosites and by light microscopy of the cells. In addition, the growth in a medium with sulphur and in medium I was positive for heterotrophs from P1 and P2. No sulphate reducing bacteria were isolated from either pulp.

The mineralogical composition of the pulps (Table 5), obtained by means of X-ray diffraction confirmed the results of chemical composition.

### 3.2. ABA static test

Results of the ABA test are shown in Table 6. These data confirmed that: the neutralization potential (NP) of sample P2 was higher than P1, the acid potential (AP) was similar in both cases and the net neutralization potential (NNP) was lower than zero. This is an indicative that both pulp samples were potentially net acid generating in the weathering test.

### 3.3. Scaled-up weathering columns

During this preliminary phase the pH in the various drainages remained between 7 and 8, indicating no tendency to acid generation, and there were no major changes in sulphate concentration. The iron, copper and zinc concentrations measured in the column effluents ranged from 0.1 to 0.3 mg/L.

This result was unexpected and appeared to conflict with the data from previous small-scale tests [18,24] in which weathering of the wastes produced acid drainages. The watering plan was therefore modified in order to study the behaviour of the system under wet/dry cycles.

The wet/dry cycle methodology is emphasised in the literature [11,25], since this makes it possible to more realistically reproduce the changing environmental conditions that affect waste after dumping.

Table 1  
Characteristics of the columns used in the weathering tests

Column	Ø (cm)	H <sub>bed</sub> (cm)	V <sub>bed</sub> (cm <sup>3</sup> )	Residue (g)	V <sub>water added</sub> (mL/cycle)	V <sub>water drained</sub> (mL/cycle)
M1	15	65	11486	9000 (P1)	2000	1800
M2	15	50	8836	7000 (P2)	2000	1800

Table 3  
Chemical composition of water contained in pulps P1 and P2

Pulp	Eh, SHE (mV)	pH	Fe (mg/L)	Cu (mg/L)	Zn (mg/L)	SO <sub>4</sub> <sup>2-</sup> (mg/L)	SO <sub>3</sub> <sup>2-</sup> (mg/L)
P1	892	6.9	0.2	0.2	4.0	2940	246
P2	52	9.2	0.4	0.1	0.8	1800	180

Table 4  
Initial microorganisms counting in pulps P1 and P2 (MNP, g<sup>-1</sup>)

Pulp	Fe-oxidising	S-oxidising	Total heterotrophs	SRB
P1	10	183.25 × 10 <sup>2</sup>	806.3 × 10	–
P2	50	20 × 10 <sup>3</sup>	734 × 10	–

(–) negative growth; SRB: sulphate-reducing bacteria.

Table 5  
Mineralogical composition of the mud (w/w, %)

Mineral	P1	P2
Chalcopyrite	1.4	1.4
Galena	0.5	0.4
Sphalerite	0.8	0.7
Pyrite	63.4	58.1
Carbohydrates and silicates	33.9	39.5

The purpose of this modification was to reproduce the effect of dry periods on the pond pulp in those areas where a part of the ore was exposed to surface weathering agents as a consequence of the pulp sedimentation conditions. Due to the climatological conditions of the area where the flotation plant is situated (dry and very hot during the summer), the pyrite waste was subject to prolonged dry, hot periods, although occasional rain could facilitate weathering of the dry solid residue. The main objectives of our research were therefore best served by altering the watering cycle.

As noted in Section 2.5, watering cycles were effected with 2 L of distilled water, which was brought into contact with the ore for 48 h with periodic drainage. Weathering in these new conditions produced a significant decrease of pH (Fig. 2, column M1) and an increase in the metal and sulphate concentration in the drainages (Figs. 3 and 4, column M1). As these figures show, the concentration of zinc, iron and sulphate increased as weathering progressed. The final concentrations in solution (20 weeks) were 640 mg/L of iron, 600 mg/L of

zinc and ~18,000 mg/L of sulphate. Copper concentrations never exceeded 0.5 mg/L, but it should be remembered that in a pyrite residue, the copper content in the waste will always be lower than the zinc content and much lower than the iron content (Table 2). The same effect has been reported in other weathering tests [18]. Another factor contributing to the different metal concentration in the water draining from the columns was the different dissolution kinetics of the three main mineral species present in the pulp. Usually, sphalerite is much more reactive in acid media than chalcopyrite. In addition, as it has been reported [26], pyrite is more sensitive to microbial attack than sphalerite and this one more than chalcopyrite.

