Effects of organic/inorganic amendments on trace elements dispersion by leachates from sulfide-containing tailings of the São Domingos mine, Portugal. Time evaluation

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ARTICLE INFO

ABSTRACT

Greenhouse pot experiments were conducted over 13 months to evaluate the effect of two amendment mixture doses (30 and 75 Mg/ha) on the geochemical dispersion of trace elements by leaching hazardous mine wastes from the São Domingos mine. Mineralogical evolution of these materials was also evaluated. Amendment mixtures containing solid wastes from agriculture (plant remains + strawberry substrate and rockwool used for the strawberry crop) and from distillation of *Ceratonia siliqua* L. and *Arbutus unedo* L. fruits were used to improve the chemical characteristics of leachates from sulfide mine wastes. Sulfide mine wastes had acidic characteristics, as well as high electrical conductivity and total element concentrations (g/kg; Al: 54.8–61.2; Fe: 104.0–110.0; Pb: 9.0–13.8; S: 63.6–68.0; As: ≈1). These features contributed to the large capacity for leaching of hazardous elements during, at least, the first four months of incubation. In the seventh month of incubation, there was a significant decrease in the leachate concentration of the majority of hazardous elements. The addition of amendments minimised trace element dispersion in leachate percolation during the first seven months (25 to 99% reduction compared to control, depending on the element and sampling period). However, the leachate characteristics were not influenced by amendment doses and no significant differences were observed in leachate composition (control and amended treatments) after 13 months. Amendment application led to differences between the solid phases of the efflorescent salts formed on the surface of the control and the amended treatments. The efflorescent salts contained very soluble aluminium sulfates, together with *alunite–jarosite*-group solid phases in amended samples, and *copiapite*-group solid phases in control. In the core materials (5 to 10 cm in depth), the mineralogy was similar in both control and amended samples. The presence of various stable solid phases from *alunite–jarosite*-group, such as jarosite and beudantite (mainly in deeper materials), can explain the low concentrations of trace elements in the leachates after thirteen months.

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1. Introduction

The intense mining activity in massive sulfides from Iberian Pyrite Belt (IPB) generates different types of wastes. In the São Domingos mine (IPB) in Portugal, large dumps attaining approximately 0.27 Tg, as well as modern and Roman slags and smelting ashes, contain pyrite-rich materials and other sulfides, which produce acid drainage all year round (Álvarez-Valero et al., 2008; Matos, 2004). The production and circulation of acid mine leachates (or acid mine drainage — AMD) are a serious environmental problem in sulfide mine areas due

to the extremely acidic conditions (frequently, pH < 1.5) they generate. The very low pH of the leachates promotes trace element dispersion to adjacent areas, preventing the establishment of vegetation, as well as harming existing vegetation or other organisms that colonise neighbouring areas, thereby decreasing biodiversity (Abreu et al., 2010; Gil Bueno et al., 1990; Pérez–López et al., 2008; Sánchez-España et al., 2005).

The AMD treatment in the IPB has been unsustainable due to its characteristics, namely, extreme acidity and high multitrace element concentrations (Sáinz et al., 2003). The large surface area of the tailings promotes sulfide oxidation and consequent AMD generation in a manner that is difficult to control. These sulfide-containing tailings also show rill and gully erosion, and lack of vegetation due to the high acidity and low fertility of these waste materials.

Different organic and inorganic wastes, like red gypsum, sugar foam, sewage sludge, biosolids, fly ashes, pig manure, marble wastes, etc., have

been evaluated as amendments to improve some physical, chemical and biological properties of mine tailings and contaminated soils (Basta et al., 2001; Forsberg et al., 2008; Pérez–López et al., 2007; Rodríguez-Jordá et al., 2012; Zanuzzi et al., 2009). Some amendments, such as waste compost and sewage sludge, can contain high concentrations of hazardous trace elements that can increase the environmental risk of their application. Therefore, their use should be carefully monitored.

Due to the different chemical behaviours of each trace element, and the specific chemical and/or mineralogical composition of the amendments, selective immobilization and redistribution of trace elements in solid phases can be achieved efficiently (Rodríguez-Jordá et al., 2010, 2012).

The application of amendment mixtures composed of several organic/inorganic wastes, instead of using a single type, can be more efficient in the rehabilitation of mining areas that contain high concentrations of several trace elements in tailings and highly contaminated leachates (Kumpiene et al., 2008). These amendment mixtures, which can make a Technosol in an attempt to create different soil functions, can reduce trace element availability and their concentrations in mine waste leachates (Macías, 2004) through the complementary effects of each amendment component. Several industrial or agro-industrial wastes, due to their intrinsic characteristics (high organic matter content and pH, and low concentration of trace elements, etc.), large available quantities and cost effectiveness, can be an economically attractive target to make a Technosol and a strategy for waste valorisation (Macías, 2004).

The ecological rehabilitation of the São Domingos mine area can be achieved by minimising the leaching element concentrations and/or improving the chemical characteristics (for instance, increase in pH and decrease in salinity) of the leachates by remediation of mine wastes containing sulfides. The use of amendments can also contribute to plant colonisation and stimulation of biogeochemical processes that promote mine waste treatment and soil remediation (Abreu and Magalhães, 2009). The success of the multielemental contaminated mine area rehabilitation depends on the combination of the trace elements in tailings and the selection of adequate amendments (Kumpiene et al., 2008).

Leachates from São Domingos and other mines in the IPB present multielemental contamination (Abreu et al., 2008, 2010; Sánchez-España, 2008; Sánchez-España et al., 2005). However, few studies are available on the effects of amendments on the leaching of cations and anions from sulfide-containing tailings (Pérez-López et al., 2007), and even less for periods of monitoring longer than one year. Therefore studies on the variation over time of the chemical composition of leachates, following amendment addition to mine wastes, are environmentally relevant for future mine rehabilitation projects.

This study aimed to evaluate the effect of two amendment mixtures (30 and 75 Mg/ha) on the availability of trace elements (cations and anions), which occurred at high concentrations in sulfide-containing tailings, over thirteen months. Understanding changes in geochemistry over time is essential in ensuring successful sulfide mine waste rehabilitation. Examining mineralogical evolution of mine wastes as a consequence of leaching and the attainment of new equilibria were also a goal of this study.

2. Materials and methods

2.1. Site characterization

Sulfide mine wastes were collected from the São Domingos mine area, an abandoned mine located in the IPB and situated in the municipality of Mértola, SE Portugal. Mining activities date from the pre-Roman period with exploitation of Ag, Au and Cu, mainly in the *gossan*. However, modern exploitation (1857–1966) occurred both in the *gossan* and massive sulfides containing Cu, Zn, As and Pb (Quental et al., 2002). The exploitation and extraction processes produced large

amounts of different mining wastes, which covered a surface area of around 3.2×10^6 m^2 (Álvarez-Valero et al., 2008). In the Portuguese IPB, São Domingos is a severe case of the environmental impact of mining due to the dimension of the areas affected by AMD and the volume of wastes and tailings (11×10^6 m^3), with high concentrations of hazardous trace elements (Álvarez-Valero et al., 2008; Matos and Martins, 2006). The sampling area is located within the mine area, SW of the open pit, near the former leaching tanks.

2.2. Experiment set-up

Composite samples of the sulfide mine wastes (MW), containing mainly crushed pyrite and smelting ashes, were collected in 2009. These materials were chosen due to their large amounts and wide distribution in the mine area, and their potential risk as a source of contamination (Álvarez-Valero et al., 2008; Quental et al., 2002). In addition, the tailings are bared and exposed to severe water erosion.

The amendments applied at 30 or 75 Mg/ha were mixtures containing distinct organic and inorganic wastes from: green agriculture (plant remains + strawberry substrate at 2:3 m/m) (AgrW), *Arbutus unedo* L. (ArbW) and *Ceratonia siliqua* L. (CerW) fruit spirit distillation; and rockwool used for strawberry crops (RW). Limestone rock wastes (LRW) with a particle size <2 mm were also used at 55 Mg/ha (except in control) to raise the mine wastes pH to ≈4. These organic and inorganic wastes were used due to their physical and chemical characteristics and the fact that they can be easily obtained in large quantities at almost "zero cost" from the vicinity of the mine.

The tailings and amendments were air-dried, mixed manually and potted. Microcosm assays were performed in pots containing around 6 kg of mine waste materials (total fraction). Three treatments were made (four replicates each): control with only mine wastes (MW); and MW + LRW + Amendment composed of AgrW + ArbW + CerW + RW (1:1:1:1) at 30 and 75 Mg/ha. All treatments were kept at 70% of water-holding capacity under controlled conditions in a greenhouse. The pots were monitored for thirteen months.

2.3. Experimental monitoring and sample analyses

Multielemental concentrations of the initial sulfide-containing mine wastes (fraction < 2 mm) and organic/inorganic wastes were analysed by atomic emission spectrometry with induced plasma (ICP-OES) and instrumental neutron activation analysis (INAA) after acid digestion with HClO$_4$ + HNO$_3$ + HCl + HF in an international accredited laboratory (Actlabs, ISO/IEC 17025, Activation Laboratories, 2011a, 2011b). The fraction < 2 mm was characterized for the total concentrations of C and N (analysed by combustion with a Leco analyser), as well as for electrical conductivity (EC) and pH, both in water suspension (1:2.5 m/V) and Extractable P and K (Povoas and Barral, 1992). Particle size distribution of mine wastes (total fraction) was also determined by sieving.

Mine waste materials (control) or the mixtures of MW and amendments were collected (0 to 5 cm of depth) with a cylindrical probe, from each pot, after collection of the surface efflorescent salts. These solids and the leachates obtained from deionised water percolation through the materials contained in the pots were collected after one, four, seven and thirteen months of incubation. At the end of the experiment (thirteen months), materials from all the treatments were also collected from a depth of around 10 cm.

Only the mine wastes (control) and amended mine wastes collected after one and thirteen months of incubation were air-dried, homogenised, sieved (<2 mm) and analysed for pH, EC, and the total concentrations of C and N by the same methodologies referred to above. Total concentration of S was also determined by combustion with a Leco analyser.

To obtain leachates by percolation, the materials in the pots were irrigated with a volume of deionised water that ensured an excess of 10% of each pot's water holding capacity, and left to percolate for 24 h.

The leachates were collected in plastic flasks linked to the bottom of the pot hole by a plastic tube. The leachates were vacuum filtrated (<0.45 μm), and pH and EC were measured. The filtrate was kept at −18 °C. The leachates were analysed for: Al, Ca, Cu, Fe, K, Mg, Mn, Na, Pb and Zn total concentrations by flame atomic absorption spectrometry; As by graphite furnace atomic absorption spectrometry; sulfates by ion chromatography; and phosphates by visible spectrophotometry using the molybdenum blue method (USEPA, 1979).

Efflorescent salts were stored, after collection, in hermetic containers at room temperature far from the sunlight. Mineralogical analysis of the efflorescent salts collected after one and thirteen months, as well as of mine waste materials (total fraction) from the end of the experiment, was performed in random powder samples by X-ray diffraction (XRD) using Cu Kα radiation. The XRD analysis was performed in samples separated under a binocular microscope, and selected by colour and general morphological aspects (lustre, habit, etc.). In spite of the methodology used for mineral identification, the samples were always heterogeneous and the solid phases were not easy to identify, owing to the amount of lines obtained in the XRD spectra. The mineralogical analysis considered the elemental composition and the pH of the leachates, the known or foreseen solubilities of the solid phases, as well as the temperature and relative humidity in the greenhouse. The same efflorescent salts were also analysed by Fourier transform infrared spectroscopy (FTIR).

