



Effect of the addition of industrial by-products on Cu, Zn, Pb and As leachability in a mine sediment

M. Paz Rodríguez-Jordá, Fernando Garrido, M. Teresa García-González*

Instituto de Ciencias Agrarias, Consejo Superior de Investigaciones Científicas, Serrano 115 dpdo, 28006 Madrid, Spain

ARTICLE INFO

Article history:

Received 6 August 2011

Received in revised form 7 January 2012

Accepted 14 January 2012

Available online 23 January 2012

Keywords:

In situ remediation

Industrial by-products

Toxic elements

São Domingos mine

Sequential extraction

ABSTRACT

A series of incubation and leaching experiments were performed to assess the feasibility of three industrial by-products (red gypsum (RG), sugar foam (SF) and ashes from the combustion of biomass (ACB)) to reduce the leachability of Cu, Pb, Zn and As in a sediment of São Domingos mine (Portugal). The changes in the element solid phase speciation were also evaluated by applying a sequential extraction procedure. All amendments significantly reduced the leachability of Zn and Cu, whereas the treatment with RG + SF + ACB also decreased the mobility of As. The reduction in Cu leachability was especially remarkable. This could be due to the great affinity of carbonates (included in SF and SF + ACB amendments) to precipitate with Cu, and maghemite and rutile (RG amendment) for acting as relevant sorbents for Cu. Pb was the least mobile element in the sediment and none of the treatments reduced its mobility. The sequential extraction reveals that the amendments induced a significant decrease in the concentration of elements associated with the residual fraction. Cu, Pb and As are redistributed from the residual fraction to the Al, Fe, and Mn hydr(oxides) fraction and Zn from the residual fraction to the water/acid soluble, exchangeable and bound to carbonates pool.

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

The oxidation of sulfide wastes produces an extremely acid drainage with a high content of potentially toxic elements in solution, known as acid mine drainage (AMD). Generation of this AMD is the main pollution process of natural watercourses in the Iberian Pyrite Belt (IPB) [1] and in other mining environments with sulfide-rich residues. The IPB is one of the largest metallogenetic provinces of massive sulfides in the world, located in the southwest of the Iberian Peninsula. In particular, the São Domingos mine, in Mértola (Beja District, South Portugal), is one of the most emblematic Portuguese mining districts in the IPB.

São Domingos mine was exploited mainly for Cu and S, although the ore was rich in other trace elements such as As, Pb, Zn and Mn [2]. The activity of this mine ceased in 1968, but it is still active from the contamination point of view. The large-scale exploitation of this deposit between 1857 and 1966 produced enormous waste dumps, around 5 Mt, where oxidation of pyrite and associated sulfides is resulting in AMD production [3]. The final acid discharge with a high content of metals and metalloids from São Domingos reaches the Chanza river, the main tributary of the Guadiana river, causing part of its pollution [4].

Although some proposals have been suggested to reduce the environmental impact associated with the AMD generation on the river basins of the IPB, treating the acidic waters is a short-term solution to the problem. The extreme acidity and high concentration of metals (mainly Fe) of these drainages rapidly saturate the treated systems [3]. However, recent investigations have been focused on direct treatment of the mine residues, as sources of this type of drainages. Specifically, the use of amendments to stabilize trace elements in sediments offers the following advantages over other remediation techniques: (1) this method is cost-effective, (2) it can be applied *in situ* on a large scale and (3) it has a lower environmental impact than other physical and chemical treatments. Experiments carried out by Pérez-López et al. [5,6] showed how the addition of fly ash material to a pyrite-rich mining residue favors the acid neutralization and metal retention in AMD. Mylona et al. [7], using column experiments, proved the efficiency of limestone in inhibiting acid generation in a pyrite-rich residue. Davis et al. [8] demonstrated that lime amendment represents a viable long-term method to mitigate acid generation in tailings. They studied how lime amendments in tailings deposited in the Clark Fork River facilitated alteration of pyrite into ferrihydrite, a process which sequesters high concentrations of As, Cu, Pb and Zn. Fernández-Caliani and Barba-Brioso [9] assessed the potential value of a waste sludge generated during the processing of marble stone for remediation of acid mine soils. They showed that in the abandoned mine site of Tharsis (Spain) this amendment, joint with lime, significantly reduced the water-soluble concentrations of Cu, Zn, Pb and Cd one

* Corresponding author. Tel.: +34 91 745 25 00; fax: +34 91 564 08 00.
E-mail address: mtgg@ica.csic.es (M.T. García-González).

month after the amendment application, remaining extremely low throughout the one-year monitoring period. Khan and Jones [10] evaluated the effectiveness of green waste compost, sewage sludge, lime and diammonium phosphate on the phytoavailability of heavy metals in a copper mine tailing site at Parys Mountain, North Wales (UK). They concluded that the extractability and phytoavailability of Pb, Zn and Cu decreased with time after amendment applications. Pérez de Mora et al. [11] reduced the leaching of Cd, Cu and Zn in a soil affected by the Aznalcóllar (Spain) mine accident using sugar beet lime, biosolid compost and municipal waste compost as amendments. Abbott et al. [12] assessed the potential co-utilization of coal fly ash and lime-stabilized biosolids for mine spoil reclamation. This study demonstrated that in an abandoned coal mine located in Tennessee, the leachate concentrations of Cu, Ni and Zn were reduced by the application of these amendments.

In previous studies, we have evaluated the use of several industrial by-products (red gypsum, RG; sugar foam, SF; and ashes from combustion of biomass, ACB) as single and combined amendments to reduce the mobility and availability of Pb, Zn, Ni, As and Se in metal and metalloid spiked acidic soils [13,14]. Our experiments show that the most effective treatments to reduce the leachability of both metalloids (As and Se) are ACB and RG. In the case of the three metals (Pb, Zn and Ni), SF and a mixture of RG and ACB (RG + ACB) gave the best results. Pursuing this further, the objective of this study is to ascertain the feasibility of these by-products as immobilizing agents of toxic elements present in a sediment of São Domingos mine. Specifically, this study aims: (i) to prove the effectiveness of the amendments in reducing the mobility of Cu, Pb, Zn and As and (ii) to describe the changes in the element solid phase speciation produced by the application of the amendments. This may result in a decrease of the potential leachability of the elements which remain in the soil matrix after the leaching procedures.

2. Materials and methods

2.1. Sediment

An alluvial superficial sediment was collected from an area of São Domingos mine located near a small pond containing acid water. The sediment was sampled at four points (2 kg per point). All these samples were air-dried, crushed and sieved through a 2-mm mesh. To obtain a homogeneous sample, the four samples of the sediment were mixed prior to characterization and use in subsequent experiments. Table 1 summarizes the most important physical, chemical and mineralogical properties of the sediment. Soil pH was measured in deionized water (pH_w), in a 1:2.5 suspension and electrical conductivity (EC) in a 1:5 suspension. Organic C (OC) was determined by wet digestion [15]. The exchangeable bases were extracted with 1 M NH₄OAc (at pH 7) [16]. The Al, Fe, Si and Mn contents in the poorly crystalline and amorphous fraction of the soils (Al_{ox}, Fe_{ox}, Si_{ox}, Mn_{ox}) were extracted with 0.2 M ammonium oxalate + 0.2 M oxalic acid solution at pH 3 [17]. The supernatants from each extraction were separated by centrifuging, acidified with HNO₃ (pH ≈ 2) and stored in polyethylene containers at 4 °C until analysis. Analyses were performed in triplicate. The Ca, Mg, Na, K, Al, Fe, Si and Mn were determined by inductively coupled plasma-atomic emission spectrometry (ICP-OES) on a PerkinElmer OPTIMA 4300DV. The texture was analyzed using the Bouyoucos method [18]. The total content of Fe, S, Mn, Cu, Pb, Zn and As in the sediment was analyzed by ICP-OES, with previous digestion of the sample in a mixture of concentrated HNO₃ and HCl [19]. The mineralogical composition of the total (≤2 mm) and clay (≤2 μm) fractions of the sediment was identified by X-ray powder diffraction (XRD) with a Philips X'Pert diffractometer with graphite-monochromated Cu-Kα

