



Potential use of gypsum and lime rich industrial by-products for induced reduction of Pb, Zn and Ni leachability in an acid soil

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ABSTRACT

This study evaluates the potential use of four industrial by-products (phosphogypsum (PG), red gypsum (RG), sugar foam (SF), and ashes from biomass combustion (ACB)), applied at two rates in single and combined amendments to reduce the mobility and availability of Pb, Zn and Ni in a metal-spiked acid soil. Leaching experiments were done to estimate leachability indexes and assess their effectiveness. Most of the treatments significantly reduced the metal leachability although only a few were effective for all metals. Based on principal component and cluster analysis, sugar foam (SF) and a mixture of RG and ACB (RG+ACB), both applied at high rate, were selected as first choices to reduce mobility and availability of the three metals. Metal sorption mechanisms involved in the reduction of their leachability were identified using scanning electron microscopy. In the SF-treated samples, the metals were found associated to amorphous Al-hydroxy polymers deposited on phyllosilicates and organic matter particles. In the (RG+ACB)-treated samples, Pb, Zn, and traces of Ni were found associated to Fe/Ti oxide phases with a significant concentration of S, suggesting the formation of metal-sulfate ternary complexes.

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1. Introduction

Different industrial by-products have been evaluated as possible amendments for the *in situ* remediation of metal contaminated soils. This approach does not diminish toxic element concentrations but it is intended to increase the soil retention capacity through element immobilization in soil's non-labile chemical pools, thus reducing the metals mobility and bioavailability. In addition, this approach reduces waste disposal through converting industrial wastes into industrial co-products [1]. Examples of industrial by-products applied to reduce contaminant leaching include: bio-fuel fly ashes [2], sewage and paper mill sludge [3,4], gravel sludge [5], ochre [6] and bovine bone meal [7]. Other by-products rich in gypsum, such as phosphogypsum and red gypsum, or rich in calcium carbonate, such as sugar foam, has also been proved to reduce mobility and availability of Cd, Cu and Pb [8], as well as As, Cd and Tl [9]. In all these cases, the immobilization of the toxic elements was induced by either the precipitation of stable solid phases such as anglesite-type minerals [10] or the *in situ* formation of new sorbent materials in the soil such as amorphous polymers which provide the soil with additional element retention capacity [11].

However, in both diffusive and point-source contaminant events an array of toxic elements are included [12]. This produces

additional difficulties to control the adverse effects of metal contamination due to the different behaviors of the elements involved. For instance, Campbell et al. [13] tested two industrial by-products (sugar foam and phosphogypsum) and phosphate rock to regulate the mobility of Pb, Cd, and Cu in an acidic soil. They concluded that the industrial by-products could be considered an option to regulate mobility of those metals in acidic soils but their effectiveness for each metal was significantly different. Similarly, Aguilar-Carrillo et al. [14], assessed the use of those two industrial by-products as immobilizing agents of As, Cd, and Tl resulting in important differences between the elements studied. Carbonell et al. [15] tested phosphogypsum to reduce the aqueous concentrations of Cd and Ni under anoxic conditions by precipitating them as sulphides. Peacock and Rimmer [16] used red gypsum as a soil amendment comparing the affinity of Pb, Cu, Zn, Cd and Ni to be adsorbed onto this by-product. In addition to the different geochemical behavior of the toxic elements, the specific chemical and mineralogical composition of the amendments involves a selective efficiency of the treatment for isolated toxic elements. As a result, new treatments applied in single or combined amendments must be tested in a view of being effective to fix multiple elements. Also, rather than only inducing changes in soil pH, these treatments should promote sequestration of metals in non-labile pools of the soils such as entrapment in clay lattices, surface complexation by covalent bonding and precipitation of stable solid phases, thus reducing both metal potential mobility and bioavailability, to avoid the restoration of the initial toxic level due to re-acidification [17].

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The objectives of this study are (1) to assess the potential use of four industrial by-products (phosphogypsum (PG), red gypsum (RG), sugar foam (SF), and ashes from the combustion of biomass (ACB)) in single and combined amendments to reduce the mobility and availability of Pb, Zn and Ni in a metal-spiked acid soil, (2) to identify those treatments that are effective to reduce both potential mobility and availability of the three elements, and (3) to explore possible sorption mechanisms through which the metals are retained in the soil matrix as a result of selected treatments.