After being analysed by XRD, the efflorescent salt samples and the mine waste materials were mixed with water (solid:water ratio of 0.033:10 and 1:10 (m/V), respectively), and shaken for 24 h. The chemical composition of the obtained aqueous solutions with pH < 3 was determined by high resolution inductively coupled plasma mass spectrometry (Actlabs, ISO/IEC 17025, Activation Laboratories, 2011c).

2.4. Data analysis

Statistical analysis was performed with the statistical programme SPSS v18.0 for Windows. All data were checked for homogeneity of variance and normality (Shapiro–Wilk test) and, when possible, a one-way ANOVA was applied. Data not satisfying assumptions for ANOVA were analysed non-parametrically using Kruskal–Wallis ANOVA by a rank test. Significant differences ($p < 0.05$) were analysed by a post-hoc Tukey's test. For statistical purposes, the results below the detection limit were assumed as half of the detection limit. Bivariate Pearson correlations were used to correlate the materials and leachate characteristics ($r > 0.95$). Quality control of the analysis was undertaken by analytical replicate samples and laboratory standards at the international accredited laboratory (Activation Laboratories).

3. Results and discussion

3.1. Characterization and time evolution of solid materials

Mine wastes are, in general, complex mixtures of heterogeneous materials, but the sulfide wastes collected from the São Domingos area did not show high variability in their chemical characteristics.

These mine wastes presented a pH ≈ 2, large EC (7.4 to 7.5 mS/cm) and low fertility (Table 1). The large total carbon concentration in mine wastes was related to the considerable presence of smelting ashes and small pieces of charcoal. Mine wastes presented 54 % of the materials in the fraction > 2 mm, distributed as follows: ≥20 mm (7 %); 10–20 mm (10 %); 8–10 mm (5 %); 5–8 mm (11 %); and 2–5 mm (21 %). The large amount of coarse materials together with the high total concentrations of trace elements (Table 2) probably contributed to the lack of vegetation, observed in the field, on dumps composed of these types of wastes.

Concentrations of As, Cu, Pb and Zn in the initial mine materials were in the same range as those reported by Álvarez-Valero et al. (2008) for pyrite-rich samples and smelting ashes from São Domingos. The physical and chemical characteristics of the mine wastes were associated with their predominant composition — materials containing sulfides, potential AMD generators.

All the organic and inorganic wastes used as amendments presented chemical characteristics considered beneficial and safe for land application and rehabilitation of mine wastes. Concentrations of total nitrogen and extractable phosphorus and potassium, in addition to pH values, were larger than those in mine wastes (Table 1), while the lowest EC was observed (0.2 to 3.5 mS/cm) in all the amendments. Wastes from spirit distillation (ArbW and CerW) showed the highest total carbon concentrations (436.7 to 442.6 g/kg). Concentrations of trace elements in the amendments were much lower than those in mine wastes (Table 2).

After one month of incubation and at the end of the experiment (thirteen months of incubation), amendment addition improved the structure of the materials by increasing the organic matter content and consequently raising the water-holding capacity. The amendments reduced EC by 31 to 53 % compared to control (Table 3). The pH of the amended mine wastes increased to 3.5–3.6 and ~2.1 after one and thirteen months of incubation, respectively (Table 3) despite the presence of limestone rock wastes in the initial composition of the amendments. However, when materials/water suspensions (1:10 m/V) from the first month of incubation were shaken for one and five days at room temperature, the measured pH was ~2.2 for control (for both shaking times) and 4.2–4.5 and 5.3–7.0 for one and five days, respectively, for the amended samples. Similar shaking experiments performed with materials after four months of incubation presented pH values (2.1 < pH < 2.5) in the same range as that of the collected leachate percolations (Fig. 1). Zanuzzi et al. (2009) in another microcosm assay involving the Brunita mine tailing pond, observed an increase in the pH of the materials following the addition of amendments, even after 24 months, from 2.8 (treatment not amended) to 7.3 (application of marble wastes + pig manure or marble wastes + sewage sludge). However, those authors applied larger doses (166.7 Mg/ha) of marble wastes with larger particles (<2 mm: 26 %; 2–5 mm: 74 %), compared to the present study (55 Mg/ha, <2 mm: 100 %). The comparison of the pH values gotten in this work, for the shaken materials/water suspensions, with the results of Zanuzzi et al. (2009) show that the presence of limestone in the amendments increases the pH to values higher than four. Thus, the pH lower than four, measured in this work,

Table 1
Characteristics of the original sulfide mine wastes from the São Domingos mine area and organic/inorganic wastes used as amendments (min–max).

	MW	AgrW	ArbW	CerW	RW
pH (H₂O)	2.1–2.3	6.6–7.2	4.9	6.1	7.1
EC (mS/cm)	7.4–7.5	0.9–3.5	1.7	0.2	3.5
Total C (g/kg)	243.8–276.1	286.1	442.6	436.7	111.0
Total N (g/kg)	3.7–4.8	9.7	8.9	11.1	9.8
Extractable P (g/kg)	<DL	0.3–3.1	0.2	0.1	7.9
Extractable K (g/kg)	0.02–0.06	0.2–6.6	3.6	9.1	0.7

EC: Electrical conductivity; MW: mine wastes; AgrW: Agriculture wastes; ArbW: residue from the liquor distillation of *Arbutus unedo* L. fruit; CerW: residue from liquor distillation of *Ceratonia siliqua* L. fruit; RW: Rockwool; DL: detection limit.

Table 2

Total concentrations of trace elements (g/kg Dry weight) in the original mine wastes from the São Domingos mine, composed of crushed pyrite and smelting ashes, and in the organic/inorganic wastes used as amendments (min–max).

	Mine wastes	AgrW	ArbW	CerW	RW
Al	54.8–61.2	4.06	1.37	0.6×10^{-3}	53.4
As	1.02–1.14	2.3×10^{-3}	1.0×10^{-3}	0.8×10^{-3}	$<0.5 \times 10^{-3}$
Ca	6.40–6.70	22.56	10.30	11.02	139.0
Cu	1.84–2.45	44.6×10^{-3}	0.124	9.4×10^{-3}	0.08
Fe	104–110	2.96	3.296	0.999	39.90
K	12.8–14.3	1.495	>1.318	0.963	6.80
Mg	1.4–1.8	2.369	1.129	>9.63	42.10
Mn	0.119–0.162	0.248	51.2×10^{-3}	43.1×10^{-3}	1.85
Na	4.20–4.60	0.310	0.404	0.404	13.10
Pb	8.97–13.80	5.0×10^{-3}	3.1×10^{-3}	0.9×10^{-3}	$<3 \times 10^{-3}$
S	63.6–68.0	Na	Na	Na	2.60
Zn	1.08–1.19	75.6×10^{-3}	27.3×10^{-3}	18.5×10^{-3}	0.201

MW: mine wastes; AgrW: Agriculture wastes; ArbW: residue from the liquor distillation of *Arbutus unedo* L. fruit; CerW: residue from liquor distillation of *Ceratonia siliqua* L. fruit; RW: Rockwool; NA: non analysed.

in the leachates from the amended materials, after one month of incubation, indicate that the limestone could not be in contact with the surrounding aqueous medium. This can be explained by the formation of a layer of calcium sulfate on the surface of the limestone grains. The calcium sulfate is the product of the reaction between the calcium carbonate and the sulfate ion present in the acid solutions generated by the pyrite oxidation. The calcium sulfate surface layer was dispersed after shaking, promoting the contact between the limestone and the aqueous solution, increasing the pH of the materials/water suspensions. However, after the fourth month of incubation the limestone was already dissolved once there was no change in the pH of the shaken materials/water suspensions. The decrease in the limestone effect at the beginning of the incubation, due to its reaction with the generated acidic leachates, was favoured by the small grain size (<2 mm) of the used material, which was therefore one disadvantage of this amendment. In fact, the kinetics of the limestone reaction increases when the size of the solid particles decreases. During the entire experiment, the acidity of mine wastes increased in all treatments, with and without amendments (Table 3). The amendments, at both doses (30 and 75 Mg/ha), were not efficient in AMD pH buffering.

After thirteen months of incubation, total sulfur concentration in the mine wastes with amendments was larger than that of control (Table 3). A significant reduction of total sulfur was only observed in the control (32%) between one and thirteen months. Efflorescent salts formed crusts on the surfaces of the controls, reaching 5 mm in thickness. On the amended surfaces, there were only a few efflorescent salts. Both surfaces displayed efflorescent salts containing mixtures of soluble sulfates, as described in Section 3.3. Besides the migration of

sulfates to the surface, leachates collected from the control contained higher concentrations of sulfates (112 g SO_4/L in leachates collected in the fourth month) than those that were treated with amendments (≈23 g SO_4/L in leachates collected also in the fourth month).

3.2. Characterization and time evolution of leachates

3.2.1. Electrical conductivity and pH

During the experimental period, pH and EC of the leachates from the treatments with amendments (pH: 1.95–2.47; EC: 4.36–21.05 mS/cm) were significantly different from those of the control (pH: 1.13–1.58; EC: 11.08–51.92 mS/cm), although both were acidic and with high EC (Fig. 1). The amendments increased the pH of leachates by more than 0.5 units and reduced the EC by more than 43 %. These values contrast with the results of Ciccu et al. (2001) and Pérez-López et al. (2007), who applied fly ashes to pyritic sludge or to soils contaminated by reddish tailings and observed an increase of more than two units for the pH of the leachates (from 2 to 7.5 and from 6 to 8, respectively) after 210 and 350 days, respectively. However, EC was only reduced in the experiments with pyritic sludge (0.30 mS/cm). Rodríguez-Jordá et al. (2012) also recorded an increase of the pH of the leachates (from 3.4 to values > 6) from São Domingos mine sediments 40 days after application of different calcium carbonate-containing amendments (sugar foam or mixtures of sugar foam + ashes from combustion of biomass or sugar foam + red gypsum + ashes from combustion of biomass). The pH values obtained by Rodríguez-Jordá et al. (2012) confirm our previous statement that the pH of amended wastes and their leachates is higher than four when calcium carbonate is present.