Table 1
Some physical, chemical and mineralogical properties of the sediment.

pH ^a	EC ^b	g kg ⁻¹				Ca ²⁺ d	Mg ²⁺	Na ⁺	K ⁺	Al _{ox} ^e	Fe _{ox}	Si _{ox}	Mn _{ox}	Fe ^f	S	mg kg ⁻¹			As	
		OC ^c	Sand	Lime	Clay											Cu	Pb	Zn		
3.3	0.2	3.9	268	400	332	0.4	0.3	0.4	0.6	4626	18,176	1721	49	101	26	114	269	5421	219	4878
		≤2 mm Fraction ^g																		
		Q	Al	HJ	PbJ	K	G								≤2 μm Fraction	HJ	PbJ	I	K	G
		46	21	9	14	7	3								Q	8	13	56	11	7
						nd									12	nd				

^a pH in water (1:2.5).

^b EC, electrical conductivity.

^c OC, organic carbon.

^d Extracted with 1 M NH₄OAc (at pH 7).

^e Al, Fe, Si and Mn oxalate-extractable content.

^f Fe, S, Mn, Cu, Pb, Zn and As total content.

^g Semi-quantitative mineralogical composition (relative %). Q, quartz; Al, albite; HJ, hidroniojarosite; PbJ, plumbojarosite; I, illite; K, kaolinite; G, gypsum; nd, no detected.

radiation. The XRD patterns were obtained from random powder mounts and various oriented aggregates of the clay fraction (air-dried, ethylene glycol-solvated, heated to 300 °C for 3 h, and heated to 550 °C for 3 h). Semi-quantitative estimates of the mineral contents were obtained from random powder and oriented aggregated patterns using the intensity factors given by Shultz [20].

2.2. Industrial by-products

Red gypsum (RG) is a waste from the industrial production of titanium dioxide (TiO₂). Sugar foam (SF) is produced by the sugar manufacturing industry. Ashes from combustion of biomass (ACB) originate in the cellulose production process.

Samples of RG, SF and ACB supplied by the companies Tioxide Europe S.A., Azucarera Ebro S.A. and ENCE S.A. respectively, were dried at 45 °C (RG) and 105 °C (SF and ACB) and processed by acid digestion and alkaline fusion [21]. The resulting standard solutions were analyzed for major and trace elements by ICP-OES, ICP-MS and ion chromatography. The chemical composition of the by-products is listed in Table 2. RG is rich in Ca and sulfate ions and because of its industrial origin from ilmenite (FeTiO₃), it contains Fe and Ti. Regarding the trace elements, Ba, Cr and Cu are present at the largest concentrations among the elements analyzed in all by-products. In addition, RG and ACB are rich in Ni and Zn. ACB is also rich in Pb. However, the heavy metal contents are much less than those established by the European Community, Council Directive 86/278/EEC on the Use of Sewage Sludge in Agriculture [22] and constitute no environmental hazard at the rates normally used in farming.

The mineralogical composition of the by-products was identified by X-ray diffraction from random powder patterns. Gypsum is the main component of RG and is accompanied by small proportions of iron and titanium minerals. An XRD study of the RG residue after dissolution of gypsum revealed the presence of maghemite (γ -Fe₂O₃) and rutile (TiO₂). SF consists mainly of calcium carbonate (CaCO₃) and traces of calcium oxide (CaO). ACB contains SiO₂, a small proportion of calcium carbonate and traces of calcium oxide.

2.3. Incubation and leaching experiments

Portions of 150 g of sediment were evenly blended with the industrial by-products as single (SF), double (SF + ACB) and triple (RG + SF + ACB) treatments. Three additional portions were maintained untreated as a control. The single SF treatment was added at 1% (w/w). In the treatments of SF + ACB and RG + SF + ACB, the amount of by-product was calculated to add similar amounts of Ca as in the SF treatment. Also, inert quartz sand, with a median grain size of 1–2 mm, was used to decrease the time of the experiments. All experiments were done in triplicate.

All these sediment samples (treated and control) were uniformly re-packed to a bulk density of 1.25 g cm⁻³ in 6.3 cm-diameter and 10 cm-length columns and maintained at room temperature (25 °C ± 2) adding 50 ml of deionized water to the surface of the columns every day, in partial volumes of 10 ml. The duration of the experiments was 40 days, and the leachates of each column were collected every two days. These leaching conditions provided non-saturated environments during the entire time of the experiments, keeping all the columns in oxidizing conditions.

After the incubation period, the columns were then dismantled and the sample homogenized and oven-dried (50 °C). The quartz sand was separated from the sediment. In order to determine the total element content of the treated and control samples they were digested in a mixture of concentrated HNO₃ and HCl [19] and the resulting solutions were analyzed for Pb, Cu, Zn, and As using ICP-OES on a PerkinElmer OPTIMA 4300DV instrument.

2.4. Study of the leachates

The leachates were filtered through 0.45 μm pore cellulose nitrate filters. Acidity of the samples was measured in deionized water (pH_w) in a 1:2.5 suspension and electrical conductivity (EC) in a 1:5 suspension. Later, the samples were acidified with HNO₃ (pH ≈ 2) and stored in polyethylene containers at 4 °C until analysis. The concentrations of Zn, Mn, Cu and Pb were determined by flame atomic absorption spectrometry on a PerkinElmer 1100B. The concentration of As was analyzed by means of graphite furnace atomic absorption spectrometry on a PerkinElmer 4110 ZL Zeeman AA.

The weight of each column (150 g) was used to estimate the amount of element leached per kg of sediment. The percentage of element concentration recovered after the leaching procedure was calculated with respect to the total concentration contained in the samples before these experiments were executed. Additionally, the percentage of retention of each toxic element in each treated column was calculated with respect to the control columns.

2.5. Element speciation in the sediment solid phase

The changes of the element solid phase speciation, resulting from the application of the amendments, were identified using samples of the dismantled columns (three columns per treatment) after the incubation period. A three-step sequential chemical extraction scheme proposed by the Standards Measurement and Testing Programme of the European Commission (BCR-SM&T) [23] was done in duplicate taking 0.75 g of subsamples from each column. This procedure delineates the following operationally defined fractions: (1) water/acid soluble and exchangeable fraction (FI, step 1), (2) reducible fraction (bound to Al, Fe and Mn (hydr)oxides) (FII, step 2), and (3) oxidizable fraction (bound to sulfides and organic matter) (FIII, step 3). A brief summary of the reagents and extracting conditions is given in Table 3. The element content in the residual fraction (R) was calculated as the difference between the total element concentration in the sediment and the sum of all previous fractions. The residual fraction corresponds to those metals or metalloids strongly associated with crystalline structures of minerals (somehow bound to the mineral matrix) which are only soluble in mixtures of strong acids. Therefore, these elements are unlikely to be released from the sediment. The results were expressed as the percentage of extraction of each fraction with respect to the total content of elements in each sample.