2. Materials and methods

2.1. Soil

Air-dried samples from the Ap horizon of an acid soil were crushed and sieved through a 2 mm mesh prior to characterization and use in subsequent experiments (Table 1). Soil pH was measured in deionized water (pH_w) and in 1 M KCl (pH_k) (in a 1:2.5 suspension). Electrical conductivity (EC) was measured in a 1:5 suspension. Organic C (OC) was determined by wet digestion [18]. The exchangeable bases were extracted with 1 M NH_4OAc (at pH 7) [19]. The Al and Fe contents in the poorly crystalline and amorphous fraction of the soils (Al_{ox} , Fe_{ox}) were extracted with 0.2 M ammonium oxalate + 0.2 M oxalic acid solution at pH 3 [20]. The supernatants from each extraction were separated by centrifuging and stored in polyethylene containers at 4 °C until analysis. Analyses were performed in triplicate. The Ca, Mg, Na, K, Al and Fe were determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES) on a Perkin Elmer OPTIMA 4300DV. The mineralogical composition of the total (≤ 2 mm) and clay ($\leq 2 \mu\text{m}$) fractions of the soil was identified by X-ray powder diffraction (XRD) with a Philips XiPert diffractometer with graphite-monochromated $\text{Cu K}\alpha$ radiation. The XRD patterns were obtained from random powder mounts and various oriented aggregates of the clay fraction (air-dried, ethylene glycol-solvated, heated at 300 °C for 3 h, and heated at 500 °C for 3 h). Semi-quantitative estimates of the mineral contents were obtained from random powder and oriented aggregated patterns using the intensity factors by Shultz (1964).

2.2. Industrial by-products

Phosphogypsum (PG) is generated in the wet-acid production of phosphoric acid from rock phosphate in the industry of fertilizers. Red gypsum (RG) is a waste from the industrial production of titanium dioxide (TiO_2). Sugar foam (SF) is the waste produced by the sugar manufacturing industry. Ashes from the combustion of biomass (ACB) are a waste from the incineration of biomass in the process of production of cellulose.

Samples of PG, RG, SF and ACB supplied by the companies Fertiberia S.A., Tióxide Europe S.A., Azucarera Ebro S.A. and ENCE S.A., respectively, were dried at 45 °C (PG and RG) and 105 °C (SF and ACB) and digested by acid digestion and alkaline fusion [21]. The resulting standard solutions were analyzed for major and trace elements by ICP-AES, ICP-MS and ion chromatography. The chemical composition of the by-products is listed in Table 2. Both gypsum-like wastes are rich in Ca and sulphate ions. In addition, because of its industrial origin from ilmenite (FeTiO_3), RG contains Fe and Ti. Regarding the trace elements, Ba, Cr and Cu are present at the largest concentrations among all elements analyzed in all by-products. In addition, RG and ACB are rich in Ni and Zn, and ACB also in Pb. However, the heavy metal contents are much less than those established by the European Community (1986) [22] for sewage sludge and constitute no environmental hazard at the rates normally used in agriculture.

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

pH _w	pH _k	EC ^a (mS cm ⁻¹)	OC ^b (g kg ⁻¹)	Sand (g kg ⁻¹)	Lime (g kg ⁻¹)	Clay (g kg ⁻¹)	Ca ²⁺ (cmol _c kg ⁻¹)	Mg ²⁺ (cmol _c kg ⁻¹)	Na ⁺ (cmol _c kg ⁻¹)	K ⁺ (cmol _c kg ⁻¹)	Al ³⁺ (cmol _c kg ⁻¹)	Al _{ox} ^c (mg kg ⁻¹)	Fe _{ox} ^c (mg kg ⁻¹)	Fraction ^d ≤ 2 mm									
														Q	G	H	Ph	Q	G	Ph	V	I	K
4.9	4.1	0.04	33	700	250	50	0.83	0.12	0.07	0.06	1.17	4772	1457	84	tr	3	13	15	9	76	11	10	55

^a EC, electrical conductivity.

^b OC, organic carbon.

^c Al and Fe oxalate-extractable contents.

^d Semi-quantitative mineralogical composition (relative%): Q, quartz; G, goethite; H, hematite; Ph, phyllosilicates; V, vermiculite; I, illite; K, kaolinite; tr, traces.

