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## Coupled thermal, hydraulic and geochemical evolution of pyritic tailings in unsaturated column experiments

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### Abstract

The evolution of pore-water and the composition of solid phases in the vadose zone of pyritic tailings was studied by means of unsaturated column experiments. Several columns of water-saturated mine tailings were dried during 125 days under controlled laboratory conditions. The columns were dismantled at four successive drying stages and the evolution of pore-water, mineralogy, water content and temperature was characterized.

Sulfide and aluminosilicate minerals present in the waste dissolved, releasing sulfate and other solutes (mainly Fe, Zn, Cu, Al, Mg and Ca) to the pore-water. Evaporation caused a crust of efflorescent, water-soluble sulfates to develop over the complete top surface of the columns and into the pores of the underlying waste material. This crust, which has also been identified in the field, changed the hydraulic properties of the tailings and produced a decrease in the evaporation rate of the columns. Moreover, these water-soluble precipitates (mainly rozenite, szomolnokite, halotrichite, hexahydrite, mirabilite and gypsum) acted as temporary sinks for Cd, Pb, Co and Ni, which could be released to the surface run-off or the groundwaters during rainfall events under field conditions.

Pore-water evolution was determined not only by geochemical processes (dissolution of sulfides and aluminosilicates, precipitation of secondary phases) but also by thermal and hydraulic processes. Progressive dilution was observed in the lower part of the columns. Dilution was caused by the thermally driven vapor flux from the top of the column to its colder bottom and subsequent condensation therein. This process, which may also occur in tailings under sub-arid climate, played a key role on the evolution of pore-water with increasing drying.

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## 1. INTRODUCTION

Oxidation of sulfide phases present in mine tailings generally leads to the release of waters with high acidity, iron, sulfate and other elements which are potentially pollutant (Acid Mine Drainage; AMD). To minimize waste weathering, mine tailings are usually kept water saturated and under a water layer during mining operations. This layer of water may disappear in the long run, which allows the access of dissolved oxygen to the sulfide minerals and, therefore, enhances the extent of oxidation reactions. This problem is especially relevant in the case of abandoned mine exploitations placed in areas with sub-arid climate, where sparse rainfall (and frequently high temperatures) favor evaporation.

There are many earlier works focused on the study of the geochemistry of pore-water and mineral phases in the water-saturated and in the vadose zone of mine tailings. The first comprehensive studies focused on the characterization of the relationship between pore-water and mineral phases in the vadose zone of mine tailings were presented by Blowes and Jambor (1990) and Blowes et al. (1991). These authors examined the geochemical evolution with depth of solutions and mineral phases in several cores of the Waite Amulet and Heath Steele mine tailings. With

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the assistance of geochemical modeling, the precipitation of the main secondary phases encountered was described and justified. More recently, other field studies have been presented using similar methodologies (Al et al., 1997; Holmström and Ohlander, 1999; Johnson et al., 2000; Moncur et al., 2005; Gunsinger et al., 2006). Other recent studies have focused especially on the characterization of the evolution of primary and secondary mineral phases at different depths in mine tailings (McGregor et al., 1998; Dold and Fontboté, 2001, 2002; McGregor and Blowes, 2002). All these earlier studies have focused more on the spatial variability of the mine tailings geochemistry (at different depths or different areas of the tailings impoundments) than on their evolution.

Most previous experimental studies have focused on water-saturated mine tailings under controlled-laboratory conditions. Simms et al. (2000) carried out water-saturated column experiments and characterized the evolution of the pore-water sampled at different depths and of the effluent water. In their laboratory study, Jurjovec et al. (2002) presented the evolution of the effluent waters from a water-saturated column filled with unoxidized tailings, in order to study acid neutralization reactions occurring in the saturated zone of tailings impoundments. A similar methodology has been more recently applied by Malmström et al. (2006) to the study of the evolution of the effluent water from water-saturated columns at reduced oxygen availability.

The studies carried out under controlled conditions and focused on the changes with time of the vadose zone of mine tailings are much scarcer in the literature. In the cases in which such studies are developed, they only focus on the evolution of the effluent waters from the unsaturated laboratory columns (Evans and Banwart, 2006) or tailings (Strömberg and Banwart, 1999; Domènech et al., 2002a; Evans et al., 2006). Furthermore, the study of the primary and secondary mineral associated with the effluent water is carried out only at the end of the experiment, once it has been dismantled.

Both types of studies, describing the variations with depth at a fixed time and the variation of effluents with time, may be unable to unravel some of the flow, transport and chemical phenomena taking place in the vadose zone. These processes may be important to interpret correctly the mineral distribution and the chemistry of the leachates. The present study is an attempt of studying unsaturated pyritic mine wastes during weathering under controlled conditions and taking into account not only the vertical variations of pore-water and mineral phases in the tailings profile, but also the variations caused by evolution of the tailings. Therefore, the main goals of this work are to study the evolution of mine tailings under conditions of variable water-saturation and to identify the main processes controlling the behavior of sulfide mine wastes during weathering under sub-arid climate. With these aims, several laboratory columns were filled with unoxidized and water-saturated mine tailings from a tailing impoundment. The columns were forced to dry under controlled thermal and hydraulic conditions and the variations with time of the pore-water and minerals precipitating within the pores and on top of the waste were characterized.

## 2. MATERIALS AND METHODS

## 2.1. Waste material preparation and characterization

Column experiments were carried out with unoxidized waste material from the Monte Romero mine tailings impoundment (Iberian Pyritic Belt, SW Spain). Several hundred kilograms of waste material from these tailings were thoroughly mixed and its moisture content was fixed at 19 wt% to ensure water saturation once packed in the columns. A comparison of the X-ray Diffraction (XRD) patterns, granulometrical distribution and chemical composition of multiple subsamples of the waste material showed that it could be considered homogenous.