Table 3

Characteristics of mine waste samples from different treatments, collected after one month of incubation and at the end of the experiment (Mean ± SD; $n = 4$). Data of the same characteristic followed by a different letter are significantly different ($p < 0.05$). Small letters indicate comparisons between treatments from the same sampling period and capital letters indicate comparisons between the same treatments from different sampling periods.

|	Control	Treatment with amendments	
		30 Mg/ha	75 Mg/ha
After one month of incubation			
pH (H_2O)	2.5 ± 0.1[bA]	3.5 ± 0.03[aA]	3.6 ± 0.1[aA]
EC (mS/cm)	8.4 ± 1.5[aA]	4.0 ± 1.0[bB]	4.3 ± 0.3[bB]
Total C (g/kg)	208.0 ± 22.0[aA]	182.0 ± 19.9[aA]	204.5 ± 18.0[aA]
Total N (g/kg)	4.1 ± 0.4[aA]	3.7 ± 0.4[aA]	4.3 ± 0.5[aA]
Total S (g/kg)	52.8 ± 2.2[aA]	51.1 ± 2.1[abA]	46.7 ± 3.7[bA]
After thirteen months of incubation			
pH (H_2O)	1.6 ± 0.1[bB]	2.1 ± 0.1[aB]	2.1 ± 0.2[aB]
EC (mS/cm)	10.9 ± 1.1[aA]	7.0 ± 1.3[bA]	7.5 ± 2.2[bA]
Total C (g/kg)	173.3 ± 7.5[aB]	154.3 ± 11.6[aA]	145.5 ± 2.9[aB]
Total N (g/kg)	3.3 ± 0.1[aB]	3.1 ± 0.1[aA]	3.1 ± 0.1[aB]
Total S (g/kg)	35.7 ± 1.3[bB]	48.7 ± 0.5[aA]	49.9 ± 1.7[aA]

EC: Electrical conductivity.
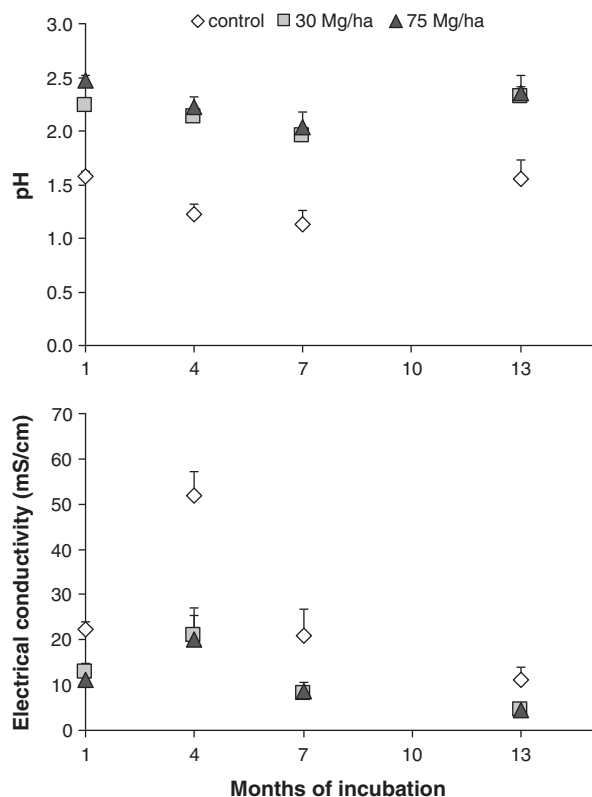
Fig. 1. Variation, with time, of pH and electrical conductivity in leachates, obtained by percolation, from sulfide mine wastes without and with amendment application at 30 and 75 Mg/ha (Mean $\pm$ SD; $n = 4$).

The pH of the leachates from control was lower and the EC values higher than those measured in the leachates from pyritic sludge by Pérez-López et al. (2007, pH $\approx$ 2; EC: 2–4 mS/cm). However, the present work results were in the same range as those reported for acid mine drainages in the IPB (Abreu et al., 2010; Sánchez-España et al., 2005, 2008).

The large quantity of sulfides in the mine wastes used in the present study can be one of the possible explanations for the great differences observed in leachate pH between this work data and those obtained by Forsberg et al. (2008) for Aitik Cu mine tailings containing only traces of metal sulfides whose pH ranged between 3.5 and 7.5.

Until the seventh month of incubation, the decrease of the leachate pH was observed in all the treatments. However, pH values at the end of the experiment (thirteen months) were similar to those of the first month of incubation. This represented a pH increase, between the seventh and thirteenth month of incubation, from 1.15 to 1.55 for control, and from $\approx$1.9 to $\approx$2.3 for amendment-treated samples. The decrease of the pH of the leachates during an experimental period of 630 days was also observed by Forsberg et al. (2008) in the Aitik Cu mine tailing leaching.

Regarding EC, the control samples exhibited a different trend compared to amended ones. Control EC values were in the same range as those reported for AMD from some IPB mines (Abreu et al., 2010; Sánchez-España et al., 2005, 2008). Control showed significant variations in EC, with a 2.5-fold increase in the fourth month (from 22.30 after the first month to 51.93 mS/cm), and a decrease to 20.78 mS/cm in the seventh month and 11.08 mS/cm in the last month. In the leachates from the control, the highest values of EC (Fig. 1) were measured in the fourth month, which agrees with the majority of the elemental total concentrations measured by other techniques. In treatments with amendments, the values of EC in the first and fourth months of incubation (11.3 and 21.1 mS/cm, respectively) were not significantly

different, but in the following months, a significant and progressive decrease was observed, reaching a value of around 4 mS/cm in the thirteenth month. The sampling made after one month of incubation occurred in spring, while the fourth and seventh month samplings occurred in summer. During spring and summer, the strong evaporation contributed to continuous crust formation of salts crystallising on the materials' surface. Irrigation usually caused complete dissolution of the efflorescent salts, but this was not complete during the warmest months, increasing the thickness of the surface crusts. The rise in the amount of surface salts could have contributed to the EC reduction observed during the experiment in all the treatments, as a result of a decrease in the concentrations of dissolved ions.

In terms of the possible biogeochemical rehabilitation effect, the increase of the amendment doses from 30 to 75 Mg/ha did not significantly modify the leachate characteristics originated by the waste materials. The environmental impact of the mine waste leachates is still very high.

3.2.2. Anion and cation concentrations

The water in contact with the mine wastes promoted the oxidation of the sulfide minerals, resulting in the formation of acid solutions and the consequent leaching and release of high amounts of cations, and anions containing mainly As and S. The leachates collected from the control presented a typical multielemental AMD composition (Figs. 2 and 3) from the IPB (taking in account both seasonal and mine variability) (Abreu et al., 2008, 2010; Sánchez-España et al., 2005, 2008) and the Valdarcas mine in the north of Portugal (Valente and Gomes, 2009).

The total concentrations of anions and cations in leachates were not related to their total concentrations in the mine wastes. However, the very low concentrations of phosphates (Fig. 2) in the leachates collected from the control suggested a low total concentration of these ions in mine wastes ([phosphate]$_{total}$ = 1.01 g PO$_4$/kg). No significant variations in phosphate concentrations were observed with time in the control (Fig. 2, 1.35–17.82 mg PO$_4$/L).

The amendments contributed to a significant increase in the phosphate total concentrations in the leachates (15.23–98.25 mg PO$_4$/L), compared to the control (1.35–17.82 mg PO$_4$/L), at least for the first three sampling periods (Fig. 2). The phosphates in the amendments (Table 1) were linked to the organic matter and nutrient solution incorporated into the rockwool, which came from strawberry cultivation in greenhouses. The amendments maintained leachate phosphate levels between 69.04 and 98.25 mg PO$_4$/L, until the seventh month of incubation. A significant reduction of more than 63 % was observed in the phosphate concentration (15.23 and 30.96 mg PO$_4$/L for 30 and 75 Mg/ha, respectively) after the thirteenth month. The crystallisation of Ca-containing phosphates in the efflorescent salts and other metal phosphates in the core materials (Section 3.3) could explain this decrease in phosphate concentrations in the leachates.

A considerable decrease in the concentration of some elements in leachates was observed following treatment with amendments, in comparison with control sample leachates (Figs. 2 and 3). The most extreme decrease, in the first month, was observed for As, which diminished by 94 % followed by Fe and Pb, whose total concentrations decreased by approximately 88 and 71 %, respectively. Sulfate and Cu concentrations decreased by around 56 %, while Al, Mn and Zn concentrations were reduced by 31, 30 and 25 %, respectively.

The total concentrations of Al, As, Cu, Fe, Pb, Zn and sulfate in the leachates from control samples were significantly higher than those in the leachates from amended ones in the fourth month of incubation (Figs. 2 and 3). In the leachates from control, the concentrations of Al, Cu, Pb, Zn and sulfate decreased significantly in the seventh and last months of the experiment (Figs. 2 and 3). A decrease of the total concentrations of Cu, Fe, Pb, Mn and Zn in the leachates was also obtained with fly ashes or bone meal application to pyritic sludge or soils
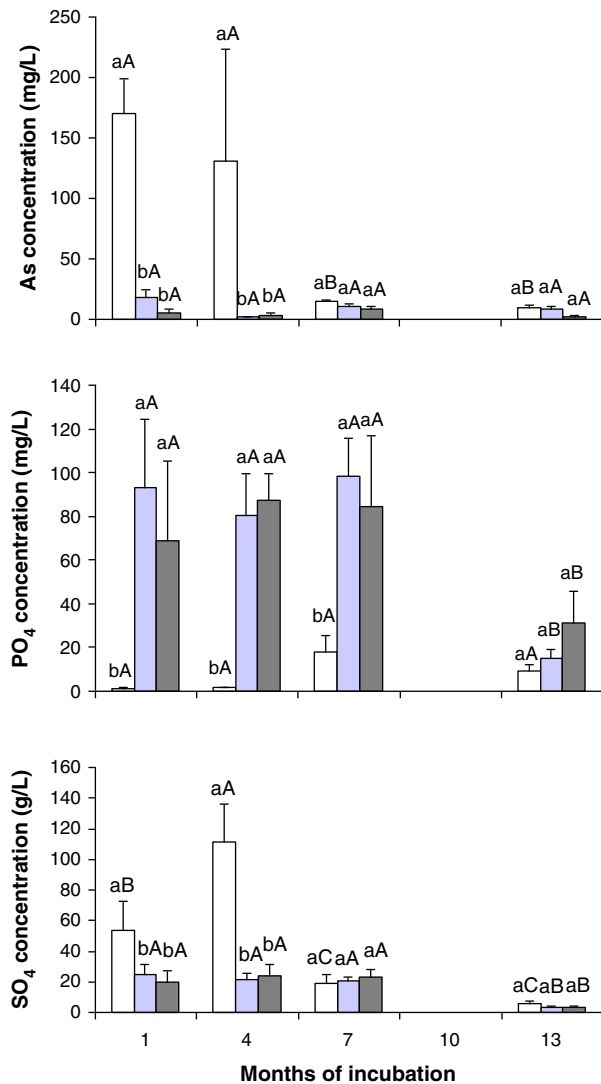
Fig. 2. Variation, with time, of anion concentrations in leachates, obtained by percolation, from sulfide mine wastes without and with amendment application at 30 and 75 Mg/ha (Mean ± SD; $n = 4$). Data followed by a different letter are significantly different ($p < 0.05$). Small letters indicate comparisons of different treatments from the same sampling period and capital letters indicate comparisons of each treatment with time.

With the exception of As and K, whose highest concentrations in leachates from control samples were found in the first and seventh months, respectively, the highest concentrations of Al, Ca, Cu, Fe, Mg, Mn, Na, Pb, Zn and sulfate were measured in the fourth month (Figs. 2 and 3). At the end of the experiment, the total concentrations of Al, As, Cu, Fe, Mg, Mn, Zn and sulfate in the leachates from control matched their concentrations in the leachates from the amended samples. In opposition to the present work results, no regular pattern was reported by Forsberg et al. (2008) in the concentrations of Al, Cu, Mn, Pb and Zn in leachates from Aitik mine tailings; however, they did note a progressive increase in their concentrations with time.

The total concentrations of K, Na and Pb in the leachates from control were always significantly higher than those in the leachates from amended samples, even at the end of the experiment (Fig. 3).