Table 2

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

	SF (g kg ⁻¹)	PG (g kg ⁻¹)	RG (g kg ⁻¹)	ACB (g kg ⁻¹)
Al ₂ O ₃	13.4 ± 0.7	14.8 ± 0.1	8.3 ± 0.4	60.1 ± 3
CaO	424 ± 13	305 ± 9	248 ± 12	171 ± 5
Fe ₃ O ₄	5.3 ± 0.3	0.2 ± 0.01	128 ± 6	16.3 ± 0.8
K ₂ O	3.0 ± 0.2	0.1 ± 0.01	0.2 ± 0.01	32.0 ± 1.6
MgO	18.6 ± 0.9	0.1 ± 0.01	8.2 ± 0.4	30.0 ± 1.5
MnO	0.3 ± 0.02	<0.1	3.8 ± 0.2	6.3 ± 0.3
Na ₂ O	0.9 ± 0.05	31.7 ± 0.2	0.7 ± 0.04	15.4 ± 0.8
P ₂ O ₅	14.6 ± 0.7	69.0 ± 0.4	0.8 ± 0.04	11.9 ± 0.6
SiO ₂	30.8 ± 2.2	17.9 ± 1.3	4.9 ± 0.2	353 ± 25
TiO ₂	0.3 ± 0.02	0.2 ± 0.01	60.2 ± 3.0	20.2 ± 0.1
F ⁻	0.08 ± 0.004	3.3 ± 0.2	<0.03	<0.1
SO ₄ ²⁻	81.4 ± 0.5	534 ± 32	425 ± 21	36.9 ± 2.2
LOI ^a	464 ± 23	221 ± 11	205 ± 10	252 ± 13
OC ^b	-	-	-	-
	SF (mg kg ⁻¹)	PG (mg kg ⁻¹)	RG (mg kg ⁻¹)	ACB (mg kg ⁻¹)
As	<2.5	<2.5	10.3 ± 0.5	7.1 ± 0.7
B	<2.5	<2.5	6.4 ± 0.3	<2.5
Ba	53.3 ± 5.3	112 ± 11	13.9 ± 0.7	396 ± 40
Be	<0.4	<0.4	<2.4	1.3 ± 0.1
Cd	<0.4	2.9 ± 0.3	<2.4	<0.4
Co	0.9 ± 0.1	<0.4	12.1 ± 0.6	5.3 ± 0.5
Cr	13.5 ± 1.4	8.7 ± 0.9	95.2 ± 4.8	36.9 ± 3.7
Cu	12.0 ± 1.2	5.2 ± 0.5	17.1 ± 0.9	45.8 ± 4.6
Mo	<0.4	1.9 ± 0.2	5.4 ± 0.3	8.7 ± 0.9
Ni	5.2 ± 0.5	2.9 ± 0.3	61.7 ± 3.1	177 ± 18
Pb	3.1 ± 0.3	2.2 ± 0.2	28.1 ± 1.4	79.0 ± 7.9
Se	<2.5	<2.5	<2.4	<2.5
Zn	19.3 ± 1.9	7.3 ± 0.7	388 ± 19	204 ± 20

^a LOI, loss on ignition (45–1000 °C).^b OC, organic carbon. (-) not detected.

The mineralogical composition of the by-products was identified by X-ray diffraction from random powder patterns. Gypsum is the main component of PG and RG and is accompanied by small proportions of iron and titanium minerals in RG. An XRD study of the RG residue after dissolution of gypsum revealed the presence of maghemite (γ -Fe₂O₃) and rutile (TiO₂). The 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. Contamination procedure

Air-dried and sieved (≤ 2 mm) soil samples were homogeneously packed to a bulk density of 1.25 g cm⁻³ into 12 methacrylate columns, 6.3-cm diameter and 20-cm length. The mass of packed soil (514 g per column) was calculated considering further experimental needs. The columns were irrigated at a constant flow rate of 30 ml h⁻¹ with 0.05 M NaNO₃ until a steady flow was achieved. Then, a front of a trielemental solution (totalizing 4 L of solution per column) containing 500 mg L⁻¹ of Pb, Zn and Ni (from analytical-grade salts Pb(NO₃)₂, Zn(NO₃)₂ and Ni(NO₃)₂·6H₂O, respectively) was applied to the surface of the columns at the same constant flow rate. Once the columns were contaminated, they were dismantled, and the topmost 3 cm was discarded to avoid uncertainties due to the possible presence of precipitates in the surface. The rest of the soil was oven-dried (50 °C) and thoroughly homogenized column by column.