The physical properties, mineral composition and chemical analyses of the waste material used in the column experiments are displayed in Tables 1 and 2. Mineral abundance was obtained by combining XRD and microprobe analyses with the normative reconstruction of the mineralogy based on chemical analyses. The waste consists of quartz, muscovite/illite, clinochlore, plagioclase (albite) and pyrite (around 12 wt%). The amount of other sulfides, namely sphalerite, chalcopyrite and galena is much smaller (2, 1.7 and 0.2 wt%, respectively). Carbonate minerals have not been detected in the waste material.

## 2.2. Experimental set-up of the column experiments

Ten columns with inner diameter of 14.2 cm, wall thickness of 0.4 cm and length of 35 cm were filled with the moist waste material up to a height of 29 cm. After preliminary trials, the waste was packed by successive compacting of 12 layers in order to ensure a 0.36 porosity and water saturation in the columns. Each column was placed with the top

Table 1

Summary of physical properties and mineral composition of the Monte Romero mine waste used in the column experiments

Mineral phase	wt%
Pyrite	11.6
Galena	0.2
Sphalerite	2.0
Chalcopyrite	1.7
Clinochlore	4.7
Albite	4.5
Muscovite/Illite	20.0
Gypsum	3.7
Quartz	51.6
Parameter	Value/description
Particle size	Average particle size = $0.031 \text{ mm}$ (50 wt% < $0.02 \text{ mm}$ , 90 wt% < $0.1 \text{ mm}$ )
Specific surface area $(m^2 g^{-1})$	$2.5\pm0.5$
Initial mass water content (wt%)	19.2
Particle density $(g \text{ cm}^{-3})$	2.94
Bulk density $(g \text{ cm}^{-3})$	2.24
Porosity <sup>a</sup>	0.36

<sup>a</sup> Based on particle density, bulk density and mass water content.

Table 2 Chemical composition of the Monte Romero mine tailings used in the column experiments

Major elem	ents (wt%)	Trace elen	Trace elements (ppm)					
Al	4.0	As	1513					
Ca	0.6	V	56					
Cu	0.6	Cd	47					
Fe	7.0	Ni	21					
К	2.1	Sb	379					
Mg	1.3	T1	64					
Na	0.3	Со	6					
Pb	0.7							
S	9.2							
Zn	1.2							
Ва	0.7							
Si	24.0							

surface of the waste material at 60 cm below an infrared bulb, used as a continuous heat source during the 125 days of experiment. Water loss by evaporation was controlled by measuring weight variations of the columns with time. Average room temperature was 34 °C and average room relative humidity was around 30%. Temperature and relative humidity at 5 cm above the top column surface were around 42 °C and 25%, respectively.

Variations of moisture content with depth, mineralogy and pore-water hydrochemistry were investigated at four drving stages, corresponding to average water saturations of 0.79, 0.71, 0.62 and 0.51. Two of the columns were dismantled at each stage. Dismantling started by mechanically removing the crust of efflorescent precipitates formed at the column top. These precipitates were weighted and stored in sealed plastic bags at 4 °C until examination by Scanning Electron Microscopy (SEM), XRD and chemical analyses. After carrying out a detailed vertical temperature profile, the column was taken out of the infrared source. Samples were taken immediately to obtain a vertical profile of moisture content in each column. In order to study the variations in the pore-water chemical composition with dryness and weathering, the remaining waste material from each column was divided into four subsamples (from below crust to 7 cm depth, 7-14 cm, 14-21 cm and 21-28 cm) after discarding the outer 2 cm of material and the bottom 2 cm, in contact with the column wall. After thoroughly homogenizing each waste subsample, a portion was separated for examination by Scanning Electron Microscopy (SEM), for XRD and for sequential extractions. The moist waste samples were then packed in hermetic containers completely filled with sample and immediately frozen and stored until pore-water extraction. The whole column dismantling procedure was carried out in less than 2 h in order to minimize water evaporation and contact of the waste material with atmospheric oxygen.

Pore-water extraction was carried out by the squeezing technique (Patterson et al., 1978) as adapted by Fernandez-Diaz et al. (2004). This technique involved pressurizing the waste samples by means of a sealed plunger connected to an inert, gas-tight tube which ended in a vacuum container closed by a septum. After discarding the first 3– 5 ml, outflowing water was collected in two separate 5 ml tubes corresponding to successively extracted water samples, with the purpose of assessing the potential chemical fractionation induced by squeezing.

Water samples were also immediately filtered at 0.1  $\mu$ m and divided into two aliquots; one of them was acidified with HNO<sub>3</sub> for major and minor element analysis and the other one was acidified with HCl for Fe(II)/(III) determination. In order to prevent further oxidation, the water samples were stored in vacuum tubes at 4 °C until analyses. Analytical results for both successively extracted samples were in very good agreement, being generally the same within 15%. Thus, the extraction technique seemed not to have induced a noticeable chemical fractionation in the water samples.

In order to assess the reproducibility of results, extraction and analysis of the pore-water from the two columns corresponding to the third dismantling stage (average water saturation of 0.62) was carried out. The analytical results in both duplicates showed good agreement, being in most cases the same within 15% error for all reported elements except Cu and Na. For these elements the difference between duplicates was around 35%.

## 2.3. Physical and analytical methods

Moisture content was determined as the weight ratio between the water lost in the oven at 105 °C during 24 h (time for constant dry weight) and the final weight of the dried solid sample. Samples of waste material were taken at eight increasing depths and its moisture content was determined. Measured moisture contents were then transformed into water saturation degrees, calculated as the ratio between the volume of liquid and the initial porosity. Specific weight or grain density of the initial solid was measured in a powdered, oven-dried sample using a pycnometer. Bulk density and porosity were determined gravimetrically. Porosity was assumed constant throughout the experiment in all the vertical profile of the column except in the top precipitates crust. The specific surface area of the initial solid sample was determined by the BETmethod (Brunauer et al., 1938) using 5-point N2-adsorption isotherms with a Micromeritics ASAP 2000. Temperature and relative humidity in the room and at 5 cm above the top column surface were measured by using a Lutron HT-3009 meter.

XRD of powdered samples was used in an attempt to identify the minerals present in each sample of waste material or efflorescent precipitates. Examination of the samples was carried out by using a Bruker D5005 diffractometer with Cu K( $\alpha$ ) radiation over a 2 $\theta$  range from 0° to 60° with a continuous scan at a rate of 0.083° 2 $\theta$  per minute.