2.6. Statistical analysis

To examine the statistical significance of the differences found in the percentages of extraction of the BCR-SM&T sequential extraction procedure, a two-way analysis of variance (ANOVA), including treatment and element, was performed. In the case of FII and FIII, the other fractions (FI and FII, respectively) were introduced as covariates. Later, the effect of the treatment in the percentages of extraction, for each element and fraction, was examined by one-way (treatment) analysis of variance (ANOVA) and the Bonferroni *post hoc* pair-tests. All statistical analyses were done using the statistic package SPSS v.17.0 (SPSS, Inc., Chicago, IL).

3. Results and discussion

3.1. Temporal evolution of pH and conductivity of the leachates and their influence in the retention of the toxic elements

The pH of the leachates remained fairly constant during the entire time of the experiments, both in control and in most of the treated columns (Fig. 1). In control samples the mean value of pH was 3.4, whereas in treated samples this value increased as

Table 2

Chemical composition of the by-products used (RG, red gypsum; SF, sugar foam; ACB, ashes from combustion of biomass).

	RG (g kg ⁻¹)	SF (g kg ⁻¹)	ACB (g kg ⁻¹)
Al ₂ O ₃	8.3 ± 0.4	13.4 ± 0.7	60.1 ± 3
CaO	248 ± 12	424 ± 13	171 ± 5
Fe ₃ O ₄	128 ± 6	5.3 ± 0.3	16.3 ± 0.8
K ₂ O	0.2 ± 0.01	3.0 ± 0.2	32.0 ± 1.6
MgO	8.2 ± 0.4	18.6 ± 0.9	30.0 ± 1.5
MnO	3.8 ± 0.2	0.3 ± 0.02	6.3 ± 0.3
Na ₂ O	0.7 ± 0.04	0.9 ± 0.05	15.4 ± 0.8
P ₂ O ₅	0.8 ± 0.04	14.6 ± 0.7	11.9 ± 0.6
SiO ₂	4.9 ± 0.2	30.8 ± 2.2	353 ± 25
TiO ₂	60.2 ± 3.0	0.3 ± 0.02	20.2 ± 0.1
F ⁻	<0.03	0.08 ± 0.004	<0.1
SO ₄ ²⁻	425 ± 21	81.4 ± 0.5	36.9 ± 2.2
LOI ^a	205 ± 10	464 ± 23	252 ± 13

	RG (mg kg ⁻¹)	SF (mg kg ⁻¹)	ACB (mg kg ⁻¹)
As	10.3 ± 0.5	<2.5	7.1 ± 0.7
B	6.4 ± 0.3	<2.5	<2.5
Ba	13.9 ± 0.7	53.3 ± 5.3	396 ± 40
Be	<2.4	<0.4	1.3 ± 0.1
Cd	<2.4	<0.4	<0.4
Co	12.1 ± 0.6	0.9 ± 0.1	5.3 ± 0.5
Cr	95.2 ± 4.8	13.5 ± 1.4	36.9 ± 3.7
Cu	17.1 ± 0.9	12.0 ± 1.2	45.8 ± 4.6
Mo	5.4 ± 0.3	<0.4	8.7 ± 0.9
Ni	61.7 ± 3.1	5.2 ± 0.5	177 ± 18
Pb	28.1 ± 1.4	3.1 ± 0.3	79.0 ± 7.9
Se	<2.4	<2.5	<2.5
Zn	388 ± 19	19.3 ± 1.9	204 ± 20

^a LOI, loss on ignition (45–1000 °C).**Table 3**

The BCR-SM&T sequential extraction scheme used for operational speciation of elements.

Fraction	Soil phases	Extractant	Shaking time and temperature
FI	Water/acid soluble and exchangeable	40 ml of 0.11 M CH ₃ COOH	16 h at room temperature
FII	Bound to Al, Fe, and Mn hydr(oxides)	40 ml of 0.5 M HONH ₂ HCl (pH 2)	16 h at room temperature
FIII	Bound to organic matter and sulfides	10 ml of 8.8 M H ₂ O ₂ (pH 2)	1 h at room temperature and 1 h at 85 °C
		10 ml of 8.8 M H ₂ O ₂ (pH 2)	1 h at 85 °C
		50 ml of 1 M NH ₄ OAC (pH 2)	16 h at room temperature

a result of the treatments. The highest pH (7.4) was observed after the SF+ACB treatment, due to the effect of the calcium carbonate contained in the sugar foam and the high liming power of the ACB by-product [24]. The lowest pH value (6.0) was detected in

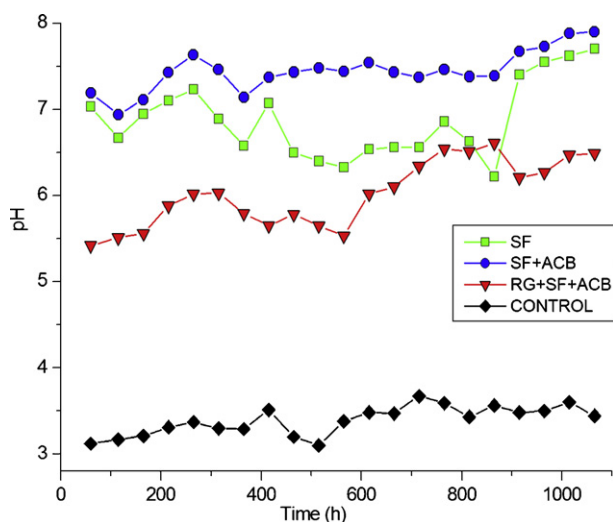


Fig. 1. pH temporal evolution of the leachates in the control and treated columns ($n=3$). SF, sugar foam; ACB, ashes from combustion of biomass; RG, red gypsum.

columns treated with RG+SF+ACB, due to the addition of RG and as a consequence of the extent of the opposing reactions of Al³⁺ and H⁺ exchange by Ca²⁺, and ligand exchange of OH⁻ by SO₄²⁻, as previously reported by Smith et al. [25] and Alcorido and Rechigl [26].

During our leaching experiments, the industrial by-products dissolution neutralized the acidity of the sediment (Fig. 1) and favored the retention of the elements Zn and Cu present in the sediment. These results coincide with the findings of Pérez-López et al. [6] in soils of the IPB treated with coal combustion fly ash. The increase of the pH favors the hydrolysis of metals, and this not only promotes their precipitation as hydroxides [27], but it also means that hydroxylated species (MOH⁺) are preferentially adsorbed as compared to the non hydrolyzed ones (M²⁺) [28]. There is also an increase of negative charges on variable charge minerals such as Fe and Al oxides [29], rising the sorption capacity of metals and consequently diminishing their mobility [30].

The temporal evolution in electrical conductivity (EC) was similar in all columns, treated and untreated (data not shown). In the first step of the experiment, the EC decreased quickly in a short period of time, and then the values decreased with a slope near to zero until a steady state was achieved. The highest values of EC were observed in samples treated with RG+SF+ACB (8.2 mS cm⁻¹), as a result of the leaching of sulfates present in red gypsum.

Table 4
Mean percentages of retention, with respect to the control, of Zn, Cu and As in the treated columns after the incubation experiments ($n = 6$).

Treatment	Zn	Cu	As
SF ^a	91.7	98.6	– ^b
SF + ACB	92.9	98.2	–
RG + SF + ACB	78.6	96.2	34.4

^a SF, sugar foam; ACB, ashes from the combustion of biomass; RG, red gypsum.