2.4. Incubation procedure

Portions of 210-g contaminated soil samples were evenly blended with the industrial by-products as single (SF, PG, RG, ACB), double (SF+PG, SF+RG, SG+ACB, PG+ACB, RG+ACB), and triple treatments (PG+SF+ACB, RG+SF+ACB). Two additional portions were

maintained untreated as control. Each treatment was applied at two rates. The single SF treatment was added at 0.5% (rate 1, SF₁) and 1% (w/w) (rate 2, SF₂), which involved the addition of 0.42 and 0.84 g of Ca for each addition rate, respectively. In the treatments of PG, RG, PG+SF, RG+SF, SG+ACB, PG+ACB, RG+ACB, PG+SF+ACB, RG+SF+ACB the amount of by-product was calculated to add similar amounts of Ca as in the SF treatment.

All these soil samples (treated and control) were uniformly re-packed to a bulk density of 1.25 g cm⁻³ in 4.4-cm-diameter and 15-cm-length columns and maintained at room temperature (25 ± 2 °C) and field capacity by adding 60 ml of deionized water to the surface of the columns every 2 days. The incubation period of 6 weeks, totalized a volume of 900 mm, equivalent to the average annual rainfall of the experimental site. After this period, the columns were then dismantled and sample homogenized and oven-dried (50 °C). Acidity of the samples was measured in deionized water (pH_w) in a 1:2.5 suspension. Lastly, the samples were digested in a mixture of concentrated HNO₃ and HCl [23] and the resulting diluted solutions were analyzed for Pb, Zn and Ni using ICP-AES on a Perkin Elmer OPTIMA 4300DV instrument. This metal concentration values were subsequently used to calculate the leachability indexes as explained below.

2.5. Leaching experiments

From each incubated column, six 20-g sub-samples were taken and re-packed in small columns for subsequent estimation of potential mobility and availability of the metals as a result of the treatments through a series of leaching experiments. Metal bioavailability was assessed by leaching one set of triplicated columns at constant flow rate with 100 ml of DTPA solution (0.005 M diethylenetriaminepentaacetic acid, 0.01 M CaCl₂ and 0.1 M triethanolamine) adjusted to pH 7.3 [24]. A similar second set was used to evaluate the potential mobility of the metals following the

Table 3
DTPA and AA-leachability indexes for Pb, Zn and Ni ($n=6$).

	Treatments													PSE ^c
	Rate ^a	C ^b	PG	RG	SF	ACB	PG+SF	RG+SF	PG+ACB	RG+ACB	SF+ACB	PG+SF+ACB	RG+SF+ACB	
Pb ^{DTPA} ^d	1	39.5	36.4	32.2	31.8	35.1	32.9	28.8	34.4	36.3	32.2	38.0	31.5	0.7
Pb ^{AA} ^e	1	6.4	6.6	5.2	2.2	5.7	3.5	2.7	5.3	4.4	1.9	3.2	2.7	0.1
Pb ^{DTPA}	2	39.5	34.1	31.8	30.1	33.7	29.9	29.6	41.7	29.1	29.8	36.6	26.8	1.0
Pb ^{AA}	2	6.4	5.1	4.5	1.3	2.6	1.9	1.6	4.0	1.6	1.4	1.5	0.8	0.06
Zn ^{DTPA}	1	19.5	13.7	14.8	21.4	24.3	23.7	19.4	12.4	23.8	19.2	20.4	22.1	0.9
Zn ^{AA}	1	11.9	7.4	6.7	7.6	14.2	11.5	7.7	5.6	11.3	5.6	6.3	9.8	0.5
Zn ^{DTPA}	2	19.5	10.3	13.1	17.0	21.3	19.3	20.7	27.0	15.8	22.1	19.8	19.9	0.9
Zn ^{AA}	2	11.9	5.8	5.1	6.6	12.1	10.0	6.1	14.6	5.0	7.4	8.9	4.4	0.3
Ni ^{DTPA}	1	21.2	17.8	19.7	25.0	31.4	23.9	19.4	8.1	23.0	51.7	16.1	56.2	0.8
Ni ^{AA}	1	11.0	7.2	7.6	6.5	14.7	8.5	6.2	2.8	8.1	7.5	4.2	18.9	0.3
Ni ^{DTPA}	2	21.2	11.4	16.4	8.3	16.4	11.8	15.3	19.8	11.4	12.0	9.0	13.1	0.5
Ni ^{AA}	2	11.0	5.1	5.7	3.0	8.4	5.3	3.4	8.7	2.9	3.6	4.2	2.5	0.2