The chemical composition of the initial waste material was determined by combining the analytical results following total acid digestion, according to the method developed by Querol et al. (1996), and X-ray fluorescence, which was carried out by using a Philips PW2400 instrument.

In order to ascertain the amount of precipitated elements associated with each mineralogical fraction, sequential extractions were carried out by adapting the procedure proposed by Dold and Fontboté (2001) to the following fractions; (1) water soluble, (2) adsorbed, organometalic and exchangeable fraction plus carbonates, (3) low-crystallinity Fe(III) phases (schwertmannite, 2-line ferrihydrite, secondary jarosite), (4) crystalline Fe(III)-phases (goethite, jarosite, hematite, highly-ordered ferrihydrite), and (5) residual fraction. Concentrations in the water soluble leachates were corrected to account for the solutes initially present in the porewater of the waste samples. For this correction, it was assumed a pore-water composition as analyzed after squeezing and with a volume equal to the measured moisture content of the corresponding wet sample. In addition, top crust precipitates were leached in double distilled water following the method used by Hammarstrom et al. (2005), and leachates were filtered and analyzed.

pH of squeezed water was measured by a pH-meter with temperature compensation and a combination glass electrode with a KCl filling solution, which was calibrated regularly with standard buffer solutions of pH 2, 4 and 7. Measurements were carried out immediately after sampling and at the average measured temperature of the column waste subsamples. Calibration of the probes was checked before and after each measurement session.

Concentrations of Fe, Cu, Zn, Ca, Mg, Al and S in solution were measured by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) using a Thermo Jarrel-Ash instrument with CID detector with detection limits of  $10 \ \mu g \ L^{-1}$  for Fe, Cu and Zn,  $100 \ \mu g \ L^{-1}$ for Ca and Mg, 200  $\mu$ g L<sup>-1</sup> for Al and 500  $\mu$ g L<sup>-1</sup> for S. Na and K concentrations were determined by Flame Atomic Absorption Spectrometry (FAAS) using a Unicam 939 equipment and the estimated detection limit was  $2 \mu g L^{-1}$ . Concentrations of As, Pb, V, Cd, Ni and Co were determined by Inductively Coupled Plasma Atomic Mass Spectroscopy (ICP-MS) using a X-series II Thermo instrument and the detection limits for these elements were in the order of  $1 \ \mu g \ L^{-1}$ . Calibration with sets of standards was performed for all the analytical techniques and regression coefficients exceeded 0.999. The analytical error was estimated to be around 4% for ICP-AES and 6% for ICP-MS and FAAS measurements. The reproducibility, accuracy and precision of results were ensured by analyzing not only blank samples and laboratory standards, but also by duplication of experiments and samples (as explained in the previous section). The quality of analytical results was checked by means of charge balance calculations, showing that charge imbalance is within  $\pm 5\%$ for all the reported water samples.

Ferrous and total dissolved iron (following reduction with hydroxylamine hydrochloride) determinations were performed by colorimetry using the ferrozine method (modified after To et al. (1999) in a UV–Vis HP Spectrophotometer within 1–4 days from sampling. Concentrations of Fe(III) were calculated by difference between Fe(tot) and Fe(II). The quality of results was assured by measuring several standards, blanks and duplicates.

The O isotope ratio of the pore-water samples was determined by equilibrium with carbon dioxide and subsequent analysis by Isotope Ratio Mass Spectrometry (IRMS). The results are expressed with respect to the V-SMOW scale and the standard deviation uncertainty was  $\pm 0.2\%$ .

#### 2.4. Geochemical modeling

Pore-water hydrochemistry was interpreted with the assistance of the code PHREEQC (Parkhurst, 1995). The ionic strength varied from around 5 to more than 15 m, well beyond the optimum range of activity corrections calculated with the Extended Debye–Hückel or the Davies equation. For this reason, the Pitzer ion-interaction approach (Pitzer, 1973) with the database compiled by Tosca et al. (2005) was used in the calculations. This database was expanded to include, among others, interaction coefficients for copper and zinc (Reardon and Beckie, 1987; Reardon, 1988). In the cases in which experimentally determined interaction parameters have not been found, published analog data for elements with similar charge and ratio have been used.

All the species present in the pore-water have been considered completely disassociated. The Pitzer ion-interaction equations, in their original form, assume complete dissociation of all ions and represent the interaction between ions solely with ion-interaction equations with parameters derived from experimental data (Ptacek and Blowes, 2000). The only exception to this treatment is the complex  $HSO_{4}^{-}$ . This aqueous complex is generally included in models using the Pitzer interaction approach in waters with low pH and high sulfate concentrations (Reardon and Beckie, 1987; Ptacek and Blowes, 2000). Solubility products and reactions were taken from the WATEQ4f database (Ball and Nordstrom, 1991) except in the cases detailed in Table 3. Thermodynamic consistency of the modified database was ensured by comparison of calculated and experimental solubility values for several single and binary salt systems (Occleshaw, 1925; Basset and Watt, 1950; Bullough et al., 1952; Moshinskii and Chibizov, 1975; Mosgovykh et al., 1984; Reardon and Beckie, 1987; Reardon, 1988; Baron and Palmer, 1996; Christov, 2004).

Hydrogeochemical calculations for each pore-water sample were performed with the measured temperature at the sampling depth while dismantling. Temperature corrections were applied on the solubility products when available. Saturation indices are expressed as  $\log(IAP/K_{sp})$ . Thus, negative saturation indices indicate undersaturation whereas positive saturation indices indicate supersaturation with respect to a given mineral phase.