The two lengthy dry periods speeded up the weathering of the waste. However, the oxidation kinetics for weathering of column M1 were slower than in previous experiments. In shake flasks and small columns pH reached values <2, metals concentration up to 20 × 10<sup>3</sup> mg/L and sulphates concentration over 120 g/L [18,27]. In order to confirm these results, a new weathering column (column M2; see characteristics in Table 2) was set up in the same conditions, but with a different residue: pulp P2 (Tables 2–5).

The evolution of the drainage composition in this new column is also shown in Figs. 2–4 for comparison with column M1.

On the whole, the evolution in column M2 was similar to that in column M1, thus confirming the initial results. The pH values measured in both drainages (Fig. 2) were comparable, both exhibiting a slow tendency to acidification. The metal concentrations in M1 and M2 were likewise similar (Fig. 3): around 500 mg/L of zinc, 600 mg/L of iron and 0.5 mg/L of Cu, which was practically constant from the outset of the experiments. The same was true for the sulphate concentration (Fig. 4). Neither column showed a clear tendency to generate acid drainages, although in column M2 the oxidation kinetics

Table 6  
Results of the ABA static tests

Sample	pH		V <sub>NaOH</sub> (mL)	V <sub>HCl reacted</sub> <sup>a</sup> (mL)	kg CaCO <sub>3</sub> /t		
	Initial	Final			NP <sup>b</sup>	AP <sup>c</sup>	NNP = NP – AP
P1 <sub>1</sub>	0.59	8.32	20.7				
P1 <sub>2</sub>	0.59	8.37	20.6				
V <sub>mean</sub>			20.65	0.94	12.2	1.175	–1.163
P2 <sub>1</sub>	0.65	8.56	19.7				
P2 <sub>2</sub>	0.60	8.33	20				
V <sub>mean</sub>			19.85	4.00	51.8	1.192	–1.140

Basis: 2 g of solid sample; HCL 0.52N added: 80 mL; excess titration with NaOH 1.98 N.

<sup>a</sup> V<sub>HCl reacted</sub> = 80 – V<sub>NaOH</sub> × N<sub>NaOH</sub>/N<sub>HCl</sub>.

<sup>b</sup> NP = V<sub>HCl reacted</sub> × (N<sub>HCl</sub>/2) × (100 g mol<sup>-1</sup>/2 g).

<sup>c</sup> AP = 31.25 × %S.



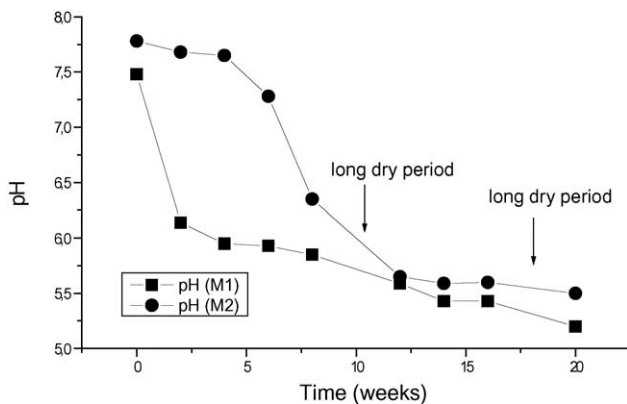


Fig. 2. pH evolution in columns M1 and M2.

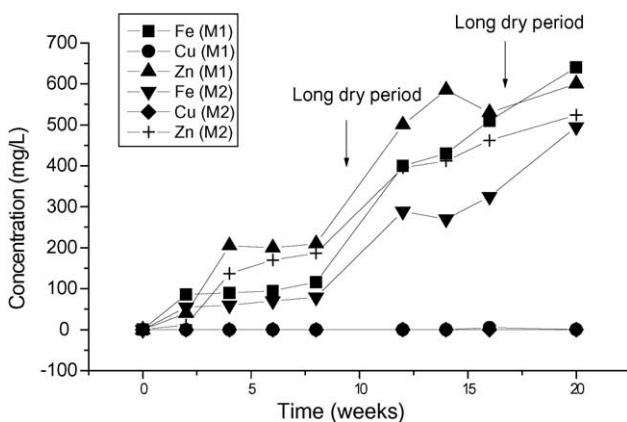


Fig. 3. Metals concentration evolution in columns M1 and M2.

were slower and more cycles (more added water) were required to attain the same concentrations as in M1. The explanation for this can be found in the pH and metal concentration data: firstly, the average particle size was slightly higher in pulp P2 (41.9  $\mu\text{m}$ ) than in pulp P1 (22.9  $\mu\text{m}$ ); and secondly, the composition of the pulps was similar but not identical. The ABA test indicated a greater neutralization potential in pulp P2 than in pulp P1.