^b % Leached higher than in the control.

3.2. Temporal evolution in Zn, Cu, Pb, and As concentrations in the leachates and effect of the treatments in the leachability of the toxic elements

Zn concentrations in the leachates of all columns showed a two-phase time-dependent behavior, with a quick decrease until a steady state was reached (Fig. 2). Pérez-López et al. [5] showed a similar temporal evolution of the Zn concentration in the leachates, when a fly ash material is added to a pyrite-rich mining residue. In our experiments the concentrations of this metal were much lower in the leachates of all treated samples than in the control ones. In the first leachate, Zn concentrations in columns treated with SF, SF + ACB and RG + SF + ACB were 4.3, 3.8 and 10.2 mg kg⁻¹, respectively, whereas in the control sample this value was 40.1 mg kg⁻¹. At the end of the incubation period, a steady state of around 0.01 mg kg⁻¹ was achieved in all the treated samples. Consequently, in the treatments with SF, SF + ACB and RG + SF + ACB, the leachability of Zn decreased 91.7%, 92.9% and 78.6%, respectively, with respect to the control samples (Table 4). These results agree with the ones obtained by Mylona et al. [7]. They studied the effectiveness of small amounts of limestone in inhibiting acid generation from a pyrite concentrate material and found a reduction in between 44% and 72% of dissolved amount of Zn as compared with the control, when the limestone content varied between 6 and 29 wt%. In our amended samples and due to the presence of calcium carbonate in the SF by-product, the coprecipitation of hydrotalcite-like compounds, such as Zn/Al-HTLC, can occur. Something similar was reported by Julliot et al. [31]. They showed, by means of EXAFS spectroscopy, in smelter-impacted soils from northern France, the formation of Zn/Al-HTLC in near-neutral pH conditions. The rapid formation and large capacity to sequester metal ions of these compounds suggest that HTLC may play an important role as a sink of Zn [32]. However in our case, the XRD analyses of the amended samples did not prove the presence of any new crystalline phase (data not shown). On the other hand, the increase in pH in the treated samples could favor the retention of Zn, according to the findings of Binay et al. [33]. They studied the leaching of elements from Indian coal fly ash and observed a higher solubility of Zn at low pH. McBride et al. [34] indicated the important role of pH in controlling the solubility of Zn in contaminated soils. Also, Clemente et al. [35] demonstrated that the addition of lime and organic amendments (cow manure and compost) successfully increased soil pH, resulting in a significant decrease of Zn solubility and promoting the natural attenuation of a recently contaminated soil by the toxic spill of pyrite residue at Aznalcóllar (Spain).

Temporal evolution in Cu concentrations was similar to the behavior of Zn (Fig. 2). Fernández-Caliani and Barba-Brioso [9] also observed a quick decrease in the Cu concentrations until a steady state was reached, when a waste sludge joint with lime was applied in an abandoned mine of Tharsis (Spain). In our experiments, the highest amounts of Cu leached were observed in control samples and all the treatments were effective in reducing the leachability of Cu. SF and SF + ACB-treated columns presented the lowest concentrations of Cu in the first leachates, with values of 0.10 and 0.14 mg kg⁻¹, respectively, whereas in the control samples this

value was 13.7 mg kg⁻¹. Therefore, both treatments reduced the leachability of this element up to 98%, with respect to the control (Table 4). This could be due to the great affinity of carbonates to precipitate with Cu, according to Kabata-Pendias and Pendias [36], who demonstrated that liming is an effective technique in decreasing the mobility of Cu in contaminated soils. Cu concentration in the first leachate of the column treated with RG + SF + ACB decreased to 0.5 mg kg⁻¹, favoring the retention of Cu up to 96.2%, with respect to the control (Table 4). Maghemite ($\gamma\text{Fe}_2\text{O}_3$) and rutile (TiO_2), components of the RG by-product, could act as relevant sorbents for Cu in agreement with the findings of Vega et al. [37], who found that Fe and Mn oxides increase the adsorption of Cu, in mine soils of Galicia (Spain). This also coincides with Kim et al. [38], who studied the effect of several factors (pH, temperature, TiO_2 concentration) in the adsorption of Cu^{2+} in the surface of titanium dioxide.

The use of a simulated laboratory weathering technique, led to Abbott et al. [12] to conclude that the application of a lime-stabilized biosolid (LSB) to an acid mine spoil (AMS) is useful for the retention of Cu and Zn. The LSB-amended AMS leachate concentrations of Cu and Zn were depressed relative to the unamended AMS leachates by several orders of magnitude. Also Pérez de Mora et al. [11] found that the use of sugar beet lime and stabilized composts (municipal waste and biosolid composts) were an effective remediation option for reducing the acidity of leachates as well as Cu and Zn leaching in a moderately contaminated soil under semiarid conditions. Incorporation of amendments reduced leaching of Cu and Zn between 40% and 70% in comparison to the untreated soil.

The concentrations of Pb were very low in the leachates of both control and treated samples (Fig. 2) and none of the treatments were effective for reducing the leachability of this metal. In the control samples Pb amounts decreased from 0.09 mg kg⁻¹ in the first leachate, to a non-detectable content (<0.005 mg kg⁻¹) by the end of the incubation period (Fig. 2). These low concentrations of Pb could be due to the great stability of plumbojarosite ($\text{PbFe}_6[(\text{OH})_6(\text{SO}_4)_2]_2$) at the pH (3.4) of the untreated samples, according to the studies of Chapman et al. [39] in acid mine drainage streams. Pb concentrations were not detected in the last leachates of all amended samples. The amount of Pb leached was higher in the amendment samples than in the control ones (Fig. 2), due to the low stability of plumbojarosite at the pH of the sediment by-products mixtures [40]. This is indicated as well by Davis et al. [8], when they assessed the efficacy of lime amendments for the geochemical stabilization of mine tailings.

Temporal evolution in As concentration was different as a function of the type of treatment. In control samples, the concentrations of As leached within the first 600 h of the incubation period were very similar (≈ 0.20 mg kg⁻¹). After which, the values decreased gradually until reaching 0.02 mg kg⁻¹ in the last leachate (Fig. 2). Arsenic concentrations increased in the leachates of SF + ACB-treated samples from 0.02 to 2.30 mg kg⁻¹ at the end of the experiment. In SF-treated samples the variation in the As concentrations was not very significant. Neither of these treatments, SF + ACB and SF, was effective, due to the increase in pH resulting from the addition of carbonates. These results agree with the findings of Clemente et al. [35], who stated the increase in the solubility of As at basic pH, in soils affected by an accidental pyrite tailing spill from the Aznalcóllar mine (Spain) and amended with lime and organic by-products. RG + SF + ACB was the only effective treatment for reducing the leachability of As. In this case, its concentration increased weakly in the first leachates reaching the value of 0.18 mg kg⁻¹ (600 h) and then its concentration remained constant (≈ 0.05 mg kg⁻¹) until the end of the experiment. Therefore, this treatment favored the retention of As up to 34.4%, with respect to the control (Table 4). This result demonstrates the benefits of the application of the joint amendment of RG + SF + ACB in reducing As leachability. Other amendments, as the mixture of waste