^a Rate 1 = 0.5%; rate 2 = 1%.^b C, control; PG, phosphogypsum; RG, red gypsum; SF, sugar foam; ACB, ashes from the combustion of biomass.^c PSE, pooled standard error ($P \leq 0.05$).^d Pb^{DTPA}, Zn^{DTPA}, Ni^{DTPA}, leachability indexes for Pb, Zn and Ni after the DTPA extraction.^e Pb^{AA}, Zn^{AA}, Ni^{AA}, leachability indexes for Pb, Zn and Ni after the acid acetic extraction.

same leaching procedure with 100 ml of an acetic acid solution at pH 4.93 (AA), corresponding to the second extracting solution used in the EPA Toxicity Characteristic Leaching Procedure (TCLP) [25]. The column total effluents were acidified with HNO₃ (pH ≈ 2) and analyzed for total Pb, Zn and Ni by ICP-AES. Both AA- and DTPA-leachability indexes for the metals (Pb^{AA}, Zn^{AA}, Ni^{AA} for identifying potential mobility and Pb^{DTPA}, Zn^{DTPA}, Ni^{DTPA} for metal bioavailability) were computed in terms of the percentage of metal concentration recovered after the leaching procedure with respect to the metal concentration contained in the samples before these leaching experiments were executed, i.e. right after the incubation procedure.

2.6. Scanning electron microscopy observations

Possible mechanisms involved in the sorption of the toxic elements in the soil matrix and differences due to the application of the amendments were investigated using scanning electron microscopy in the backscattered electron mode (SEM-BSE). Contaminated and amended samples were oven-dried (50 °C) and embedded in a low-viscosity acrylic resin (LR-Whyte, medium grade). Blocks of the resin-embedded samples were polished using a commercially available low-viscosity oil/water emulsion as lubricant and subsequently observed under a DMS 940A Zeiss microscope equipped with BSE detector. Semi-quantitative elemental analyses, using point analyses, were done by energy dispersive spectrometry (EDS) with a Link Isis microanalytical system on the SEM.

2.7. Statistical analysis

Different statistical tests were done in order to identify the optimum treatment and application rate (dose) to reduce both acid acetic and DTPA extractability of the three metals. First, the statistical differences in the leachability of each metal as a result of the treatments as compared to the untreated samples were assessed for each application rate by a one-way analysis of variance (ANOVA) and the Bonferroni or Tamhane *post hoc* pair-tests (depending on the particular variance homogeneity).

On the other hand, a principal component analysis (PCA) was done to identify homogeneous responses (high correlations) in terms of metal leachability and to obtain a reduced number of variables. In addition, a new variability factor was defined by joining both treatment and dose (treat × dose).

On the basis of this PCA, a K-means cluster analysis (CA) was used to find those groups of treatment conditions (treat × dose) showing similar responses with respect to the principal components. The different treat × dose experimental conditions considered were projected over the two-dimension principal component plot to identify those treat × dose clusters that operates reducing both AA and DTPA leachability of the three metals (optimum treat × dose). Lastly, the statistical differences of the metal leachability obtained upon this selected treatments were assessed by a one-way ANOVA and *post hoc* tests. All statistical analyses were done using the statistic package SPSS v. 15.0 (SPSS, Inc., Chicago, IL).

3. Results and discussion

3.1. Effect of treatments on metal leachability

Metal leachability varies significantly as a function of the metal, leaching conditions, and soil treatment (Table 3). In the control samples, Pb is removed from columns to a greater extent than Zn and Ni after leaching with the DTPA solution showing the stronger affinity of Pb for the chelating agent than that of Zn [26] and Ni. On the contrary, Zn and Ni leachability indexes are almost twice lead's index after the leaching procedure with the acid acetic solution at pH 4.93. Lead is known to have a large tendency to be retained through inner-sphere complexes in available hydroxyl groups of clay minerals and organic particles that remain stable at the extracting pH [27]. Due to this affinity, competing cations coexisting in the soil solution are retained in exchangeable positions to a greater extent thus becoming easily displaceable in leaching conditions [28].