#### 3. RESULTS AND DISCUSSION

#### 3.1. Evolution of water content and temperature

All columns displayed very similar evaporation trends (differences smaller than 3% weight variations) throughout the 125 days of experiment (Fig. 1). Precipitation of whitish salts on the top surface of all columns was observed as early as the second day. Efflorescent precipitates continued growing thereafter, creating a continuous crusted surface which kept increasing in thickness throughout the experiment. In one of the columns, the salts precipitated at the top surface of the column were mechanically removed every 3–10 days throughout the experiment, with the aim of assessing the role of the crust on evaporation rates. In this column, the

Table 3

Solubility j	products	and so	olid pha	ses from	other	sources	than	the	WATEQ4f	database	(Ball an	d Nordstrom,	1991)	for the	geochemical
modeling o	of the colu	umn po	ore-wate	r											

Phase	Reaction	log <i>K</i> (25 °C)
Alunogen	$Al_2(SO_4)_3 \cdot 17H_2O \rightarrow 2Al^{3+} + 3SO_4^{2-} + 17H_2O$	$-6.204^{a}$
Bilinite	$Fe^{2+}Fe^{3+}_{2}(SO_{4})_{4} \cdot 22H_{2}O \rightarrow Fe^{2+} + 2Fe^{3+} + 4SO_{4}^{2-} + 22H_{2}O$	$-15.9641^{d}$
Copiapite	$Fe^{2+}Fe^{3+}(SO_4)_6(OH)_2 \cdot 20H_2O + 2H^+ \rightarrow Fe^{2+} + 4Fe^{3+} + 6SO_4^{2-} + 22H_2O$	$-22.8912^{d}$
Coquimbite	$Fe_2(SO_4)_3 \cdot 9H_2O \rightarrow 2Fe^{3+} + 3SO_4^{2-} + 9H_2O$	26.2707 <sup>d</sup>
Epsomite	$MgSO_4 \cdot 7H_2O \rightarrow Mg^{2+} + SO_4^{2-} + 7H_2O$	$-1.858^{a}$
Halotrichite	$FeAl_2(SO_4)_4 \cdot 22H_2O \rightarrow Fe^{3+} + 2Al^{3+} + 4SO_4^{2-} + 22H_2O$	$-8.68^{a}$
Hexahydrite	$MgSO_4 \cdot 6H_2O \rightarrow Mg^{2+} + SO_4^{2-} + 6H_2O$	$-1.7268^{b}$
Kornelite	$Fe_2(SO_4)_3 \cdot 7H_2O \rightarrow 2Fe^{3+} + 3SO_4^{2-} + 7H_2O$	23.211 <sup>d</sup>
Pickeringite	$MgAl_2(SO_4)_4 \cdot 22H_2O \rightarrow Mg^{2+} + 2Al^{3+} + 4SO_4^{2-} + 22H_2O$	$-8.06^{\rm a}$
Rozenite	$FeSO_4 \cdot 4H_2O \rightarrow Fe^{2+} + SO_4^{2-} + 4H_2O$	$-2.0181^{d}$
Schwertmannite	$Fe_8O_8(OH)_{4.5}(SO_4)_{1.75} + 20.5H^+ \rightarrow 8Fe^{3+} + 1.75SO_4^{2-} + 12.5H_2O$	$-10.5^{\circ}$
Siderotil	$FeSO_4 \cdot 5H_2O \rightarrow Fe^{2+} + SO_4^{2-} + 5H_2O$	$-2.284^{d}$
Szomolnokite	$FeSO_4 \cdot H_2O \rightarrow Fe^{2+} + SO_4^{2-} + H_2O$	-1.5885 <sup>d</sup>

<sup>a</sup> Reardon (1988).

<sup>b</sup> Delany and Lundeen (1990).

<sup>c</sup> Yu et al. (1999).

<sup>d</sup> Tosca et al. (2005).



Fig. 1. Accumulated water loss (expressed as weight variation in the columns) as a function of time during the experiments.

average evaporation rate was more than double of the evaporation rate in the rest of the columns and, consequently, this part of the experiment only lasted for 59 days (Fig. 1).

Measured vertical profiles of moisture content are presented in Fig. 2 for the four dryness stages considered. Two samples were taken in each of the two columns dismantled at each depth. Determined moisture contents in the four samples (two samples in each of the two columns) were the same within a 5% error. As can be observed in Fig. 2, there were no important vertical variations in the water saturation degree for each dryness stage.

The evolution of temperature profiles is displayed in Fig. 2. Temperatures increased throughout the experiment in parallel to water desaturation, especially in the top part of the column. The bottom surface of the columns remained at almost constant temperature of 38-39 °C but the temperature at depth of one centimeter increased from 43 °C to 47 °C (approx.) between the first and the last dis-

mantling stage. Therefore, the average thermal gradient became steeper throughout the experiment.

## **3.2.** Evolution of crusts precipitated at the top surface of the columns

According to XRD results, the main phases identified in the crust at the top of the columns in the first two stages of evolution (corresponding to water saturation of 0.79 and 0.71, respectively) were rozenite (FeSO·4H<sub>2</sub>O), halotrichite (FeAl<sub>2</sub>(SO<sub>4</sub>)·22H<sub>2</sub>O), and hexahydrite (MgSO·6H<sub>2</sub>O) with minor amounts of mirabilite (Na<sub>2</sub>SO·10H<sub>2</sub>O), melanterite (FeSO·7H<sub>2</sub>O) and gypsum (CaSO·2H<sub>2</sub>O). The main iron sulfates identified in the last two stages of evolution (water saturation of 0.62 and 0.51) were halotrichite and szomolnokite (FeSO·H<sub>2</sub>O) with only traces of rozenite and melanterite. Pickeringite (MgAl<sub>2</sub>(SO<sub>4</sub>)<sub>4</sub>·22H<sub>2</sub>O) was also detected in the crust during the last two stages of evolution. Similar mineralogical paragenesis have been



Fig. 2. Vertical profiles of water saturation and temperature at the four studied stages during the column experiments. Error bars show the difference between profiles in duplicate experiments (5% for water saturation and 1 °C for temperature). Water saturation in the precipitate crust is not displayed.

identified at field scale in the efflorescent precipitates of the Monte Romero mine and in other mine environments of the Pyritic Belt (Buckley et al., 2003), as well as in other metallogenic provinces in the world (Jambor et al., 2000; Hammarstrom et al., 2005). The observed reduction in the hydration degree of iron sulfate salts from rozenite and melanterite to szomolnokite with time is consistent with the increase of temperature at the top surface of the column and with a reduction in the water activity owing to increasing concentrations and acidity in the pore-water (Jambor et al., 2000) although some dehydration prior to XRD determinations cannot be ruled out.