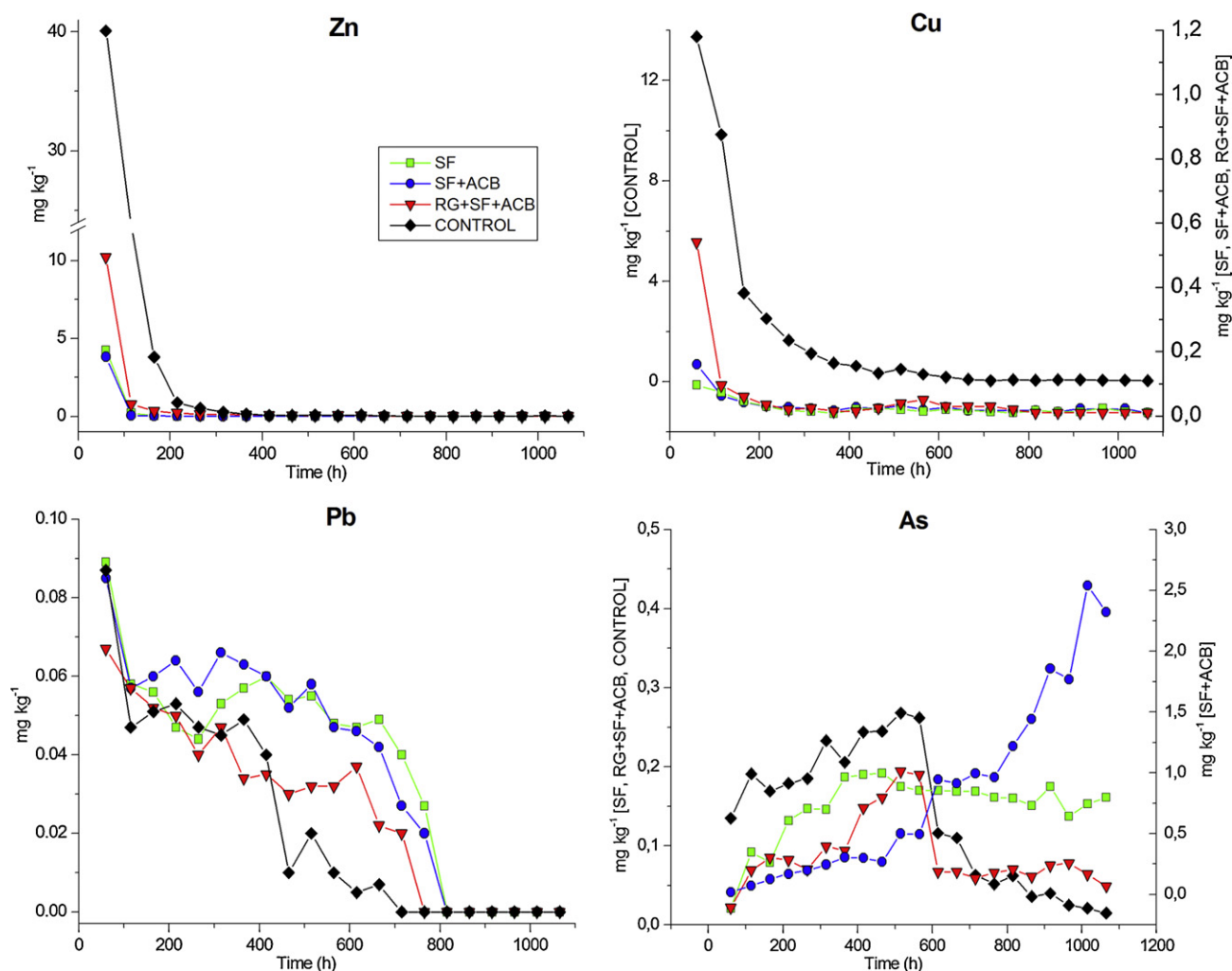


Fig. 2. Temporal evolution of the concentration of Zn, Cu, Pb and As in the leachates of control and treated columns ($n=3$). SF, sugar foam; ACB, ashes from combustion of biomass; RG, red gypsum.

sludge, produced in the processing of marble stone, and lime were no effective for As immobilization in the mine of Tharsis (Spain), as reported by Fernández-Caliani and Barba-Brioso [9].

Although it has not been confirmed in this work, the addition of calcium from these by-products could induce the formation of stable precipitates of Ca–As with different solubility, as farncolite minerals ($\text{CaHAsO}_4 \cdot 2\text{H}_2\text{O}$) [41]. On the other hand, maghemite ($\gamma\text{Fe}_2\text{O}_3$) and rutile (TiO_2), components of the RG by-product, could act as relevant sorbents for As, in agreement with the findings of Hartley et al. [42], who found that maghemite increases the adsorption of As. Further, O'Reilly et al. [43] and Pena et al. [44] demonstrated that arsenate can be sorbed onto micron-sized particles of rutile, proving this mineral is effective for As removal. Another mechanism that cannot be disregarded for reducing As mobility in the samples treated with RG+SF+ACB, could be the formation of an amorphous iron arsenate ($\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$) [45,46]. Additionally, the retention through ligand exchange of the As species for OH_2 and OH^- in the coordination spheres of surface structural Fe atoms [47] could be considered. Moreover, the presence of substantial amounts of SO_4^{2-} could cause a decrease in the adsorption of As considering that As competes with sulfate for sorption/coprecipitation sites [45]. This competitive sorption between sulfate and arsenate ions for the sorption sites could lead As anions toward more specific sorption positions [48].

3.3. Effect of the treatments in the speciation of the toxic elements

The addition of the amendments induced a significant decrease in the percentage of Zn, Cu, Pb and As associated to the residual fraction (R), with respect to the control (Table 5). This fraction corresponds to those elements strongly associated with crystalline compounds, which are therefore unlikely to be leached. Nevertheless, the increase of pH as a result of the treatments (Table 6) favored the dissolution of some crystalline compounds present in the sediment, and the subsequent release of the toxic elements contained in those phases.

The amount of Pb and As associated to the water/acid soluble and exchangeable fraction (FI), both in treated and control samples, was very low (Table 5). These results agree with the ones observed in the studied leachates, where a low leachability of Pb and As was detected, despite the high concentration of both elements in the sediment. A high percentage of Pb and As was found in the residual fraction (R), whereas the percentage in the reducible fraction (FII), bound to Fe and Mn (hydr)oxides was lower (Fig. 3). The observed decrease of Pb in the residual fraction of the treated samples, with respect to the control, could be explained by the dissolution of plumbojarosite ($\text{PbFe}_6[(\text{OH})_6(\text{SO}_4)_2]_2$), stable at acid pH [40], which could be dissolved at the pH of the treatments (Table 6). Abbott et al. [12] indicated that in an acid mine spoil Pb was primarily bound to the carbonate and residual fractions, averaging