Figs. 2 and 3 show that increasing the dose of amendments did not significantly affect the multielemental composition of the leachates. The variations in the leachate pH with time did not correlate with the concentrations of anions and cations in all the treatments.

In general, the concentrations of cations in leachates were variable and difficult to predict and explain, due to the complexity of solid-phase trace element composition and concentrations, aqueous solution characteristics, rates of acid generation relative to neutralisation, and the possible existence of various physico-chemical conditions (Sullivan and Yelton, 1988). In the present work, a decrease in the concentrations of the hazardous chemical elements was evident with time, but Pérez-López et al. (2007) found an increase in Pb concentration from 3 to 35 mg/L in leachates from pyritic sludge. Rodríguez-Jordá et al. (2012) also observed an increase in As concentrations, with time in leachates from São Domingos sediments amended with sugar foam + biomass ash. Cao et al. (2003), Forsberg et al. (2008), Pérez-López et al. (2007) and Rodríguez-Jordá et al. (2012) reported, as in the present work, decreased concentrations of several chemical elements in leachates following the application of amendments. However, Forsberg et al. (2008) reported that adding sewage sludge to mine tailings from Aitik copper mine did not lead to the immobilization of Al, Cu, Mn and Pb during all leaching cycles. The different results obtained with different amendments could be attributed to the elemental chemical composition as well as to the physico-chemical properties of the amendments and substratum (soils and/or mine wastes) (McBride, 2003). Systems with different chemical compositions promote different behaviours.

The amendments obviously interact with the mine waste materials. For example, limestone reacts with the acid generating media and also organic matter. In spite of the small increase in pH of mine waste leachates following amendment application, interactions between the mine wastes and amendments can be perceived. The experiments discussed in Section 3.1 show that limestone was not present in the amended materials in the fourth month of incubation. On the other hand, the organic matter of the amendments can be oxidized, originating weak organic acids with some buffering capacity. The small increase in pH of the leachates from amended mine wastes, when compared to control, can be explained by the action of those organic acids. The organic matter can also inhibit the possible oxidation of the sulfide minerals. Residues of crystalline organic compounds were proposed in the preliminary computer analysis of the X-ray diffractograms of the amended wastes, described in Section 3.3. The decrease of the total concentrations of As and sulfate in the leachates from amended samples following the addition of organic matter is not easy to explain by surface adsorption mechanisms, since the presence of mainly negatively charged organic molecules or ions will not attract the negatively charged As or S containing ions. Hydronation of organic molecules can occur at low pH, but As ions are also hydronated into neutral species, diminishing the possibility of surface adsorption. Fitz and Wenzel (2002) stated that they did not see evidence of the organic

contaminated with reddish tailings (Ciccu et al., 2001; Pérez-López et al., 2007; Sneddon et al., 2006). Rodríguez-Jordá et al. (2012) also observed a decrease of the total concentrations of Cu and Zn in the leachates from São Domingos mine sediments after applying sugar foam-containing amendments. However, these authors noted an increase in the total concentrations of As and Pb in leachates after amendment application, which are in contrast to the results of the present study.

The total concentrations of As and Fe in the leachates from amended samples showed no significant variations with time. There was no noticeable decrease in the first month, in the concentrations of Ca, K and Na in these leachates when compared to control, with Na and K exhibiting very low concentrations in the leachates from amended samples all the time (Fig. 3). However Ciccu et al. (2001) and Pérez-López et al. (2007) observed an increase in the total concentrations of Ca, K and Na in leachates from the amended treatments.

The concentration of Mg in the leachates from control was lower than that in the leachates from samples treated with 75 Mg/ha of amendments in the first month, due to the fact that the amendments had high total concentration of Mg (Table 2, Fig. 3).

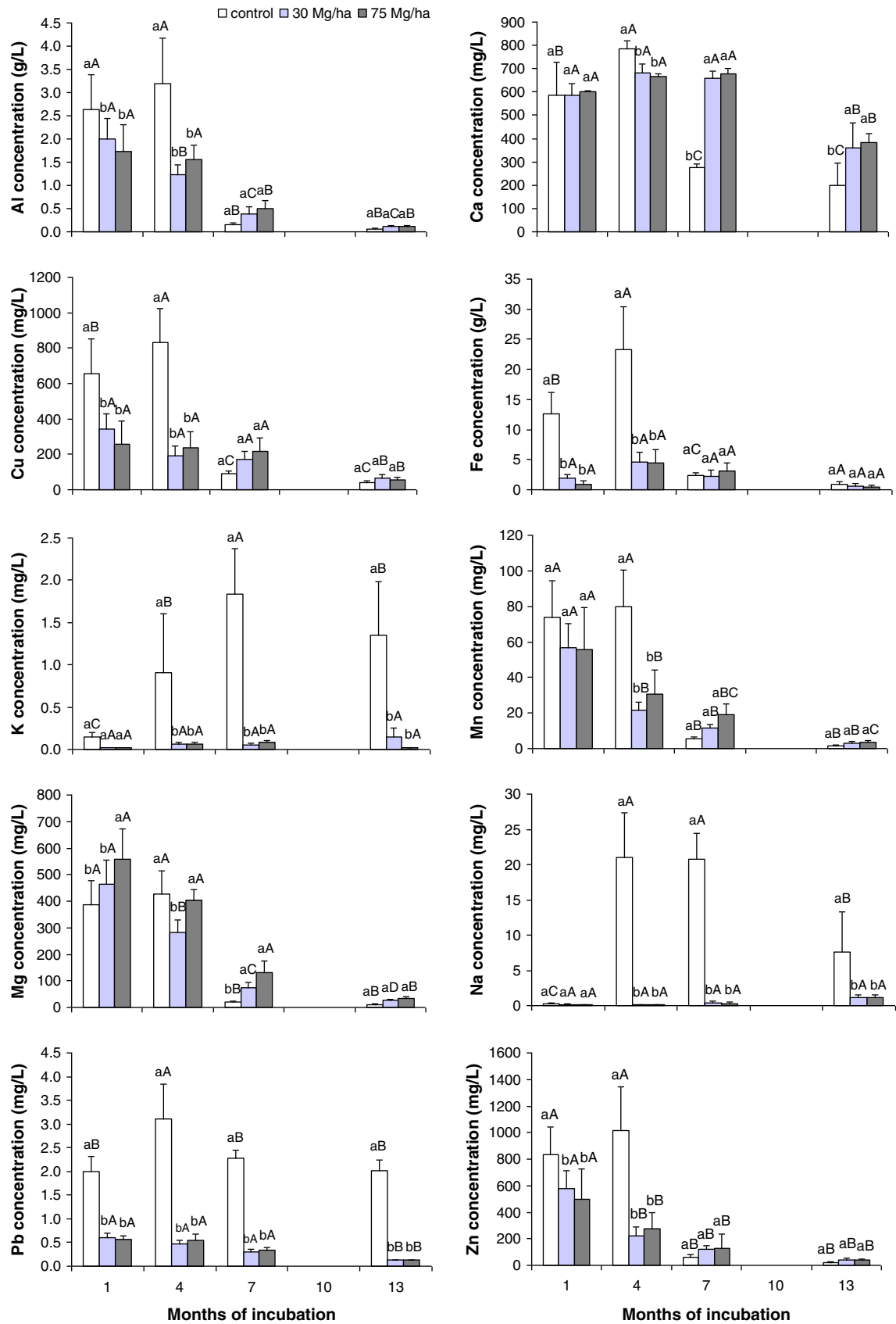**Fig. 3.** Variation, with time, of cation concentrations in leachates, obtained by percolation, from sulfide mine wastes without and with amendment application at 30 and 75 Mg/ha (Mean ± SD; $n = 4$). Data followed by a different letter are significantly different ($p < 0.05$). Small letters indicate comparisons of different treatments from the same sampling period and capital letters indicate comparisons of each treatment with time.

matter contribution to the sorption of significant amounts of As in soils. The same mechanism of hydronation of organic groups neutralising their negative charges or even, at very low pH, becoming positively charged could explain the possible lack of sorption of the positive metal ions in very acidic media. Besides the sorption mechanisms, ions can be immobilised by the formation of insoluble secondary solid phases (metal arsenates) (Abreu et al., 2009; Kabata-Pendias and Pendias, 2001; Kumpiene et al., 2008; Santos et al., 2012). The decrease of the total concentrations of Al, Cu, Fe, K, Mn, Na, Pb and Zn in the leachates from samples treated with both doses of amendments, compared to control, is also well explained by the crystallisation of solid phases.

During thirteen months of incubation, the sulfide materials (Table 2) from control lost cumulatively in the leachates, 4.8 % of their total concentration of S and ~1.7% of their total concentrations of As and Fe (Figs. 2 and 3). However, after amendment application, the fraction of these elements lost by leaching from the sulfide materials decreased significantly to about 2.5% of the total concentration of S and less than 0.5% for As and Fe.

3.3. Mineralogical characterization

The maintenance of the water-holding capacity during the experimental period kept the core materials continuously wet in an acidic media, promoting the dissolution of some solid phases and the crystallisation of new ones with compositions different from those of the parent materials. The contact of the constantly moist mine waste with atmospheric oxygen promoted the oxidation of sulfide minerals, the decrease of the pH of the leachates, mineral dissolution, and chemical element leaching. Hazardous chemical elements can be retained by the formation of the secondary solid phases or become available depending on the composition of the leaching solutions. Hazardous chemical element retention in the solid phases can be explained by the crystallisation of metal arsenates, phosphates and sulfates. The most soluble solids, under specific chemical and physical conditions, crystallise at the surface as efflorescent salts, while the less soluble solids crystallise in the core materials contained in the pots. However, the solubility of arsenates and phosphates strongly depends on pH as a result of the hydrolysis of the anions and consequent displacement
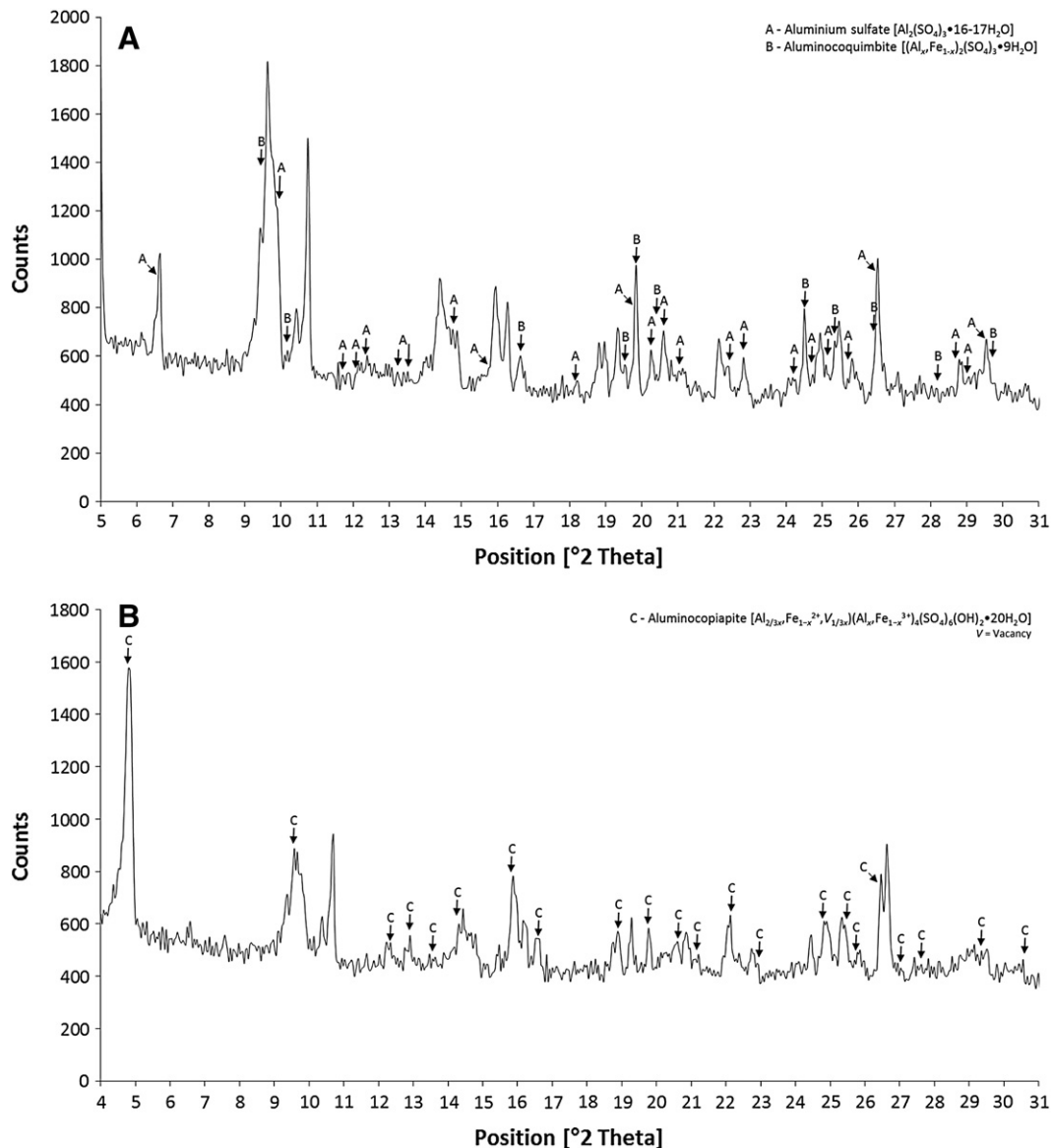