Water-soluble leachates of the crusts showed that these precipitates are very rich in Fe, Ca, Al, Na, Mg, Zn, Al and S (Table 4). This composition was consistent with the mineralogical identification carried out by XRD. The wt% of each phase in the precipitates can be estimated by assuming that all water-soluble calcium in the crust precipitates as gypsum, sodium as mirabilite, all the magnesium as hexahydrite, aluminium as halotrichite and all the zinc plus the rest of iron (after substracting the amount present in halotrichite) included in iron and zinc sulfates (Table 4). In spite of the large amount of zinc present in the crust precipitates (Table 4), no pure zinc sulfates have been identified by XRD. Nevertheless, zinc may be present in the structure of iron sulfates in substitution of Fe(II) (Jamieson et al., 1999; Jambor et al., 2000 and references therein). This element has been reported to substitute Fe(II) up to 39 mol% in the structure of szomolnokite in Iron Mountain (Jamieson et al., 1999) or up to 57 mol% in zinc-melanterite. It may be also present in dietrichite (the zinc-rich member of the halotrichite group). Similar availability to substitute Fe(II) in the structure of iron sulfates has also been described for copper (Jambor et al., 2000). It is worth noting that small amounts of magnesium may also be included in melanterite, rozenite, szomolnokite or halotrichite (Jambor et al., 2000) instead of in hexahydrite or pickeringite.

As shown in Table 4, the estimated mineralogical proportions in the crusts were fairly constant at the different stages of evolution. Regarding the trace element content, these crusts have up to 135 ppm of lead, 35–60 ppm of nickel and cobalt and 645 ppm of cadmium. This is important because, under field conditions, these water-soluble crust precipitates act only as temporary sinks for trace elements, which could be released to the surface run-off or the groundwaters during rainfall events, with potentially damaging effects for the environment.

The precipitates crust was easily removable from the waste underneath in all the stages of evolution. The thickness of this layer increased from 6 mm in the second stage of dryness to around 20 mm at the end of the experiment and its weight increased from 150 g to 500 g during the same time (Fig. 3).

XRD patterns in all the samples showed that very minor amounts of the mineral phases originally present in the waste (sulfides and aluminosilicates) were detectable in the crusts of the first two drying stages. Consistently, the water insoluble residue represented less than 20 wt% in those samples. However, the XRD spectrum of the crust corresponding to the last two stages of evolution showed a greater proportion of pyrite and aluminosilicates. Consistently, the water-insoluble residue increased, reaching around 35 wt%. These evidences suggested that crust precipitates grew initially over the top surface of the waste material and, subsequently, into the pores of the underlying material.

Thermal and hydraulic processes controlling the column evolution can be derived from these observations. During the first two drying stages, the moisture content remained Table 4

	Sample				
	Crust stage 1	Crust stage 2	Crust stage 3	Crust stage 4	
Water saturation	0.79	0.71	0.62	0.51	
Ca	4442	4419	4583	9297	
Mg	39,962	39,517	38,974	37,064	
Zn	62,900	62,235	61,533	90,730	
Fe	110,733	114,032	113,542	73,479	
Al	43,059	42,177	43,043	39,564	
Cu	4197	1262	2434	10,800	
S	221,298	219,334	221,291	211,080	
Κ	181	65	147	138	
Na	18,828	18,883	18,801	26,444	
Pb	135	70	115	65	
Cd	605	505	470	645	
As	10	5	5	5	
Co	35	40	40	45	
Ni	50	50	50	60	
Gypsum	2	2	2	3	
Mirabilite	6	6	6	9	
Halotrichite	39	39	39	37	
Hexahydrite	20	20	19	19	
(Fe,Zn)-SO <sub>4</sub>	33	35	34	32	

Chemical analyses and estimated proportions of the mineral phases in the water soluble fraction of the dried crust precipitates grown at the top surface during the column experiments

The concentration of all the elements is expressed in ppm and the deduced proportion of soluble mineral phases is expressed in wt%.



Fig. 3. Precipitate crust created in one of the columns at the end of the evaporation experiment (125 days). The weight of the crust is around 500 g.

high and water flowed by capillarity to the column top, leading to sulfate precipitation on the top surface. As the column dried out, the evaporation front receded and precipitation occurred progressively further from that surface. This caused a reduction in porosity and permeability but also an increase in the capillary rise, which caused the evaporative process to slow down. Since evaporation is the main cooling mechanism, its reduction produced an increase of temperatures.

All these processes observed during the evolution of the columns must drive the evolution of pyritic tailings under subarid field conditions, since progressive drying by heating, evaporative concentration of pore-water near the surface and precipitation of very similar crusts on top of the waste to those observed in our experiments has already been described in many earlier field works.

# 3.3. Evolution of solid phases and pore-water chemistry at different depths

#### 3.3.1. Evolution of major elements

Pore-water extraction by squeezing was only possible in the three first stages of the experiment. The composition and chemical parameters obtained in the pore-water samples are displayed in Figs. 4 and 5. The pH of the porewater remained between 2.3 and 2.9 throughout the whole experiment, decreasing with time in the top layers of the columns and increasing in the bottom part throughout the experiment. This evolution is the result of the complex interaction between the hydraulic and thermal processes (changing the amount of solvent by evaporation) and geochemical processes, whether acid-producing (dissolution of sulfide minerals, precipitation of Fe(III)-(oxy-hydroxy-) sulfates) or acid-consuming (mainly dissolution of aluminosilicates).

The evolution of the oxygen isotopes during the experiment is shown in Fig. 6. The pore-water displayed a progressive enrichment in  $O^{18}$  with time in the top of the columns, as expected from evaporation. Surprisingly, the pore-water in the bottom part of the column showed in the third stage of evolution a decrease in the  $O^{18}/O^{16}$  ratio when compared to the previous two stages. This indicates a dilution process in the column bottom.