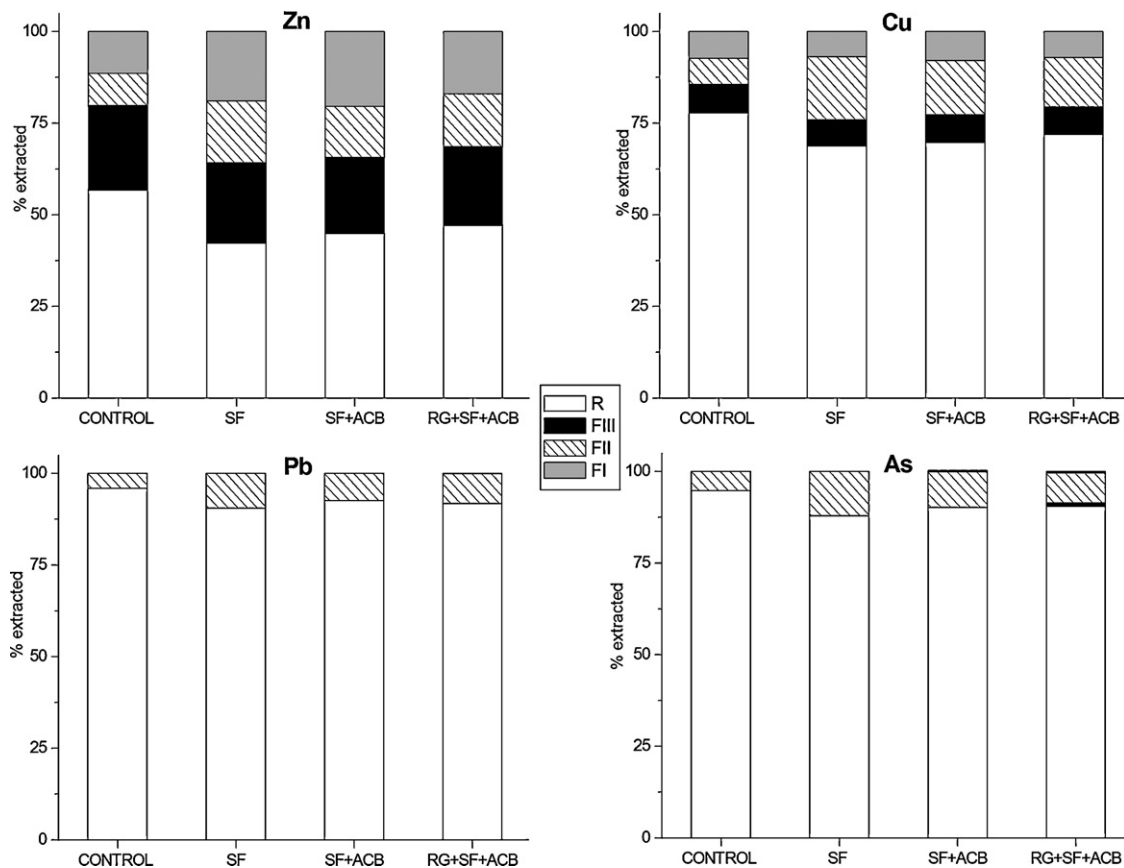


Fig. 3. Percentage extracted of Zn, Cu, Pb and As, in control and treated samples, in each step of the sequential extraction procedure ($n=6$). SF, sugar foam; ACB, ashes from combustion of biomass; RG, red gypsum. FI, water/acid soluble and exchangeable fraction; FII, bound to Al, Fe, and Mn hydr(oxides) fraction; FIII, bound to sulfides and organic matter fraction; R, residual fraction.

Table 5

Element distribution in the sediment solid phase as estimated by the sequential extraction procedure after the incubation experiments. Percentage respect to the total amount in each sample ($n=6$).

		Control	SF ^a	SF + ACB	RG + SF + ACB	PSE ^b
Zn	FI ^c	11.4	18.9 [*]	20.4 [*]	16.9 [*]	1.19
	FII	8.8	16.9 [*]	13.9 [*]	14.4 [*]	1.08
	FIII	23.1	21.9	20.9	21.6	1.51
	R	56.7	42.3 [*]	44.9 [*]	47.1 [*]	1.58
Cu	FI	7.4	6.8	7.8	7.1	0.29
	FII	7.1	17.3 [*]	14.8 [*]	13.5 [*]	0.87
	FIII	7.9	7.1	7.6	7.5	1.12
	R	77.8	68.9 [*]	69.7 [*]	71.9 [*]	0.66
Pb	FI	<0.1	- ^{d,*}	<0.1	<0.1	0.01
	FII	4.1	9.5	7.4 [*]	8.1 [*]	0.48
	FIII	-	-	-	-	-
	R	95.9	90.5	92.6 [*]	91.8 [*]	0.57
As	FI	-	-	0.1 [*]	0.5 [*]	0.01
	FII	5.2	12.1	9.8 [*]	8.1 [*]	0.18
	FIII	-	-	-	1.0 [*]	0.002
	R	94.8	87.9	90.1 [*]	90.4 [*]	0.001

^{*} Indicate statistically significant differences with the control to each fraction and element ($p < 0.05$).

^a SF, sugar foam; ACB, ashes from combustion of biomass; RG, red gypsum.

^b PSE, pooled standard error ($p < 0.05$) for each element and fraction and within the same row.

^c FI, water/acid soluble and exchangeable fraction; FII, bound to Al, Fe and Mn (hydr)oxide fraction; FIII, bound to organic matter and sulfides fraction; R, residual fraction.

^d not detected.

20% and 74% of the total content, respectively. The application of a lime-stabilized biosolid and a coal-fly ash produced minor effects on the distribution of Pb in these two fractions. The stability of Pb-bearing phases illustrated by the selective extraction results is consistent with the data of the leachate analyses, where Pb was below detectable levels throughout the study [12].

In SF + ACB and RG + SF + ACB-treated samples, the percentage of As extracted in the water/acid soluble and exchangeable fraction (FI) increased significantly with respect to the control (Table 5). At the pH raised by the treatments (Table 6), the solubility of As could increase by the competitive sorption between the anions and negative surface sites in the sediment [48].

The distribution of Cu in the FI and FIII fractions was not affected by the addition of the amendments (Table 5). Nevertheless, the amount of Cu bound to Al, Fe and Mn (hydr)oxides (FII fraction) was greater in all treated samples than in the control ones (Fig. 3). In all samples, the higher content of Cu was found in the residual fraction ($\approx 70\%$) (Fig. 3).

Table 6

pH_w values for the sediment-by-products mixtures and control, before the application of the sequential extraction procedure ($n=6$).

Treatments	pH _w
Control ^a	3.5
SF ^b	6.9
SF + ACB	7.2
RG + SF + ACB	6.1

^a Sediment without by-products.

^b SF: sugar foam; ACB: ashes from biomass combustion; RG: red gypsum.

In the treated samples, a considerable percentage of Zn was found in the fraction bound to Fe and Mn (hydr)oxides (FII), whereas in the control samples, the majority of Zn content was in the residual fraction. The amount of Zn associated with the oxidizable fraction (FIII) was similar in the treated and control samples (Table 5), and higher than in the other toxic elements (Fig. 3). The water/acid soluble and exchangeable pool of Zn (FI) increased significantly in comparison to the control (Table 5). FI fraction not only represents the water/acid soluble and exchangeable fraction, but also includes a fraction associated with carbonates according to Kartal et al. [49], who studied the fractionation of metals in street sediment samples by using the BCR sequential extraction procedure. To confirm that Zn could be associated to carbonates, the treated samples (in a 1:4 suspension) were kept at pH 4 and 5, during 18 h, using an autoburette. To maintain these pH values, solutions of HNO₃ 0.5 M and NaOH 0.2 N, were used. The low concentrations of Cu, As and Pb extracted at pH 4 (data not shown) proved that these elements are bound to amorphous Fe (hydr)oxides, which are stable at that pH value [46,50]. However, the high amounts of Zn extracted at pH 4 (data not shown) explained its retention as carbonates, soluble at acid pH, such as hydrozincite (Zn₅(CO₃)₂(OH)₆) or smithsonite (ZnCO₃) [40]. Zn bound to amorphous Fe (hydr)oxides are stable at that pH value [51]. However, our XRD results on the amended samples did not confirm the presence of Zn carbonates. Abbott et al. [12] found a significantly increase (by 10–15%) of the Zn content associated to the carbonate fraction at the expense of both the exchangeable-soluble and residual fraction of an acid mine spoil amended with a lime-stabilized biosolid.