Fig. 4. X-ray diffractograms of two samples (A and B) of the surface efflorescent salts identified in control collected after one month of incubation.

Table 4

Multielemental composition of surface effluorescent salts from sulfide mine wastes without (control) and with amendments application at 30 and 75 Mg/ha.

Samples	Al (mg/g)	As (μg/g)	Ca (mg/g)	Cu (mg/g)	Fe (mg/g)	K (μg/g)	Mg (mg/g)	Mn (mg/g)	Na (μg/g)	Pb (μg/g)	Zn (mg/g)
After one month of incubation											
Control-A*	14.96	80.71	0.86	1.26	58.16	210.27	0.46	0.15	108.39	468.84	3.12
Control-B*	4.06	78.18	0.58	0.25	9.42	156.38	1.65	0.19	237.69	444.23	1.13
Amended at 30 Mg/ha-A	31.20	1.85	2.94	5.68	4.04	33.20	6.28	1.13	73.00	0.55	13.02
Amended at 75 Mg/ha-A*	29.00	1.83	27.64	4.47	2.46	73.71	7.43	1.14	101.08	0.25	10.84
Amended at 75 Mg/ha-B*	44.51	4.42	3.53	5.66	3.84	130.35	10.49	1.61	84.68	0.19	15.20
After thirteen months of incubation											
Control-A*	1.84	154.61	0.65	0.43	0.31	197.22	0.17	0.19	93.28	362.76	1.28
Control-B*	5.68	294.17	0.93	1.67	45.44	381.55	0.58	0.19	323.30	675.73	2.27
Amended at 30 Mg/ha-A	10.21	109.30	2.28	5.52	46.60	368.17	1.35	0.26	284.18	871.52	3.83
Amended at 30 Mg/ha-B	6.16	22.79	1.43	3.96	19.24	612.75	1.34	0.28	77.91	3.66	3.74
Amended at 75 Mg/ha-A*	8.07	43.57	1.54	5.06	17.72	51.23	2.04	0.34	78.31	0.58	4.27
Amended at 75 Mg/ha-B*	15.41	33.62	145.01	3.11	23.99	54.70	1.85	0.30	96.01	2.12	3.05
Amended at 75 Mg/ha-C*	7.58	1.36	6.27	2.21	2.68	114.21	1.20	0.20	144.67	1.33	2.31

*Samples indicated with asterisk correspond to salts analysed by DRX.
The determination of multielemental composition of other salts from amended treatment at 30 Mg/ha, after one month of incubation, was not possible due to insufficient sample.