The behavior of the major elements can be divided into five different trends. First, zinc concentrations increased in the pore-water throughout the experiment. This increase



Fig. 4. Pore-water concentrations of major elements and pH evolution at the three studied stages of evolution. Error bars correspond to the difference between duplicates (15% for all displayed elements except Cu and Na, for which they represent 35%) and to 0.05 units for pH.

was more evident in the shallower part of the column, where evaporation was taking place (Fig. 4). Zinc concentrations in the third stage of evolution reached 52 g kg<sup>-1</sup>, among the highest values ever reported in the literature for tailings pore-water (a compilation can be found in Moncur et al., 2005). The main process releasing zinc to the pore-water is sphalerite dissolution. Geochemical calcula-

tions show that all pore-waters (Table 5) are undersaturated with respect to the main zinc sulfate salts described in mine tailings (namely zincosite, gunningite, bianchite and goslarite). In contrast with the observed association in the crust precipitates, zinc coprecipitation with other water-soluble phases in the waste pores can be neglected, since zinc was not detected at significant concentrations in the water-solu-



Fig. 5. Pore-water concentrations of trace elements at the three studied stages of evolution. Error bars correspond to the difference between duplicates (15% for all displayed elements).

ble leachates (after pore-water correction). In the light of the sequential extraction results (Fig. 7), the association of zinc with water-insoluble iron (oxy-hydroxy-)sulfates can also be considered negligible compared to the amount of zinc that remained dissolved in the pore-water.

In the second place, the concentrations iron decreased in the pore-water throughout the experiment, especially in the bottom part of the column, where the concentrations at the third stage of evolution are more than seven times smaller than in the first stage (Fig. 4). Pyrite is the main sulfide phase present in the tailings and the main iron source to the pore-water. Since the dissolution rates for pyrite and sphalerite are similar (Acero et al., 2007), one should have expected an increase in iron concentrations, analogous to that of zinc. The decrease of iron concentrations can be explained by the precipitation of (oxy-hydroxy-)sulfates or crystalline iron oxides, which were detected during sequential extractions and also by XRD (in the case of jarosite). This is also in agreement with the geochemical modeling results, which showed that all the pore-waters were supersaturated with respect to K-jarosite, H<sub>3</sub>O-jarosite, Na-jarosite, goethite and schwertmannite. Some pore-waters were also close to saturation with respect to copiapite and bilinite (Table 5). The precipitation of Fe(III)-bearing phases explains also the low proportion of Fe(III) measured in all the pore-waters (Fe(II) between 80% and 90% of total iron). In agreement, the amount of iron associated to amorphous and crystalline iron phases in the sequential extractions is significant (Fig. 7).

A third type of behavior is observed for copper and potassium. For these elements, concentrations first remained unchanged or decreased slightly at the second stage and then increased in the last part of the experiment, especially in the upper part of the columns owing to evaporation (Fig. 4). The observed increase in the third stage of the experiment can be explained by the dissolution of chalcopyrite (for copper) and aluminosilicates (for potassium). At present we do not have a clear explanation for the behavior of these elements at the second stage. One possibility would be their incorporation to secondary phases.



Fig. 6. Evolution with time and in depth of  $\delta^{18}$ O in the pore-water of the column experiments at the first three studied stages.

Copper association with iron oxides or oxy-hydroxy-sulfates has been reported in earlier studies (Dutrizac, 1984; McGregor et al., 1998) and can be deduced in the light of the sequential extraction results from the column experiments (Fig. 7). In the case of potassium, the concentrations were below the detection limit for all the fractions in the sequential extraction except in the residual fraction. However, although not confirmed by sequential extractions, potassium precipitation as K-jarosite is possible according to the geochemical calculations (Table 5).

The fourth type of behavior is observed for calcium. Calcium pore-water concentrations first remained unchanged during the first two stages and then decreased slightly in the last part of the experiment (Fig. 4). The main sources of calcium should have been the milling reagents or the aluminosilicate minerals, since carbonate minerals were not detected in the initial waste. Geochemical calculations performed using PHREEQC (Table 5) showed that all the pore-waters sampled in this study were close to equilibrium with respect to gypsum. Calcium and sulfate were the main ions present in the water-soluble fraction obtained by the sequential extraction procedure (Fig. 7) and the ratio between them in that fraction was consistent with the stoichiometry of gypsum. Moreover, XRD spectra showed the presence of traces of gypsum in the samples from the vertical profiles. Gypsum has also been described in earlier works as the phase controlling calcium concentrations in the pore-water of other mine tailings (Blowes and Jambor, 1990; Al et al., 1997; McGregor et al., 1998; Dold and Fontboté, 2002; Hammarstrom et al., 2005). Therefore, it seems reasonable that gypsum precipitation is the process controlling calcium concentrations and responsible for their decrease in the last stage of the column experiment.

Finally, the rest of major elements studied (Al, Mg, S and Na) remained almost unchanged during the three studied stages (Fig. 4). As for calcium, the main sources for sodium should have been the milling reagents or the aluminosilicate minerals. The dissolution of those phases and the precipitation of Na-jarosite (not unambiguously detected but thermodynamically possible according to geochemical calculations) are probably the main processes controlling the evolution of sodium in the pore-water. For Al, Mg and S, the pore-water concentrations increased only in the third stage and especially in the upper part of the column (evaporation zone). The observed increase of concentrations at this latter stage can be explained by the combined effects of water loss by evaporation (decrease in the relative mass of solvent) and dissolution of sulfides and aluminosilicates (increase in the mass of solutes). Since the dissolution rates for aluminosilicates are much slower (White and Brantley, 2003) than the rates for sphalerite (Domènech et al., 2002b; Acero et al., 2007), the increase of concentrations observed for aluminium and magnesium throughout the experiment was much slower than the increase observed for zinc. Another interesting trend observed in the evolution of the aluminium, magnesium and sulfate concentrations is the progressive decrease in their pore-water concentrations in the lower part of the columns. This dilution has been clearly observed in duplicate experiments and in previous tests. However, this important process is missed in earlier field or experimental works, which only describe the distribution of solutes at a particular time, neglecting the previous conditions. The dilution at the lower part of the column can only be attributed to thermally driven flux of vapor from the column top and by the subsequent condensation of the mobilized vapor in that colder, bottom part. This explanation is also in agreement with the observed evolution for oxygen isotopes (Fig. 6).