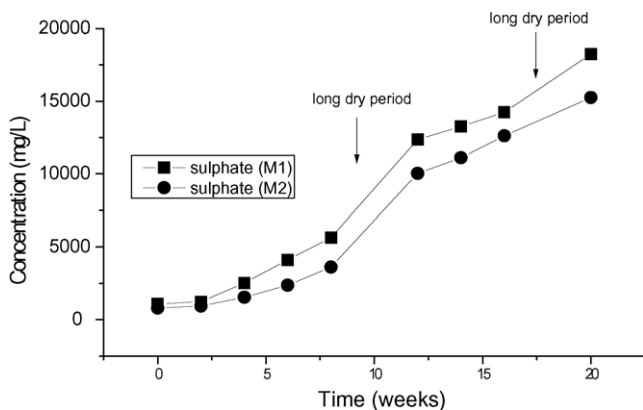


Fig. 4. Sulphate concentration evolution in columns M1 and M2.

The pH of the drainages from both columns was not too low. However, this pH is not the only factor indicating weathering, which could be due to the neutralization potential of the waste itself [28–30]. In this connection, sulphate concentration is the key factor confirming the presence of acid rock drainages. The kinetics of pyrite transformation was very slow in both systems, as confirmed by the presence of around 15,000 mg/L of sulphate (Fig. 4) in the column drainages.

When the residue was subjected to long dry periods, the concentration of metals and sulphate in the column drainages increased considerably. In both columns, this can be explained by the formation of holes and channels constituting a preferential route for water circulation [31]. It was in these channels that surface oxidation of the pyritic residue occurred, observable visually in the formation of brown and reddish precipitates. Watering following a long dry period resulted in dissolution of the different compounds formed and consequently the generation of acidity [32]. Moreover, because of these channels, not all of the water added in each dry/wet cycle contacted and soaked all of the residue; some of that water circulated through the channels and drained straight out. This would also explain the low metal and sulphate concentrations detected in the drainages.

The role of microbial catalysis in the weathering of columns M1 and M2 was not relevant. Lithoautotroph bacteria were detected in pulps P1 and P2; however these microorganisms need oxygen to survive and attach themselves to the mineral surface. As Eqs. (1)–(3) indicate, oxygen is crucial to direct attack and to the generation of ferric ions. As explained earlier, columns M1 and M2 were saturated with water (anaerobic conditions) for most of the time, and mineral oxidation was detected only under extreme conditions (long dry periods). Consequently, the pH value was not extremely acid and the metal concentration was much lower than would be the case if there were active microbial catalysis of the system. In previous experiments [18,27], assays of microbial activity in shake flasks and small columns produced extreme values for pH and metal concentrations.

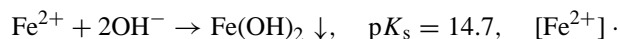
### 3.4. Oxidation kinetics of ferrous iron contained in the drained solutions

The samples drained from the columns were transparent at the time of collection. However, after several hours they turned yellow; in some cases reddish-brown precipitates appeared if the solution was left in contact with the air, depending on the time. Transformation occurred after several hours (2–3 h), becoming more intense thereafter and clearly appreciable after 24 h. This phenomenon has been observed and described by other authors [33] who attribute it to oxidation of the iron in the solutions. This aspect was studied to determine whether colouring was due to the oxidation of ferrous to ferric iron and consequent precipitation of  $\text{Fe}^{3+}$

hydroxides and similar compounds, or directly to ferrous iron precipitation. The first possibility seemed debatable given the apparent slowness of  $\text{Fe}^{2+}$  oxidation kinetics. To elucidate this, we studied the stability of both iron species at the pH of the drainages, and also the  $\text{Fe}^{2+}$  oxidation kinetics.