of the chemical equilibria related to the dissolution processes. The very acidic aqueous solutions have very high leaching capacities and can dissolve the solid arsenates and phosphates with low solubility in almost neutral aqueous solutions. These solutions move to the surface by the capillarity phenomena and the very soluble solid phases then crystallises due to water evaporation.
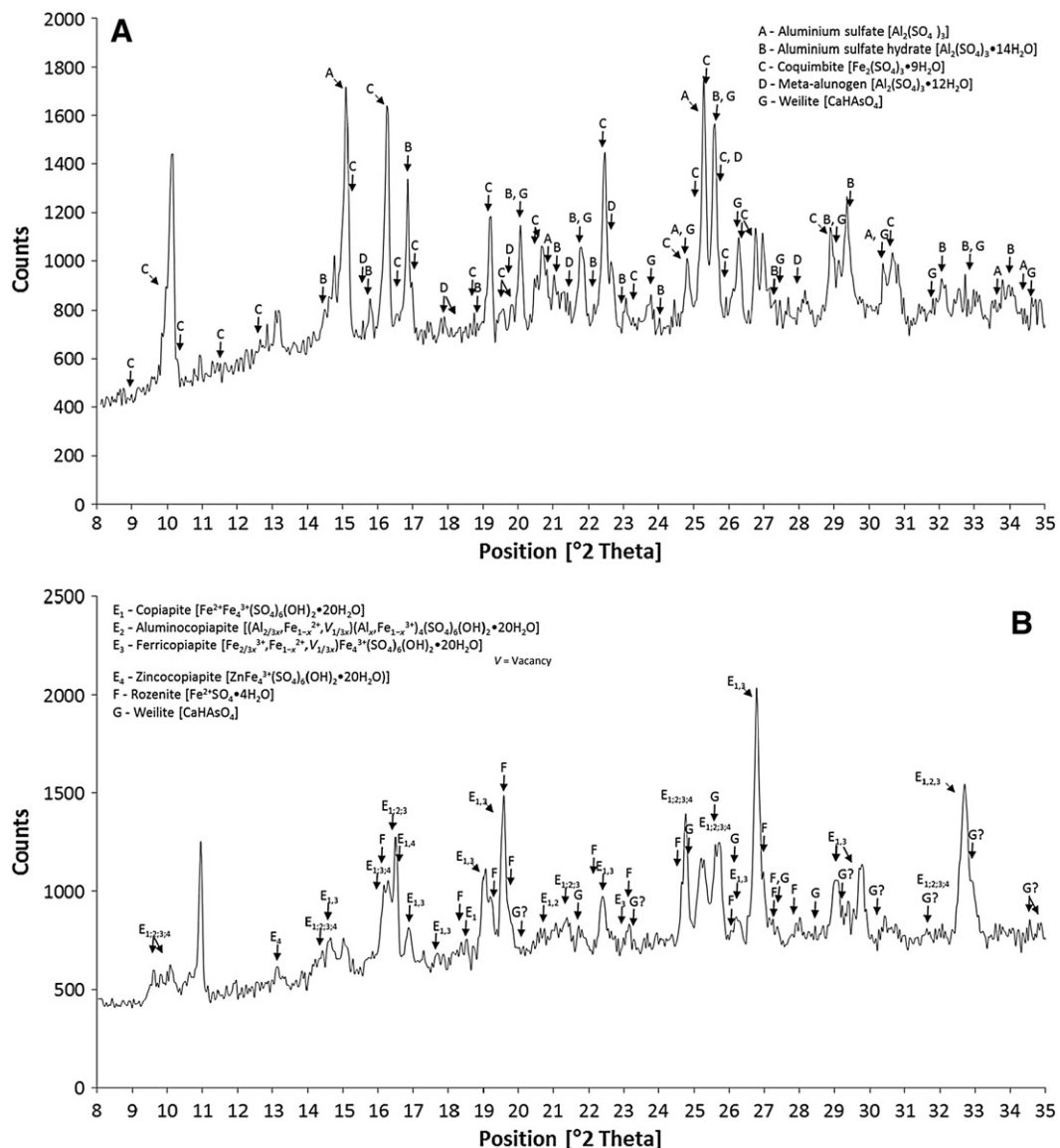
Fig. 5. X-ray diffractograms of two samples (A and B) of the surface effluorescent salts identified in control collected after thirteen months of incubation.
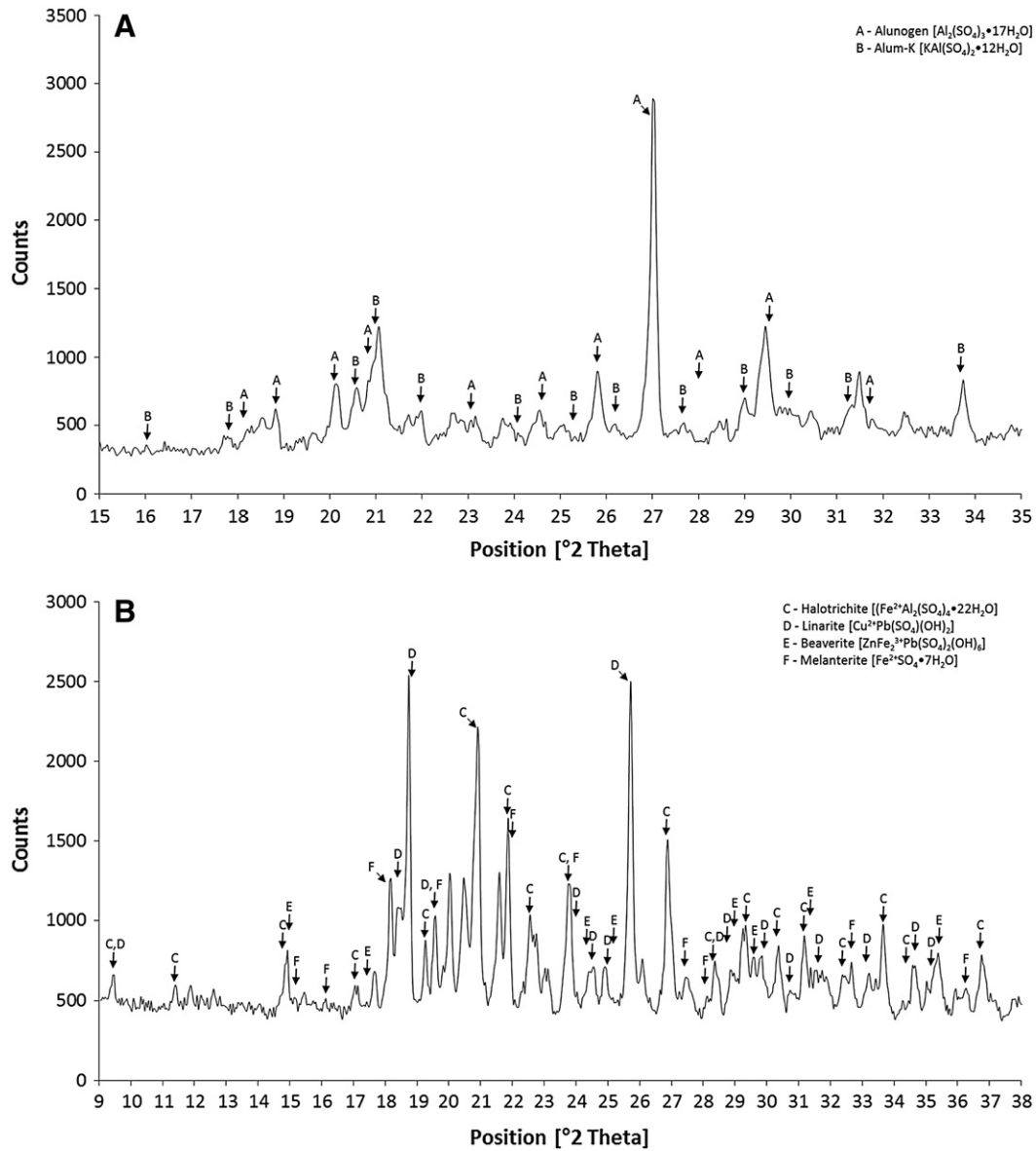
Fig. 6. X-ray diffractograms of two samples (A and B) of the surface efflorescent salts identified in amended materials collected after one month of incubation.
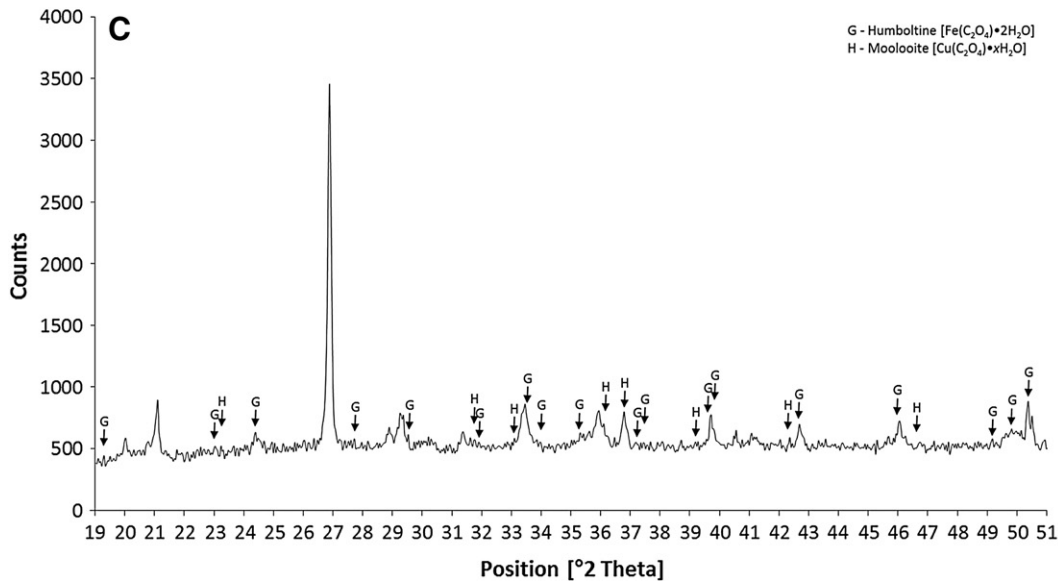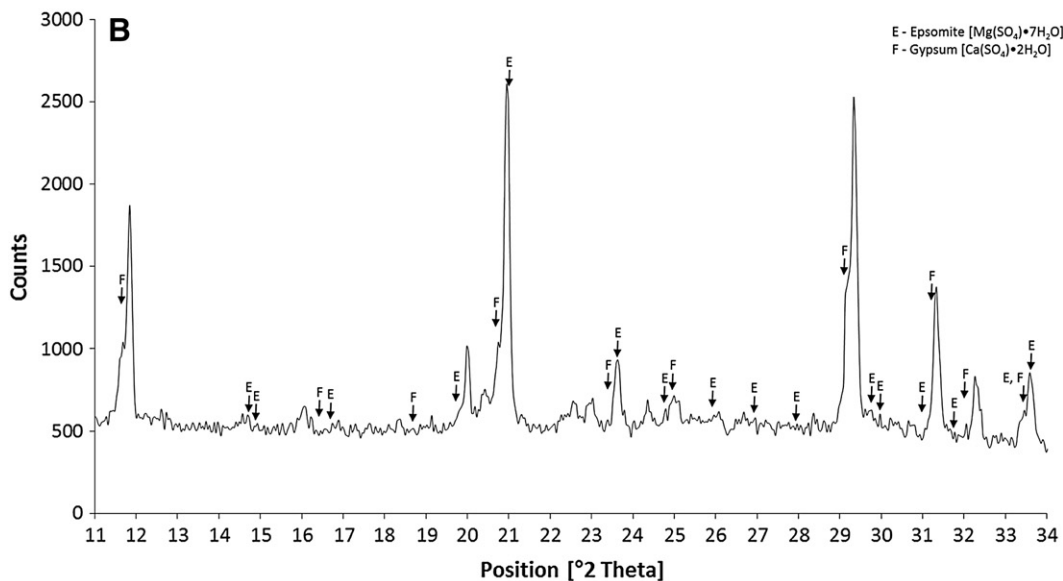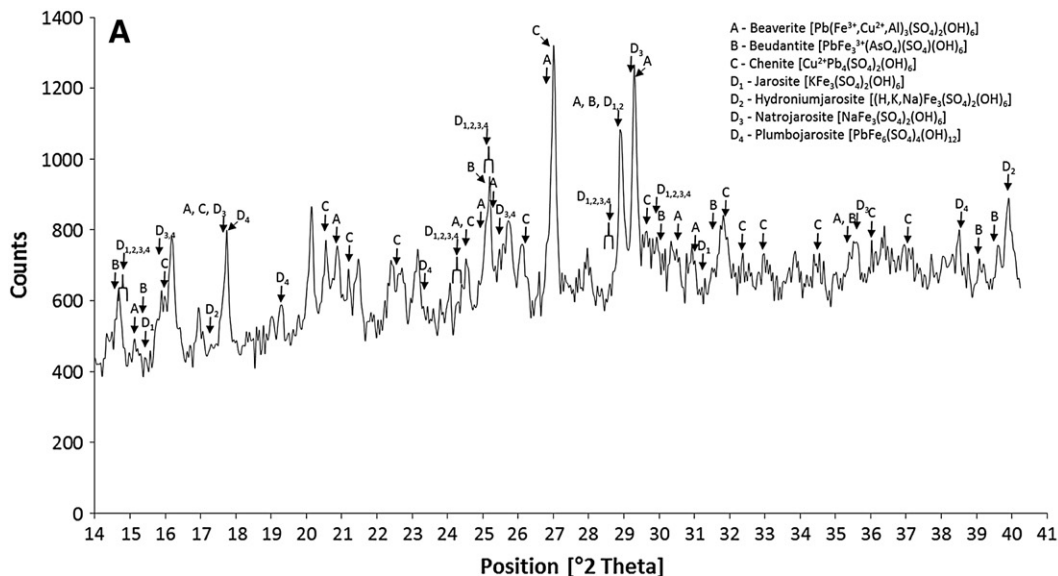
3.3.1. Efflorescent salts

The formation of efflorescent soluble salts on the materials of the surface of each pot began when the atmospheric temperature increased and air humidity decreased, promoting dryness of the surface, in spite of the constant watering to meet the water-holding capacity of the materials inside the pots. The thickness of the surface crust was higher in the control than in the amended samples as a consequence of the higher ionic concentrations in the control pore aqueous solution. In all pots, the thickness of the surface crusts increased during the hottest months, undergoing partial re-dissolution during irrigation. Under similar atmospheric conditions, in the Iberian Pyrite Belt mining areas, very soluble crusts are formed on the surfaces of mine wastes, leaching lagoon banks and beds, and river beds (Abreu et al., 2010; Romero et al., 2006). However, the first rainfalls completely dissolve the efflorescent salts, leading to increased levels of trace elements in the mine drainage water (Abreu et al., 2010; Álvarez-Valero et al., 2008; Nieto et al., 2007; Sánchez-España, 2008; Sánchez-España et al., 2005).

Different efflorescent salts were identified depending on the pH and other ionic composition of the crystallisation medium, the presence or absence of organic matter, and the duration of contact between the water and solid phases. Air temperature and humidity can also influence the composition of the efflorescent solid phases.

After one month of incubation, the efflorescent salts of the control were identified as the secondary new phases aluminium sulfates ($Al_2(SO_4)_3 \cdot 16$–$17H_2O$), aluminocopiapite (($(Al_{2/3x},Fe^{2+}_{1-x},V_{1/3x})(Al_x, Fe^{3+}_{1-x})_4(SO_4)_6(OH)_2 \cdot 20H_2O$) and aluminocoquimbite (($(Al_x,Fe_{1-x})_2 (SO_4)_3 \cdot 9H_2O$) with different degrees of substitution of Al in the Fe positions (Fig. 4). The data presented in Table 4, obtained from the dissolution of the efflorescent salts, show that these solid phases must contain mainly Al and Fe. Some of the other chemical elements presented in Table 4 can be in the lattice of the reported solid phases in trace amounts. Other solid phases must also be present but their tiny amounts did not allow their identification by X-ray diffraction.

After thirteen months of incubation, a higher diversity of soluble sulfates was identified among other solids (quartz, weilite ($CaHAsO_4$), metal sulfides, etc.) (Fig. 5). The existence of high total concentrations of S, Al and Fe ions in the mine waste materials (Table 2) produced sulfates with different chemical composition and structure, such as aluminium sulfate ($Al_2(SO_4)_3$), meta-alunogen ($Al_2(SO_4)_3 \cdot 12H_2O$),

A - Beaverite [Pb(Fe^{3+},Cu^{2+},Al)$_3$(SO$_4$)$_2$(OH)$_6$]
B - Beudantite [PbFe$_3$$^{3+}$(AsO$_4$)(SO$_4$)(OH)$_6$]
C - Chenite [Cu^{2+}Pb$_4$(SO$_4$)$_2$(OH)$_6$]
D$_1$ - Jarosite [KFe$_3$(SO$_4$)$_2$(OH)$_6$]
D$_2$ - Hydroniumjarosite [(H,K,Na)Fe$_3$(SO$_4$)$_2$(OH)$_6$]
D$_3$ - Natrojarosite [NaFe$_3$(SO$_4$)$_2$(OH)$_6$]
D$_4$ - Plumbojarosite [PbFe$_6$(SO$_4$)$_4$(OH)$_{12}$]

E - Epsomite [Mg(SO$_4$)•7H$_2$O]
F - Gypsum [Ca(SO$_4$)•2H$_2$O]