Sodium concentrations were below the detection limits in all the fractions of the sequential extractions except in the residual fraction. In the case of magnesium and aluminium, the sequential extraction results showed that more than 80 wt% Mg and 95 wt% Al remained in the residual fraction, being the rest of these elements mainly present in the pore-water (Fig. 7). According to the performed geochemical calculations, all the studied pore-waters were undersaturated (Table 5) with respect to any (hydroxy-)sulfate of magnesium or aluminium except jurbanite and alunite. However, there were no evidences of the precipitation of these phases, since they have not been detected by XRD or sequential extraction. With regard to sulfur, its evolution in the pore-water throughout the experiment can be explained by the same combined effect of evaporation and sulfide dissolution (which tend to increase sulfate concentrations), and the precipitation of water-soluble phases (gypsum) and especially iron oxy-hydroxy-sulfates (which tend to reduce its pore-water concentrations). As explained above, the precipitation of sulfur-bearing phases is supported by geochemical calculations, showing supersaturation with respect to gypsum and to several iron oxy-hydroxy-sulfates, and by the detection of jarosite and gypsum by XRD.

## Table 5 Saturation indexes with respect to the main mineral phases in the pore-water of the three first stages of the column experiments

		Stage 1/Water saturation 0.79				Stage 2/W	ater saturat	ion 0.71		Stage 3/Water saturation 0.62			
Sample Temperature (°C)		ST10107 42	ST10714 41	ST11421 40	ST12128 39	ST20107 44	ST20714 42	ST21421 40	ST22128 39	ST30107 46	ST30714 43	ST31421 40	ST32128 39
Depth range (cm		1-/	/-14	14-21	21-28	1-/	/-14	14-21	21-28	1-/	/-14	14-21	21-28
Phase	Min. formula	Saturation	n index										
Alum	$KAl(SO_4)_2 \cdot 12H_2O$	-3.89	-4.21	-4.30	-4.29	-3.88	-4.00	-4.21	-4.30	-2.71	-3.27	-3.30	-3.78
Alunite	$KAl_3(SO_4)_2(OH)_6$	4.73	2.44	2.88	2.60	4.28	3.63	3.13	3.32	7.27	6.77	6.01	5.96
Alunogen	$Al_2(SO_4)_3 \cdot 17H_2O$	-2.55	-3.30	-3.30	-3.27	-2.64	-3.21	-3.24	-3.55	-1.53	-2.64	-2.81	-3.67
Anglesite	PbSO <sub>4</sub>	-0.27	0.01	-0.11	-0.17	-0.32	-0.14	-0.10	-0.16	0.07	-0.05	-0.04	0.02
Bianchite	ZnSO <sub>4</sub> ·6H <sub>2</sub> O	-1.20	-1.51	-1.51	-1.52	-1.05	-1.35	-1.40	-1.50	-0.49	-0.91	-0.97	-1.24
Bilinite	Fe <sup>2+</sup> Fe <sup>3+</sup> <sub>2</sub> (SO <sub>4</sub> ) <sub>4</sub> ·22H <sub>2</sub> O	0.87	0.22	-0.03	0.23	0.23	-0.26	-0.13	-0.65	0.35	-1.51	-1.36	-2.83
Chalcantite	CuSO <sub>4</sub> ·5H <sub>2</sub> O	-1.48	-1.65	-1.60	-1.55	-1.49	-1.73	-1.76	-1.75	-0.67	-1.11	-1.27	-1.43
Copiapite	$Fe^{2+}Fe^{3+}_{4}(SO_{4})_{6}(OH)_{2}\cdot 20H_{2}O$	2.03	0.57	0.13	0.73	0.73	0.01	0.19	-0.37	1.27	-1.72	-1.42	-3.43
Coquimbite	Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> ·9H <sub>2</sub> O	-38.37	-38.79	-39.07	-38.79	-38.82	-39.13	-39.07	-39.35	-38.60	-40.19	-39.98	-40.97
Epsomite	MgSO <sub>4</sub> ·7H <sub>2</sub> O	-1.06	-1.33	-1.34	-1.32	-1.08	-1.32	-1.32	-1.47	-0.70	-1.14	-1.20	-1.62
Fe(OH) <sub>3</sub>	Fe(OH) <sub>3</sub>	-1.76	-2.39	-2.40	-2.15	-2.29	-2.18	-2.15	-1.89	-2.31	-1.97	-1.90	-1.58
Goethite	FeOOH	4.73	4.06	4.11	4.23	4.26	4.30	4.26	4.49	4.34	4.55	4.52	4.80
Goslarite	ZnSO <sub>4</sub> ·7H <sub>2</sub> O	-1.17	-1.46	-1.47	-1.46	-1.03	-1.31	-1.34	-1.42	-0.52	-0.88	-0.92	-1.17
Gypsum	CaSO <sub>4</sub> ·2H <sub>2</sub> O	0.19	0.02	0.01	0.04	0.14	0.05	0.02	-0.04	0.45	0.13	0.07	-0.04
Halotrichrte	FeAl <sub>2</sub> (SO <sub>4</sub> ) <sub>4</sub> ·22H <sub>2</sub> O	-2.86	-3.95	-3.91	-3.91	-3.15	-4.00	-3.95	-4.53	-1.85	-3.52	-3.80	-5.23
Hexahydrite	MgSO <sub>4</sub> ·6H <sub>2</sub> O	-1.06	-1.35	-1.34	-1.35	-1.07	-1.33	-1.34	-1.50	-0.64	-1.13	-1.21	-1.65
H <sub>3</sub> O-Jarosite	$(H_3O)Fe_3(SO_4)_2(OH)_6$	4.82	3.33	3.37	3.47	3.88	3.58	3.40	3.52	4.37	3.38	3.25	2.96
K-Jarosite	$KFe_3(SO_4)_2(OH)_6$	6.47	4.87	4.79	5.07	5.39	5.37	5.07	5.41	6.54	5.88	5.88	5.81
Na-Jarosite	NaFe <sub>3</sub> (SO <sub>4</sub> ) <sub>2</sub> (OH) <sub>6</sub>	2.99	1.44	1.43	1.63	2.45	1.87	1.78	2.02	2.87	2.20	2.03	2.00
Jurbanite	AlOHSO <sub>4</sub>	2.09	1.49	1.54	1.58	1.94	1.66	1.64	1.59	2.71	2.27	2.14	1.90
Komelite	Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> ·7H <sub>2</sub> O	-35.25	-35.70	-35.98	-35.71	-35.71	-36.04	-35.99	-36.27	-35.42	-37.09	-36.88	-37.90
Melanterite	FeSO <sub>4</sub> ·7H <sub>2</sub> O	-0.82	-1.11	-1.10	-1.08	-1.03	-1.26	-1.17	-1.42	-0.93	-1.39	-1.46	-1.99
Mirabilite	Na <sub>2</sub> SO <sub>4</sub> ·10H <sub>2</sub> O	-7.99	-7.71	-7.82	-7.85	-6.88	-7.56	-7.48	-7.49	-7.27	-7.09	-7.22	-7.17
Pickeringite	MgAl <sub>2</sub> (SO <sub>4</sub> ) <sub>4</sub> ·22H <sub>2</sub> O	-3.45	-4.51	-4.49	-4.48	-3.55	-4.40	-4.43	-4.91	-1.98	-3.61	-3.87	-5.18
Rozenite	FeSO <sub>4</sub> ·4H <sub>2</sub> O	-0.75	-1.09	-1.06	-1.08	-0.94	-1.23	-1.16	-1.44	-0.72	-1.31	-1.43	-2.01
Schwertmannite	Fe <sub>8</sub> O <sub>8</sub> (OH) <sub>6</sub> SO <sub>4</sub>	25.16	20.47	20.24	22.07	21.27	21.72	21.90	23.49	21.74	22.68	23.20	24.69
Siderotil	FeSO <sub>4</sub> ·5H <sub>2</sub> O	-0.51	-0.84	-0.81	-0.83	-0.70	-0.98	-0.90	-1.18	-0.51	-1.07	-1.18	-1.75
Szomolnokite	FeSO <sub>4</sub> ·H <sub>2</sub> O	-1.10	-1.48	-1.45	-1.47	-1.30	-1.62	-1.55	-1.84	-0.96	-1.67	-1.80	-2.41
Zincosite	ZnSO <sub>4</sub>	-5.07	-5.50	-5.41	-5.60	-4.84	-5.30	-5.43	-5.59	-3.97	-4.74	-4.96	-5.34
Gunningite	ZnSO <sub>4</sub> ·H <sub>2</sub> O	-1.85	-2.25	-2.20	-2.31	-1.66	-2.07	-2.17	-2.30	-0.87	-1.55	-1.70	-2.05