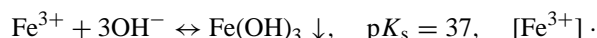
#### 3.4.1. Theoretical chemical stability of iron species in aqueous solution

Assuming that a pH of 5.5 is representative of the drainages produced by column M1, the stability of ferrous and ferric ions will be as follows [34]:



$$[\text{OH}^-] = 10^{-14.7}, \quad [\text{Fe}^{2+}] = \frac{10^{-14.7}}{10^{-17}} = 10^{2.3}$$

Therefore at pH 5.5,  $\text{Fe}^{2+}$  can exist in solution without precipitating, even at relatively high concentrations. However,  $\text{Fe}^{3+}$  cannot exist in solution at this pH:



$$[\text{OH}^-]^3 = 10^{-37}, \quad [\text{Fe}^{3+}] = \frac{10^{-37}}{10^{-25.5}} = 10^{11.5}$$

#### 3.4.2. $\text{Fe}^{2+}$ oxidation kinetics

The oxidation rate of ferrous iron is highly dependent on the pH [35–38]. This dependence is described by the following relationship at 25 °C:

$$-\frac{d[\text{Fe}^{2+}]}{dt} = K[\text{Fe}^{2+}][\text{OH}^-]^2 p_{\text{O}_2}, \quad K = 8.0 \\ \times 10^{13} \text{ L}^2 \text{ mol}^{-2} \text{ atm}^{-1} \text{ min}^{-1}$$

If  $p_{\text{O}_2}$  is considered constant (1 atm) and pH = 5.5:

$$-\frac{d[\text{Fe}^{2+}]}{dt} = 8.10^{13} \times 10^{-17} [\text{Fe}^{2+}], \\ -\ln \frac{[\text{Fe}^{2+}]_f}{[\text{Fe}^{2+}]_i} = 8 \times 10^{-4} t$$

Therefore, the time required ( $t$ , min) to reduce the initial concentration of ferrous iron ( $C_i$ ) to its thousandth part ( $C_f$ ) will be:

$$t = -\frac{1}{8 \times 10^{-4}} \left( \ln \frac{10^{-3} C_i}{C_i} \right) = 8.636 \text{ min} \cong 6 \text{ days}$$

The  $\text{Fe}^{2+}$  concentrations before and after the appearance of colour in the effluents were therefore measured along with the respective pH values of several samples from the drainage of the columns where this effect was observed. In the case of a sample with an initial pH of 6.4 and an initial concentration of ferrous iron of 20.5 mg/L, the  $\text{Fe}^{2+}$  concentration in the coloured solution was 1.1 mg/L. Therefore, according to the above equations, oxidation of this concentration of  $\text{Fe}^{2+}$  to

$\text{Fe}^{3+}$  will take approximately 69 min. In other words, oxidation of ferrous ion can take as little as 1 h at the mentioned pH. This timing is consistent with that observed for the appearance of colour in the samples during experimentation in the laboratory. This was verified by X-ray diffraction analysis of the precipitate, which showed iron oxides ( $\text{Fe}_2\text{O}_3$ ) and jarosites.

## 4. Conclusions

ABA test results are a guide, but they can never be used as definitive parameters to evaluate the behaviour of a given residue. In the present work, the ABA test indicated a strong tendency towards acid generation in both pulps, however, in the two columns tested (M1 and M2) a slow oxidation kinetics and a weak weathering was observed. As the data revealed (pH close to 5.25, metals concentration ~550 mg/L and sulphate concentration close to 17,000 mg/L), the drainage from the columns was far from the acidity indicated by ABA test results.

Current results and previous experiments [27] carried out by the group using columns of different sizes concluded that the height of the columns chosen was the determinant factor contributing to the weak pulp weathering. Column height influences residue weathering in such a way that oxidation is much slower in large columns because they retain water thus hindering penetration by the oxygen necessary for sulphide oxidation.

The weathering time in columns M1 and M2 was insufficient to produce the acidity attained in smaller columns with a smaller bed volume under the same conditions. To achieve the same results with columns M1 and M2 would require longer times and a greater number of weathering cycles. This raises reasonable doubts as to the usefulness of working with large columns, given the excellent results obtained with medium size columns over shorter times.

The influence of microbial activity on pulps weathering was insignificant; the values of pH reached (close to 5), the metals and sulphate concentration (<550 and <17,000 mg/L respectively) were far from those determined in previous experiences (pH close to 2, metals concentration up to  $20 \times 10^3$  mg/L and sulphate concentration up to 120 g/L), where bacteria were present, in activity and bioleaching the pulp [27].

Finally, the use of dry/wet cycles clearly increases the weathering of a pyritic residue, with the added advantage that the behaviour of the residue in a natural environment can be reproduced.

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