G - Humboltine [Fe(C$_2$O$_4$)•2H$_2$O]
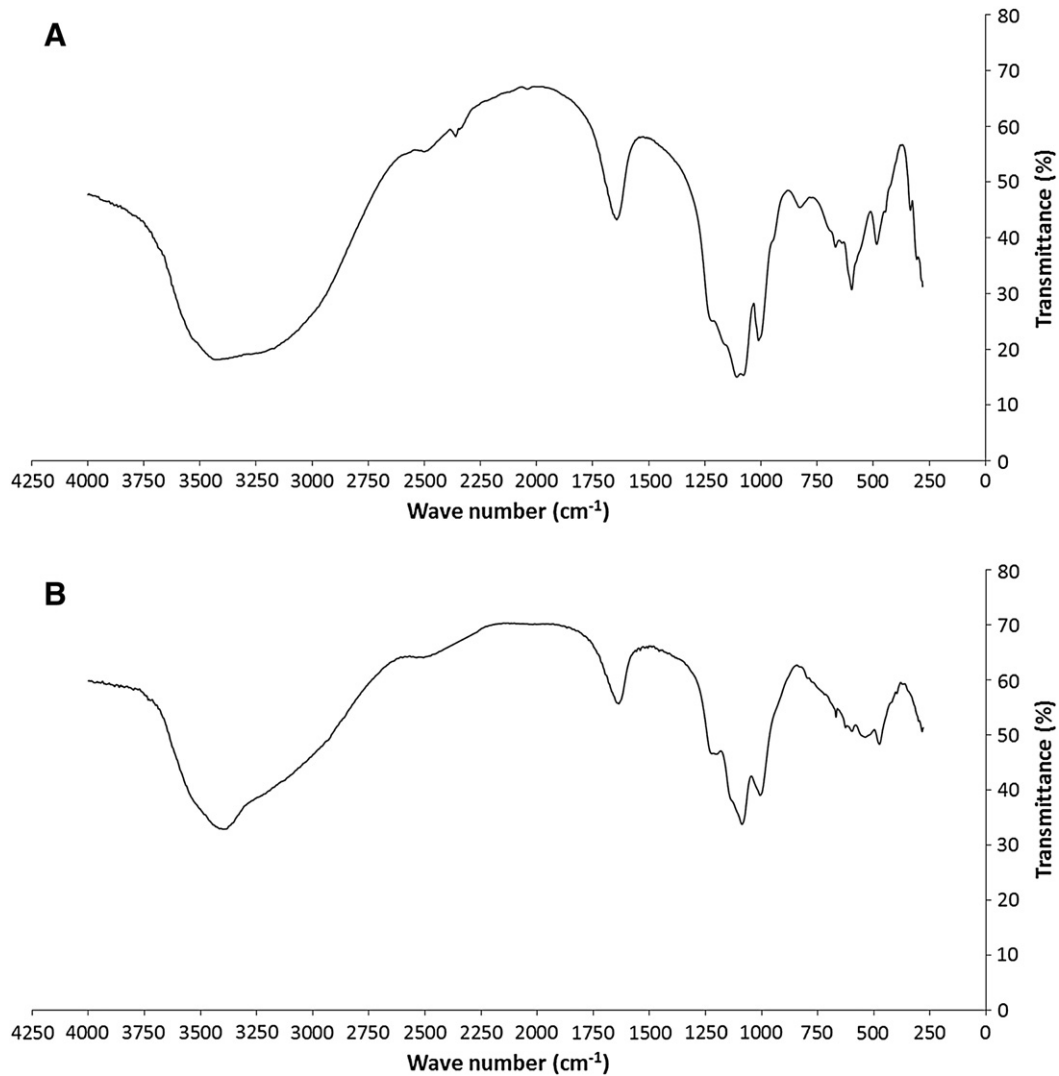H - Moolooite [Cu(C$_2$O$_4$)•xH$_2$O]

Fig. 8. Infrared spectra of surface efflorescent salts containing *copiapite*-group (A: control treatment after thirteen months of incubation) and *jarosite*-group (B: amended treatment after thirteen months of incubation).

tamarugite ($NaAl(SO_4)_2 \cdot 6H_2O$), coquimbite ($Fe_2(SO_4)_3 \cdot 9H_2O$), several solid phases or solid solutions (with different degrees of metal ions substitution) of the *copiapite*-group [aluminocopiapite, copiapite ($Fe^{2+}Fe_4^{3+}(SO_4)_6(OH)_2 \cdot 20H_2O$), ferricopiapite (($Fe_{2/3x}^{3+}, Fe_{1-x}^{2+}, V_{1/3x}$) $Fe_4^{3+}(SO_4)_6(OH)_2 \cdot 20H_2O$) and zincocopiapite ($ZnFe_4^{3+}(SO_4)_6(OH)_2 \cdot 20H_2O$)], rozenite ($Fe^{2+}SO_4 \cdot 4H_2O$) and probably poitevinite ((Cu, Fe^{2+}) $SO_4 \cdot H_2O$) (Fig. 5). The slight increase of the concentration of several ions in the aqueous solutions, obtained from the dissolution of the efflorescent salts, in relation to the values obtained after one month of incubation (Table 4) explains the variety of the solid solutions identified by XRD. On the other hand, the changes in the environmental humidity and temperature during the elapsed time of the experiment (13 months) justify the existence of solid phases with similar composition but different degrees of hydration. Some of these minerals, e.g., coquimbite, aluminocopiapite, ferricopiapite, rozenite and poitevinite, were also reported in mine wastes from São Domingos (Abreu et al., 2010; Álvarez-Valero et al., 2008; Sánchez-España, 2008), other IPB mines and the Valdarcas mine (Romero et al., 2006; Sánchez-España, 2008; Sánchez-España et al., 2005; Valente and Gomes, 2009). *Copiapite*-group minerals are common in the extremely acid

environments of sulfide mine areas, where associations with iron sulfates such as melanterite and coquimbite are frequent (Jamieson et al., 2005a; Romero et al., 2006). The pH values of the waste materials in the control (Table 3) in the first and thirteenth months, coupled with the pH values of the leachates collected from control (Fig. 1), indicate that all the solid phases crystallised on the materials of the surface of the control samples are stable under extremely acidic conditions (pH < 1.5), as the abovementioned field data also corroborate (Abreu et al., 2010). The pH of the pore waters at the surface of the materials in the control decreased as the superficial water evaporated, increasing the concentrations of the dissolved ions and promoting the crystallisation of very soluble salts.

In the efflorescent secondary salts following amendment treatments (30 and 75 Mg/ha) after one month of incubation, mainly aluminium-, copper- and iron-containing sulfates, such as alum-K ($KAl(SO_4)_2 \cdot 12H_2O$), alunogen ($Al_2(SO_4)_3 \cdot 17H_2O$), beaverite ($Pb(Cu^{2+}, Fe^{3+})_3(SO_4)_2(OH, H_2O)_6$), halotrichite ($Fe^{2+}Al_2(SO_4)_4 \cdot 22H_2O$), linarite ($Cu^{2+}Pb(SO_4)(OH)_2$) and melanterite ($Fe^{2+}SO_4 \cdot 7H_2O$), were identified (Fig. 6). The chemical composition of the minerals agrees with the data presented in Table 4.

Fig. 7. X-ray diffractograms of three samples (A, B and C) of the surface efflorescent salts identified in amended materials collected after thirteen months of incubation. Peaks not identified should be attributed to organic compounds from amendments.

After thirteen months of incubation, arsenate, oxalate, phosphate and sulfate minerals were identified in the efflorescent salts crystallising on the amended materials (Fig. 7): several minerals from the *alunite–jarosite*-group [beaverite, beudantite $(Pb(Fe^{3+})_3(AsO_4)(SO_4)(OH)_6)$, corkite $(Pb(Fe^{3+})_3(PO_4)(SO_4)(OH)_6)$, (hydronium-, natro-) jarosite $(H_3O,K,Na)(Fe^{3+})_3(SO_4)_2(OH)_6)$, plumbojarosite $(Pb(Fe^{3+})_6(SO_4)_4(OH)_{12})$, chenite $(Cu^{2+}Pb_4(SO_4)_2(OH)_6)]$, epsomite $(MgSO_4 \cdot 7H_2O)$, gypsum $(CaSO_4 \cdot 2H_2O)$, humboldtine $(Fe^{2+}C_2O_4 \cdot 2H_2O)$, moolooite $(Cu^{2+}C_2O_4 \cdot nH_2O$ $(0 < n < 1))$ and weilite $(Ca(HAsO_4))$. Once more, the chemical composition of the minerals agrees with the data presented in Table 4. The existence of solid phases containing sulfates was confirmed by infrared (Mindat, 2013; Moenke, 1962), as shown in the spectra of Fig. 8.

Alunogen, *alunite–jarosite*-group minerals, epsomite, gypsum and melanterite were also reported in Valdarcas, São Domingos and other mine areas from IPB at sites with pH > 1.5 (Abreu et al., 2010; Álvarez-Valero et al., 2008; Matos and Martins, 2006; Romero et al., 2006; Rosado et al., 2008; Sánchez-España, 2008; Sánchez-España et al., 2005; Valente and Gomes, 2009). Halotrichite was reported in the mining areas and river banks with pH values from 1.5 to 2.5 (Sánchez-España, 2008; Sánchez-España et al., 2005; Valente and Gomes, 2009). Gypsum is found in the referred mines often associated with copiapite and jarosite. Jamieson et al. (2005b) observed that jarosite was frequently found in mine waste environments with pH > 2, but not in mine areas with pH < 1.

The organic matter included in the amendments can retain more water and allow the formation of more hydrated phases than the meta-alunogen and rozenite identified in the efflorescent salts from control. This is due to the increase in water activity, which consequently raises the pH. The pH of the leachates collected from amended samples was higher (2.0 < pH < 2.5) than that of the leachates from control (Fig. 1).

The stability field diagram of melanterite (Knoll et al., 2005) shows that this solid phase can be associated with minerals of the *alunite–jarosite* group, which are stable phases at a pH between 1.5 and 4 (Knoll et al., 2005), as well as with minerals of the *copiapite*-group, which only exist at a pH < 1.5.