The addition of the amendments does not greatly change the metal sorption and leaching behavior but a significant reduction of metal leachability is achieved in most of the experimental cases. In general, the application of the amendments at high rate (rate 2) induced a greater reduction of the leachability of the three metals than when they were applied at low rate (rate 1), although only the RG+ACB treatment consistently produced greater leachability indexes of the three metals at the higher application rate. The maximum reduction of the Pb^{DTPA}-leachability index is obtained upon the RG+SF treatment. The addition of this joint amendment decreased in up to 27% the Pb^{DTPA} value with respect to the control and up to 10% those values obtained after the addition of the by-products isolated. On the other hand, after the SF treatment, Pb^{AA} index values were reduced by up to 80% the index

Table 4
Correlation matrix of the DTPA and AA-leachability indexes ($n = 66$).

Correlation coefficient (r^2) ^a						
	Pb ^{DTPAb}	Zn ^{DTPA}	Ni ^{DTPA}	Pb ^{AAc}	Zn ^{AA}	Ni ^{AA}
Pb ^{DTPA}	1	0.237	0.043	0.537**	0.507**	0.245*
Zn ^{DTPA}		1	0.352**	-0.292*	0.704**	0.416**
Ni ^{DTPA}			1	0.049	0.234	0.790**
Pb ^{AA}				1	0.241	0.341**
Zn ^{AA}					1	0.623**
Ni ^{AA}						1

^a The probability values (P -value) of regression are shown after r^2 values.

^b Pb^{DTPA}, Zn^{DTPA}, Ni^{DTPA}, leachability indexes for Pb, Zn and Ni after the DTPA extraction.

^c Pb^{AA}, Zn^{AA}, Ni^{AA}, leachability indexes for Pb, Zn and Ni after the Acid Acetic extraction.

* $P < 0.05$.

** $P < 0.01$.

value obtained in the untreated samples. Both Zn and Ni leachability indexes were also significantly reduced as a result of the addition of various amendments. Greatest reduction of Zn^{DTPA} was obtained upon PG, RG, and RG+ACB treatments (up to 47% reduction in the case of the PG treated columns) while Zn^{AA} index is specially reduced as a result of the RG+SF+ACB treatment (63% as compared to the control samples) in addition to the other three. The application of carbonate-rich and gypsum-rich amendments to acidic soils produces the formation of non-crystalline Al-hydroxy polymers [29] on which surface the adsorption of Zn²⁺ is enhanced by the presence of inorganic ligands such as sulphate anions through the formation of stable Zn-sulphate ternary complexes [11,30]. In addition, Voegelin and Kretzschmar [31] found evidence for the predominant formation in a near neutral contaminated soil of a new Zn-layered double hydroxide phase in the presence of amorphous Al(OH)₃ whose stability is favoured when bicarbonate is contained in the interlayer (hydratocite-like minerals). Lastly, both Ni^{DTPA} and Ni^{AA} are specially reduced after the SF treatment (60% and 74% reduction with respect to the control samples, respectively) along with the RG+ACB and PG+SF+ACB treatments. In addition to the insolubilization as hydroxide due to the increase in pH resulting from the addition of carbonates, calcium carbonate also induces Ni retention through a co-precipitation process leading to Ni/Ca carbonate double salts and mixed Ni/Al hydroxides and carbonates formation (hydratocite-like minerals) [32].

Overall, taking into account all experimental cases except for the control, DTPA and AA-leachability indexes significantly correlate

Table 5

The most effective treatments in the DTPA and acid acetic (AA) extraction, based on the principal component analysis (PCA) and the K-means cluster analysis (CA).

DTPA	AA
RG ₁ ^a	
PG ₂	
SF ₂	SF ₂
PG ₂	
RG+SF ₁	RG+SF ₁
PG+ACB ₁	
RG+SF ₂	RG+SF ₂
PG+SF ₂	PG+SF ₂
SF+ACB ₂	SF+ACB ₂
RG+ACB ₂	RG+ACB ₂
RG+SF+ACB ₂	RG+SF+ACB ₂
	SF ₁
	SF+ACB ₁
	PG+SF+ACB ₁
	PG+SF+ACB ₂

Rate 1 = 0.5%; rate 2 = 1%.

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

for each element (Table 4). On a second level, positive significant correlations between Zn and Ni leachability indexes show that sorption and leaching behavior of both metals are closer to each other than to those of Pb regardless the treatment applied to the soil.