The calculations have been carried out using the PHREEQC code (Parkhurst, 1995) and the databases from Tosca et al. (2005)) and WATEQ4f (Ball and Nordstrom, 1991), with the modifications explained in the text.



Fig. 7. Distribution of elements between the different solid phases and pore-water in the four stages of evolution in the column experiments. In the fourth stage, the "pore-water" fraction represents the sum of the content in pore-water and the content in the water-soluble precipitates except for calcium, copper and sulfur. For these three elements the sum of pore-water and water-soluble fraction is represented as "water soluble".

## 3.3.2. Evolution of trace elements

Three different groups of trace element behavior in the pore-water were observed. First, lead concentrations showed no significant variations throughout the experiment (Fig. 5). The main process releasing lead to the pore-water is galena dissolution. As shown in Fig. 7, the amount of

lead present in the pore-water or associated to the water soluble fraction is negligible compared with the proportion of this element in the rest of solid phases. The lack of variation in the lead pore-water concentration throughout the experiment can be attributed to the small amount of galena initially present in the tailings or to the adsorption or coprecipitation of lead with the solid phases, for which lead showed a clear affinity (Fig. 7). Precipitation of anglesite is also possible, since most of the pore-waters are close to equilibrium with respect to this phase (Table 5).

The second type of behavior is represented by arsenic. Pore-water concentrations of this element decreased during the column experiment except in the uppermost sample at the third stage (Fig. 5). Arsenic is present in small amounts in the structure of pyrite and it is released to pore-water owing to pyrite dissolution. The progressive decrease of arsenic in the pore-water throughout the experiment can be explained by the adsorption of coprecipitation of this element with crystalline or amorphous iron phases. These iron phases retained a half of the arsenic present in the tailings material (Fig. 7). The ability of schwertmannnite, iron oxy-hydroxides, jarosite or goethite to retain arsenic is well known and it has been described in several earlier works (Dold and Fontboté, 2002; Fukushi et al., 2003; Savage et al., 2005; Acero et al., 2006). Under the studied conditions, arsenic showed a clear affinity for crystalline over amorphous iron phases (Fig. 7).

Finally, pore-water concentrations of the rest of trace elements reported (Cd, Co, Ni) remained almost unchanged during the two first dismantling stages and then increased at the third stage, especially in the uppermost part of the columns (Fig. 5). In the case of cobalt and nickel, these elements have been reported to replace iron in the structure of pyrite and zinc in sphalerite (Deer et al., 1992). More than 70 wt% of cobalt and nickel remained in the residual fraction throughout the experiment, while the rest of these elements was present mainly in the pore-water and the water-soluble fractions (Fig. 7). As far as cadmium is concerned, this element usually replaces zinc in the structure of sphalerite (Vaughan and Craig, 1978) and it is therefore released to the pore-water as a consequence of sphalerite dissolution. As in the case of zinc, most of the mobilized fraction of cadmium remained in the pore-water preferentially over the solid phases throughout the column experiments.

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