Humboldtine and moolooite can be formed by the reaction of metal ions with the oxalic acid produced by the fungi that grew in the organic amendments during the present experimental assay. Gadd (1999)
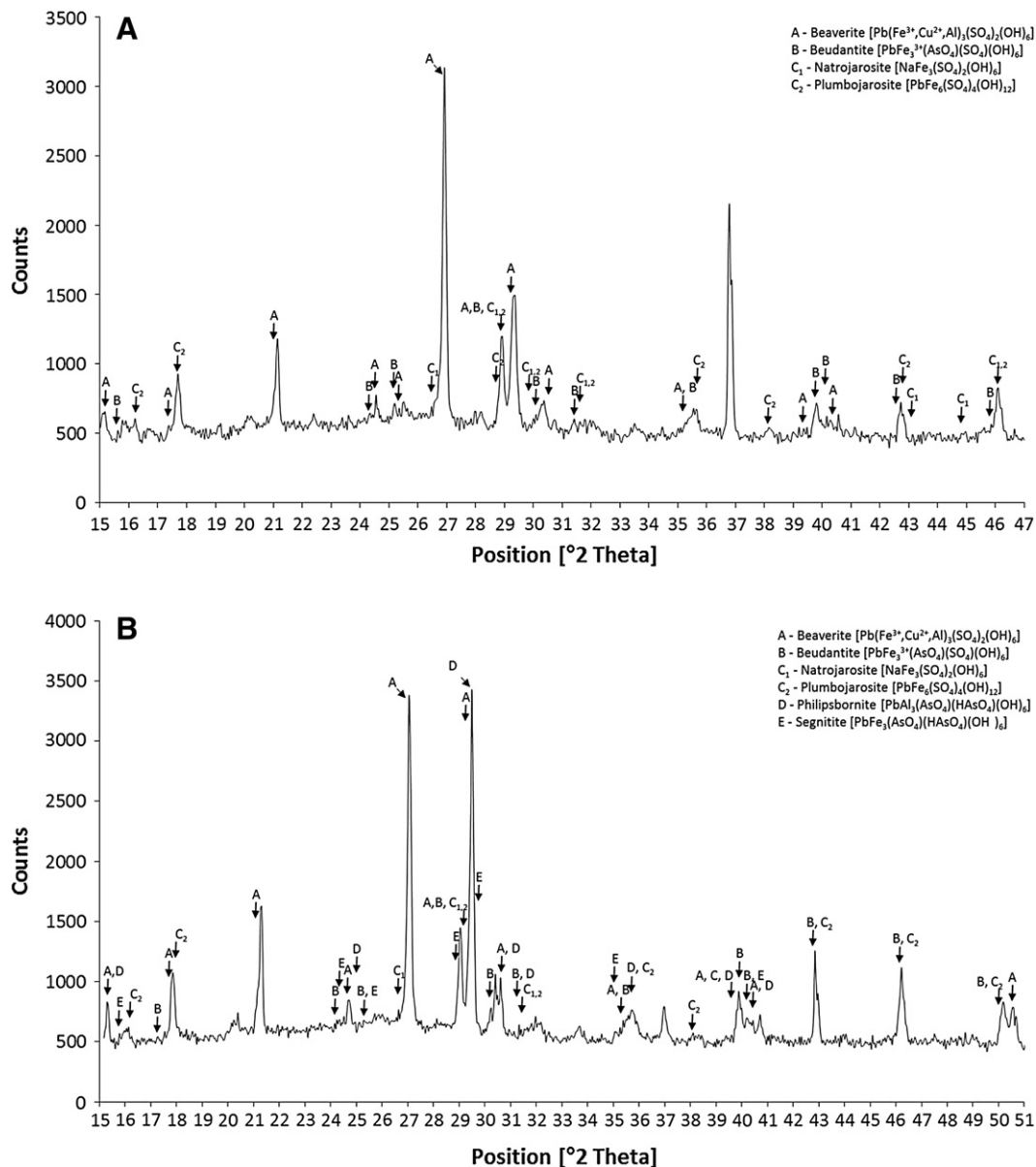

Fig. 9. X-ray diffractograms of the minerals identified in control mine waste materials, collected in two depths (A: <5 cm; B: ≈10 cm) after thirteen months of incubation.

analysed the biogeochemical importance of the sparingly soluble iron and copper oxalates produced by fungi.

3.3.2. Solid phases in the pots' core materials

In general, the same secondary solid phases were identified in materials from both depths (superficial: 0–5 cm; pot's core: $\approx$10 cm), and from control and amended samples (30 and 75 Mg/ha) (Figs. 9 and 10), which had a similar composition to that of the efflorescent salts from amended samples (Figs. 4–7). Several solid phases or solid solutions (with different degrees of metal ion substitution) belonging to the *alunite–jarosite*-group [beaverite, beudantite, (hydronium-, natro-, plumbo-) jarosite and segnitite ($Pb(Fe^{3+})_3H(AsO_4)_2(OH)_6$)] were the most common both in control and amended samples. Belonging to the *alunite–jarosite*-group, it is probable that philipsbornite ($PbAl_3H(AsO_4)_2(OH)_6$) crystallises in the control (Fig. 9), and corkite in the amended samples (Fig. 10). In addition to the abovementioned solid phases, it is highly likely that arsenbrackebuschite ($Pb_2(Fe^{2+},Zn)(AsO_4)$ $(HAsO_4)(OH)$), berlinite ($AlPO_4$) and the minerals of the *apatite*-group [hedyphane ($Ca_2Pb_3(AsO_4)_3Cl$) and mimetite ($Pb_5(AsO_4)_3(OH)$]

crystallised in the core of the amended samples (Fig. 10). The pH values of the waste materials (Table 3) and the leachates during the thirteen months of incubation (Fig. 1) indicate that all the core solid phases were under conditions (pH > 1.5) that promoted the crystallisation of the observed solid phases. The wastes in the pot core were kept moistened (water-holding capacity), but were not waterlogged during the time span of the experiment. This allows the creation of very localised microsystems with very specific and different environments (e.g., moist content and oxidation–reduction potential) generated by the pore system (different pore sizes), creating a diversity of chemical conditions (pH, aqueous ionic concentrations, water activity) that can produce multiple solid phases stable under each particular condition.

A global analysis of the results shows that the minerals of the *alunite–jarosite*-group were the stable solid phases under the physical and chemical experimental environments used. The presence of these minerals, both in the core materials and as efflorescent salts on the amended wastes, means that they are moderately soluble, since the solutions that rise to the surface by capillarity can generate the same solid

A - Beaverite [$Pb(Fe^{3+}, Cu^{2+}, Al)_3(SO_4)_2(OH)_6$]
B - Beudantite [$PbFe_3^{3+}(AsO_4)_2(OH)_6$]
C$_1$ - Natrojarosite [$NaFe_3(SO_4)_2(OH)_6$]
C$_2$ - Plumbojarosite [$PbFe_6(SO_4)_4(OH)_{12}$]

A - Beaverite [$Pb(Fe^{3+}, Cu^{2+}, Al)_3(SO_4)_2(OH)_6$]
B - Beudantite [$PbFe_3^{3+}(AsO_4)_2(OH)_6$]
C$_1$ - Natrojarosite [$NaFe_3(SO_4)_2(OH)_6$]
C$_2$ - Plumbojarosite [$PbFe_6(SO_4)_4(OH)_{12}$]
D - Corkite [$PbFe_3^{3+}(PO_4)(SO_4)(OH)_6$]
E - Arsenbrackbushite [$Pb_2(Fe^{2+}, Zn)(AsO_4)(AsO_3OH)(OH)$]
F - Hedyphane [$Ca_{1.84}Pb_{3.16}(AsO_4)_{0.27}(PO_4)_{2.73}Cl$]
G - Mimetite [$Pb_5(AsO_4)_3OH$]

Fig. 10. X-ray diffractograms of the minerals identified in amended mine waste materials, collected in two depths (A: <5 cm; B: $\approx$10 cm) after thirteen months of incubation.

Table 5
Multielemental composition of minerals (μg or mg/g Dry weight) from sulfide mine wastes without (control) and with amendment application at 30 and 75 Mg/ha, collected in two depths (A: <5 cm; B: ≈10   cm) after thirteen months of incubation.

Samples	Al (mg/g)	As (μg/g)	Ca (mg/g)	Cu (mg/g)	Fe (mg/g)	K (μg/g)	Mg (mg/g)	Mn (mg/g)	Na (μg/g)	Pb (μg/g)	Zn (mg/g)	SO₄ (mg/g)	PO₄ (μg/g)
Control-A*	0.22	26.68	4.01	0.18	4.06	2.34	0.05	0.07	42.23	18.79	0.12	58.84	48.63
Control-B*	0.32	1.53	2.82	0.06	0.87	1.32	0.02	0.004	6.54	1.44	0.05	Nd	Nd
Amended at 30 Mg/ha-A	0.92	5.74	4.31	0.43	3.83	2.15	0.19	0.22	<0.60	<2.5	0.27	34.96	27.98
Amended at 30 Mg/ha-B	0.52	3.12	8.06	0.14	1.23	1.06	0.06	0.01	4.22	0.74	0.12	Nd	Nd
Amended at 75 Mg/ha-A*	1.36	9.54	4.53	0.55	3.88	2.20	0.31	0.07	<0.60	<2.5	0.41	35.01	44.21
Amended at 75 Mg/ha-B*	0.30	2.62	8.88	0.12	0.95	1.24	0.05	0.01	4.41	0.16	0.07	Nd	Nd

Nd: not determined. *Samples indicated with asterisk correspond to the samples analysed by DRX.

phases. However, the significant retention of trace elements in solid phases (Tables 4 and 5) and therefore the decrease of their concentration in leachates (Figs. 2 and 3) can be explained by the formation of these stable solid phases, under these experimental conditions.

The amount of trace elements leached in each sampling period is not enough to explain the sharp decrease in elemental concentrations in the leachate samples collected in the thirteenth month.

Although iron oxides occur usually in mines after sulfide oxidation (Abreu et al., 2010; Rosado et al., 2008; Sánchez-España, 2008; Sánchez-España et al., 2005; Valente and Gomes, 2009), no iron oxides were identified due to the low pH of the waste materials. The abovementioned identified solid phases, as for instance melanterite and jarosite, show that the iron was in the structure of those solids.

4. Conclusions

The waste dumps containing sulfides displayed a very low pH and a large capacity to leach chemical elements due to the continuous generation of acid mine drainage, and their large multielemental concentrations.

The amendments had very low pH buffer capacity in relation to the acid generated by the mine wastes. They were efficient in decreasing the elemental concentrations in leachates, compared to control, but only for a short period. However, during the thirteen months, the leached fraction of As, Fe and S from the amended sulfide materials were significantly decreased when compared to the control. The organic materials from the amendments improved the material structure, increased water retention and prevented excessive dryness with the appearance of local and very high acidic conditions (pH < 1).

Low concentrations of trace elements in leachates from all treatments after thirteen months could be due to the presence, mainly in the core materials, of several solid phases with moderate solubility. Melanterite can be associated with *copiapite*-group minerals and also with *alunite–jarosite*-group minerals. Nevertheless, the higher solubility of the minerals of the *copiapite*-group than those of the *alunite–jarosite*-group means that the former solid phases crystallise from more concentrated solutions with lower pH and lower water activity. For a pH lower than 1.5, it is very likely that rozenite is a more stable solid phase than melanterite, which contains more crystallisation water molecules.

The presence of *copiapite*-group minerals in the efflorescent salts of control samples indicates the existence of more extreme conditions (pH < 1.5, high elemental concentrations and low water activity) compared to the other situations (control core materials, and efflorescent salts and core materials in amended wastes) where the *alunite–jarosite*-group minerals were identified. Despite the moderate solubility of the *alunite–jarosite*-group minerals, their crystallisation, together with arsenbrackebuschite, berlinite and the *apatite*-group minerals hedyphane and mimetite-(OH), can be used to explain the sharp decrease in the concentrations of the studied trace elements in the leachates collected in the thirteenth month of incubation. A deep

analysis of the final values attained after this time, combined with the leachates pH, illustrated that the crystallisation of these solid phases was not suitable for environmental remediation, due to the high elemental concentrations still present in the leachates. On the other hand, the stability of jarosite in the pH range between ~1.5 and ~4.5 confirms the previous conclusion that this solid phase, as well as the majority of the minerals of the *alunite–jarosite*-group, are not suitable for chemical element immobilization, as they will change to different solid phases when the pH increases.

The amendments improved, in general, the chemical characteristics of the mine wastes. The dose of the amendments did not influence leachate characteristics during the entire experiment. Other organic and inorganic wastes, as well as their rate of application, should be studied over a longer time span in order to reduce AMD generation and chemical element leaching and spread from sulfide mine wastes.

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