3.2. Identification of the most effective treatments

In order to select those most effective treatments in reducing potential leachability and bioavailability of the three metals, principal component analysis (PCA) followed by a K-means cluster analysis (CA) on the basis of a new variability factor (treat × dose) were done. The results of the PCA showed that Zn and Ni leachability indexes could be grouped into one component for each leaching condition while the Pb ones behave independently so that it constitutes as a second component for both DTPA and AA leaching conditions. This way, for the DTPA indexes, 44% and 36% of the total variance were explained by the first (Zn × Ni^{DTPA}) and second components (Pb^{DTPA}), respectively, while in the case of the AA indexes,

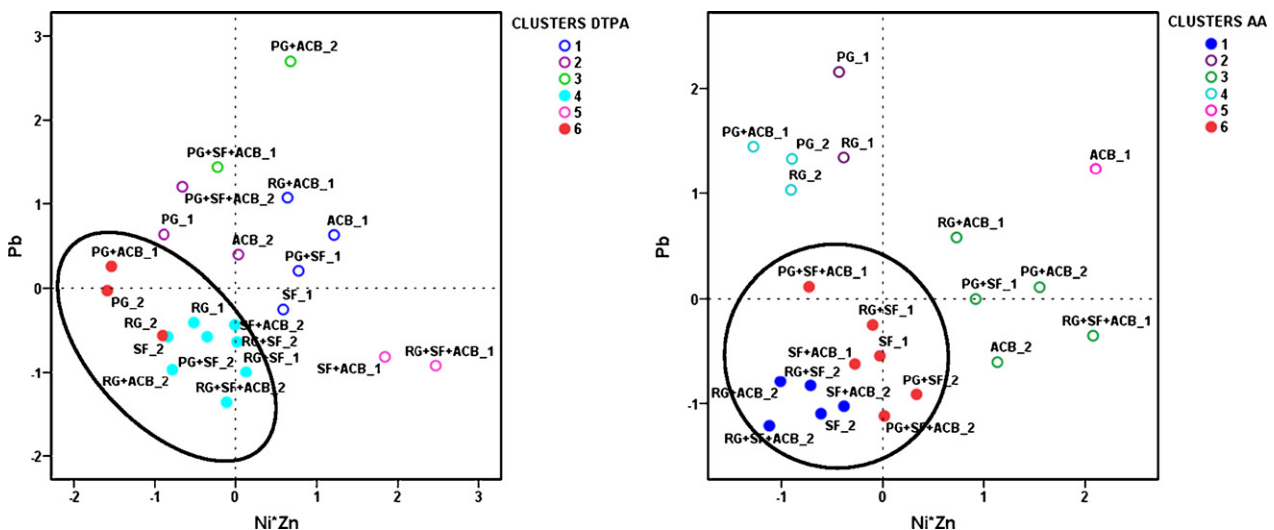


Fig. 1. Principal components analysis (PCA) and K-means cluster analysis (CA) for DTPA and AA leaching procedures.

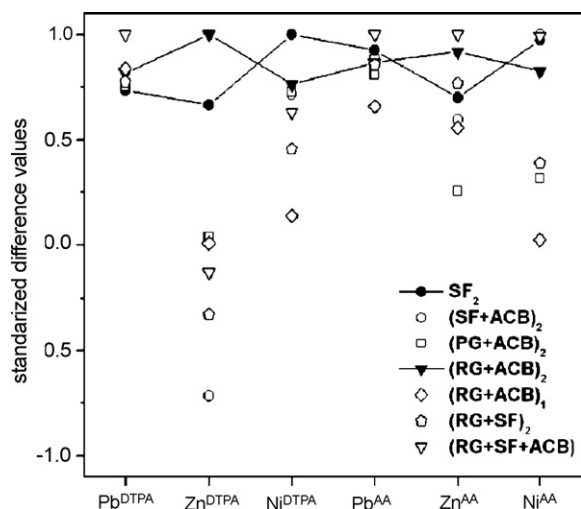


Fig. 2. Representation of the differences between the mean leachability indexes in the control and treated samples standardized with respect to the maximum difference value for each metal and leaching condition.

both components explained 87% of the total variance (53% the first component, $Zn \times Ni^{AA}$, and 34% second component, Pb^{AA}). Based on these results, CA divided all treatments into six clusters that distribute onto the factorial planes corresponding to each leaching condition as it is shown in Fig. 1. Optimum treatments for reducing the Pb, Zn and Ni leachability indexes are those approximately localized within the bottom left-hand quadrant on each factorial plane. The set of treatments that are included in these relative positions on both the DTPA and AA factorial planes were defined as effective treatments of the three elements upon the two leaching conditions, thus reducing both potential mobility and bioavailability of the three elements (Table 5).