4. Conclusions

The present study evaluates the potential use of three industrial by-products (red gypsum, RG; sugar foam, SF; and ashes from the combustion of biomass, ACB) in reducing the leachability of Cu, Zn, Pb and As in a sediment of the São Domingos mine (Portugal). Our results have been compared, wherever possible, with the ones published by other authors. The application of the treatments (SF, SF+ACB and RG+SF+ACB) neutralized the acidity of the sediment, and significantly reduced the leachability of Zn and Cu. In all amended samples, and due to the presence of calcium carbonate in the SF by-product, coprecipitation of Zn-hydroxalate-like compounds can occur. SF and SF+ACB treatments reduced the leachability of Cu up to 98% as a consequence of the great affinity of carbonates, to precipitate with Cu. In addition, in the RG+SF+ACB-treated samples, maghemite (γ-Fe₂O₃) and rutile (TiO₂), components of the RG by-product, could further act as relevant sorbents for Cu. This treatment was the only effective one for reducing the leachability of As. Although not confirmed in this work, the addition of calcium from the by-products could induce the formation of stable precipitates of Ca-As with different solubility, as pharmacolite minerals (CaHAsO₄·2H₂O). On the other hand, maghemite and rutile could also act as relevant sorbents for As. Pb was the least mobile toxic element in the sediment and none of the treatments were effective for reducing its leachability.

The results of the sequential extraction procedure reveal that the amendments induced a significant decrease in the concentration of elements associated with the residual fraction. The increase of pH as a result of the treatments favored the dissolution of some crystalline compounds present in the sediment, and the subsequent release of the toxic elements contained in those phases. Cu, Pb and As are redistributed from the residual fraction to the Al, Fe, and Mn hydr(oxides) fraction and Zn from the residual fraction to the water/acid soluble, exchangeable and bound to carbonates pool.

In summary, both SF and its mixture with ACB and RG are feasible treatments in reducing the potential leachability of toxic anions and cations in mine environments. However, the mechanisms that are induced in the sediments treated with these amendments produced a redistribution of toxic elements from an inert fraction, from the point of view of the contamination, to more mobile fractions. Therefore, this increase of the concentration of contaminants into more mobile fractions could enhance the effectiveness of other remediation strategies of contaminated areas, such as phytoremediation, in which the toxic elements must be in solution.

Acknowledgments

This work was supported by the Spanish Ministry of Science and Innovation, research project AGL2005-07017-C03-03. MPRJ acknowledges a fellowship from CSIC (Spain). We are especially grateful to Laura Barrios for her assistance in the statistical treatment of the data. Thanks to Prof. Macias for the facilities given to obtain several analytical measurements. Azucarera Ebro S.A., Tioxide Europe S.A. and ENCE S.A. are also acknowledged for supplying the waste samples.

References

- [1] M. Olías, C.R. Cánovas, J.M. Nieto, A.M. Sarmiento, Evaluation of the dissolved contaminant load transported by the Tinto and Odiel Rivers (South West Spain), *Appl. Geochem.* 10 (2006) 1733–1749.
- [2] M.T. Tavares, A.J. Sousa, M.M. Abreu, Ordinary kriging and indicator kriging in the cartography of trace elements contamination in São Domingos mining site (Alentejo, Portugal), *J. Geochem. Explor.* 98 (2008) 43–56.
- [3] A.M. Álvarez Valero, R. Pérez-López, J. Matos, M.A. Capitán, J.M. Nieto, R. Sáez, J. Delgado, M. Caraballo, Potential environment impact at São Domingos mining district (Iberian Pyrite Belt, SW Iberian Peninsula): evidence from a chemical and mineralogical characterization, *Environ. Geol.* 55 (2008) 1797–1809.
- [4] R. Pérez-López, A.M. Álvarez Valero, J.M. Nieto, R. Sáez, J.X. Matos, Use of sequential extraction procedure for assessing the environmental impact at region scale of the São Domingos Mine (Iberian Pyrite Belt), *Appl. Geochem.* 23 (2008) 3452–3463.
- [5] R. Pérez-López, J.M. Nieto, G.R. Almodóvar, Utilization of fly ash to improve the quality of the acid mine drainage generated by oxidation of a sulphide-rich mining waste: column experiments, *Chemosphere* 67 (2007) 1637–1646.
- [6] R. Pérez-López, J. Cama, J.M. Nieto, C. Ayora, The iron-coating role on the oxidation kinetics of a pyrite sludge doped with fly ash, *Geochim. Cosmochim. Acta* 71 (2007) 1921–1934.
- [7] E. Mylona, A. Xenidis, I. Paspaliaris, Inhibition of acid generation from sulphidic wastes by the addition of small amounts of limestones, *Miner. Eng.* 13 (2000) 1161–1175.
- [8] A. Davis, L.E. Eary, S. Helgen, Assessing the Efficacy of lime amendment to geochemically stabilize mine tailings, *Environ. Sci. Technol.* 33 (1999) 2626–2632.
- [9] J.F. Fernández-Caliani, C. Barba-Brioso, Metal immobilization in hazardous contaminated mine soils after marble slurry waste application. A field assessment at the Tharsis mine district (Spain), *J. Hazard. Mater.* 181 (2010) 817–826.
- [10] M.J. Khan, D.L. Jones, Effect of composts, lime and diammonium phosphate on the phytoavailability of heavy metals in a copper mine tailing soil, *Pedosphere* 19 (2009) 631–641.
- [11] A. Pérez de Mora, P. Burgos, F. Cabrera, E. Madejón, In situ amendments and revegetation reduce trace element leaching in a contaminated soil, *Water Air Soil Pollut.* 185 (2007) 209–222.
- [12] D.E. Abbott, M.E. Essington, M.D. Mullen, J.T. Ammons, Fly ash and lime stabilized biosolid mixtures in mine spoil reclamation: simulated weathering, *J. Environ. Qual.* 30 (2001) 608–616.
- [13] M.P. Rodríguez-Jordá, F. Garrido, M.T. García-González, Potential use of gypsum and lime rich industrial by-products for induced reduction of Pb, Zn and Ni leachability in an acid soil, *J. Hazard. Mater.* 175 (2010) 762–769.
- [14] M.P. Rodríguez-Jordá, F. Garrido, M.T. García-González, Assessment of the use of industrial by-products for induced reduction of As and Se potential leachability in an acid soil, *J. Hazard. Mater.* 175 (2010) 328–335.
- [15] A. Walkley, A.I. Black, An examination of the Degtjareff method for determining soil organic matter, and a proposed modification of the chromic acid titration method, *Soil Sci.* 37 (1934) 29–38.
- [16] G.W. Thomas, Exchangeable cations, in: A.L. Page (Ed.), *Methods of Soil Analysis. Part 2. Chemical and Microbiological Properties*, American Society of Agronomy, Madison, 1982, pp. 159–164.
- [17] R. Mackay, T.A. Cooper, A.V. Metcalfe, P.E. O'Connell, Contaminant transport in heterogeneous porous media: a case study. 2. Stochastic modelling, *J. Hydrol.* 175 (1996) 429–452.
- [18] G.S. Campbell, R.D. Jackson, M.M. Mortland, D.R. Nielsen, *Methods of Soil Analysis. Part 1. Physical and Mineralogical Methods*, Soil Science Society of America, Madison, 1986.

- [19] M. Chen, L.Q. Ma, Comparison of three aqua regia digestion methods for twenty florida soils, *Soil Sci. Soc. Am. J.* 65 (2001) 491–499.
- [20] L.G. Schultz, Quantitative interpretation of mineralogical composition from X-ray and chemical data for the Pierre Shale, US Geological Survey Professional Paper 391-C, 1964, pp. C1–C31.
- [21] L.R. Hossner, Dissolution for total elemental analysis, in: D.L. Sparks (Ed.), *Methods of Soil Analysis. Part 3. Chemical Methods*, American Society of Agronomy, Madison, 1996, pp. 49–64.
- [22] European Community, Council directive 86/278/EEC on the use of sewage sludge in agriculture, *Off. J. Eur. Communities Luxemb.* L181 (1986) 6–12.
- [23] G. Rauret, J.F. López-Sánchez, A. Sahuquillo, R. Rubio, C. Davidson, A. Ureb, Ph. Quevauviller, Improvement of the BCR three step sequential extraction procedure prior to the certification of new sediment and soil referent materials, *J. Environ. Monit.* 1 (1999) 57–61.
- [24] D. Dermatas, X. Meng, Utilization of fly ash for stabilization/solidification of heavy metals contaminated soils, *Eng. Geol.* 70 (2003) 377–394.
- [25] C.J. Smith, M.B. Peoples, G. Keerthisinghe, T.R. James, D.L. Garden, S.S. Tuomi, Effect of surface applications of lime, gypsum and phosphogypsum on the alleviating of surface and subsurface acidity in a soil under pasture, *Aust. J. Soil Res.* 32 (1994) 995–1008.
- [26] I.S. Alcorido, J.E. Rechcigl, Phosphogypsum in agriculture: a review, *Adv. Agron.* 49 (1993) 55–118.
- [27] M.B. McBride, Reactions controlling heavy metals solubility in soils, *Adv. Soil Sci.* 10 (1989) 1–56.
- [28] V. Schwertmann, R.M. Tylor, Iron oxides, in: J.B. Dixon, S.B. Weeds (Eds.), *Minerals in Soil Environments*, Soil Science Society of America, Madison, WI, 1989, pp. 379–438.
- [29] C.W. Gray, S.J. Dunham, P.G. Dennis, F.J. Zhao, S.P. McGrath, Field evaluation of in situ remediation of a heavy metal contaminate soil using lime and red mud, *Environ. Pollut.* 142 (2006) 530–539.
- [30] E. Madejón, A. Pérez De Mora, E. Felipe, P. Burgos, F. Cabrera, Soil amendments reduce trace element solubility in a contaminated soil and allow regrowth of natural vegetation, *Environ. Pollut.* 139 (2006) 40–52.
- [31] F. Julliot, G. Morin, P. Ildefonse, T.P. Trainor, M. Benedetti, L. Gadoisy, G. Calas, G.E. Brown, Occurrence of Zn/Al hydroxalite in smelter-impacted soils from northern France: evidence from EXAFS spectroscopy and chemical extractions, *Am. Miner.* 88 (2003) 509–526.
- [32] T.P. Trainor, G.E. Vrown Jr., G.A. Parks, Adsorption and precipitation of aqueous Zn (II) on alumina powders, *J. Colloid Interface Sci.* 231 (2000) 359–372.
- [33] K.D. Binay, S. Khanra, D. Mallick, Leaching of elements from coal fly ash: Assessment of its potential for use in filling abandoned coal mines, *Fuel* 88 (2009) 1314–1323.
- [34] M. McBride, S. Sauvé, W. Hendershot, Solubility control of Cu, Zn, Cd and Pb in contaminated soils, *Eur. J. Soil Sci.* 48 (1997) 337–346.
- [35] R. Clemente, C. Almela, M.P. Bernal, A remediation strategy based on active phytoremediation followed by natural attenuation in a soil contaminated by pyrite waste, *Environ. Pollut.* 143 (2006) 397–403.
- [36] A. Kabata-Pendias, H. Pendias, *Trace Elements in Soils and Plants*, CRC Press, Boca Raton, FL, 2001.
- [37] F.A. Vega, E.F. Covelo, M.L. Andrade, Competitive sorption and desorption of heavy metals in mine soils: influence of mine soil characteristics, *J. Colloid Interface Sci.* 298 (2006) 582–592.
- [38] M.O. Kim, K.M. Hong, J.G. Chung, Removal of Cu(II) from aqueous solutions by adsorption process with anatase-type titanium dioxide, *Water Res.* 37 (2003) 3524–3529.
- [39] B.M. Chapman, D.R. Jones, R.F. Jung, Processes controlling metal ion attenuation in acid mine drainage streams, *Geochim. Cosmochim. Acta* 47 (1983) 1957–1973.
- [40] W.L. Lindsay, *Chemical Equilibria in Soils*, John Wiley & Sons, New York, 1979.
- [41] V.G. Alexandratos, E.J. Elzinga, R.J. Reeder, Arsenate uptake by calcite: macroscopic and spectroscopic characterization of adsorption and incorporation mechanisms, *Geochim. Cosmochim. Acta* 71 (2007) 4172–4187.
- [42] W. Hartley, R. Edwards, N.W. Lepp, Arsenic and heavy metal mobility in iron oxide-amended contaminated soils as evaluated by short and long-term leaching tests, *Environ. Pollut.* 131 (2004) 495–504.
- [43] S.E. O'Reilly, D.G. Strawn, D.L. Sparks, Residence time effects on arsenate adsorption/desorption mechanisms on goethite, *Soil Sci. Soc. Am. J.* 65 (2001) 67–77.
- [44] M.E. Pena, G.M. Korfiatis, M. Patel, L. Lippincott, X. Meng, Adsorption of As(V) and As(III) by nanocrystalline titanium dioxide, *Water Res.* 39 (2005) 2327–2337.
- [45] L. Carlson, J.M. Bigham, U. Schwertmann, A. Kyek, F. Wagner, Scavenging of As from acid mine drainage by schwertmannite and ferrihydrite: a comparison with synthetic analogues, *Environ. Sci. Technol.* 36 (2002) 1712–1719.
- [46] W. Hartley, R. Edwards, N.W. Lepp, Arsenic and heavy metal mobility in iron oxide-amended contaminated soils as evaluated by short and long-term leaching test, *Environ. Pollut.* 131 (2004) 495–504.
- [47] A. Jain, K.P. Raven, R.H. Loeppert, Arsenite and arsenate adsorption on ferrihydrite: surface charge reduction and net OH⁻ release stoichiometry, *Environ. Sci. Technol.* 33 (1999) 1179–1184.
- [48] J. Aguilar-Carrillo, F. Garrido, M.T. García-González, Sorption of As, Cd and Tl as influenced by industrial by-products applied to an acidic soil: equilibrium and kinetic experiments, *Chemosphere* 65 (2006) 2377–2387.
- [49] S. Kartal, Z. Aydin, S. Tokalioglu, Fractionation of metals in street sediment samples by using the BCR sequential extraction procedure and multivariate statistical elucidation of the data, *J. Hazard. Mater.* 132 (2006) 80–89.
- [50] B. Doušová, A. Martaus, M. Filippi, D. Koloušek, Stability of arsenic species in soils contaminated naturally and in an anthropogenic manner, *Water Air Soil Pollut.* 187 (2008) 233–241.
- [51] P. Trivedi, J.A. Dyer, D.L. Sparks, K. Pandya, Mechanistic and thermodynamic interpretations of zinc sorption onto ferrihydrite, *J. Colloid Interface Sci.* 270 (2004) 77–85.