Among these selected treatments, to identify those most effective, the resulting differences between the mean leachability indexes obtained in control and treated samples were standardized with respect to the maximum difference value for each metal and leaching condition and plotted (Fig. 2). As can be seen, SF and (RG+ACB), both amendments applied at rate 2, stand out within this selected set of treatments due to a more homogeneous effect over all variables (metal and leaching conditions) than the rest of the treatments ((RG+SF)₁, (RG+SF)₂, (PG+SF)₂, (SF+ACB)₂ and (RG+SF+ACB)₂) and thus both amendments could be considered as

first choice in order to reduce the potential leachability of Pb, Zn and Ni in contaminated soils.

3.3. Induced sorption mechanisms of metals after the SF and RG+ACB treatments: SEM observations

Among all the by-products applied, only SF₂ was an effective treatment as single amendment in reducing both potential mobility and availability of Pb, Zn and Ni. Different sorption mechanisms may be involved in the overall reduction of metal leachability shown after this treatment. SEM-BSE analysis of the SF₂-treated samples confirmed the formation of non-crystalline Al-hydroxy polymers containing the three metals and associated with phyllosilicates and organic matter particles (Fig. 3). To elucidate whether the metals remain retained on hydroxyl groups of the surface of these amorphous phases or, through kinetic-controlled processes (migration into micropores, solid state diffusion into crystal lattices or physical occlusion of elements) [33,34], become part of hydrotalcite-like minerals including carbonate anions in their structure is out of the scope of this study. However, long-term studies on the stability of these new solid phases should be performed to assess the feasibility of this treatment for in situ remediation of contaminated soils. In addition, theoretical modelling using the geochemical code Visual MINTEQA2 [35] predicted the formation of cerussite ($PbCO_3$), hydrocerussite ($Pb_3(CO_3)_2(OH)_2$), smithsonite ($ZnCO_3$) and $NiCO_3$ as possible sorption mechanisms of the metals due the amount of CO_3^{2-} added by the sugar foam and the increment in pH_w (from 4.7 to 7.6 in the control and SF₂-treated samples, respectively) (Table 6). However, XRD analyses of the amended samples did not prove the presence of any of these compounds (data not shown).

The joint addition of RG and ACB at rate 2 also produced a significant reduction of the leachability indexes of the three metals upon both leaching conditions (Fig. 2). SEM-BSE observations revealed different features within the corresponding treated samples. Firstly, the three metals were frequently found associated with particles mainly composed of phyllosilicates and organic matter. Also, on the one hand, the formation of Al-hydroxy polymers was produced to a lesser extent as compared to the SF₂-treated samples and none of the metals were found associated to this new solid phase. On the other, the presence of maghemite and rutile in the RG by-product provides reactive surface sites for sorption of heavy metals [36]. In accordance to this, Pb and Zn as well as traces of Ni were found associated to Fe/Ti oxide phases in which elemental composition, a significant concentration of S is also a remarkable

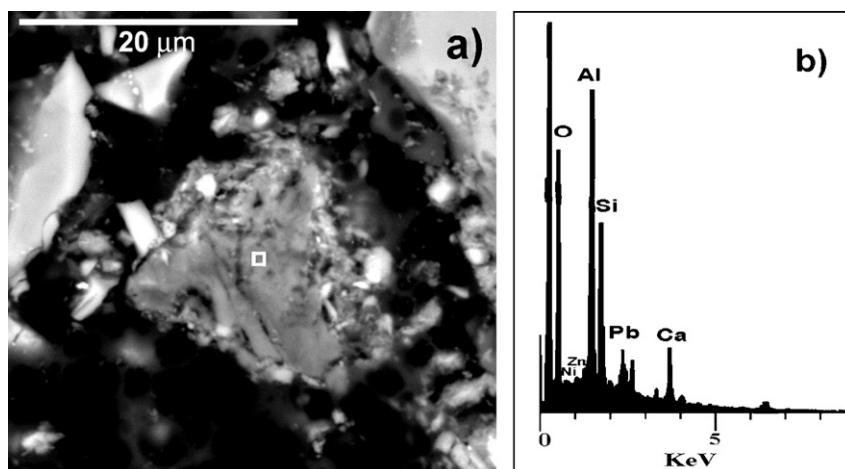


Fig. 3. (a) SEM-BSE image of a massive formation of Al-hydroxy polymers in SF₂-treated soil samples and (b) EDS X-ray spectrum of the zone marked with square showing the presence of Al, Pb, Zn and Ni.

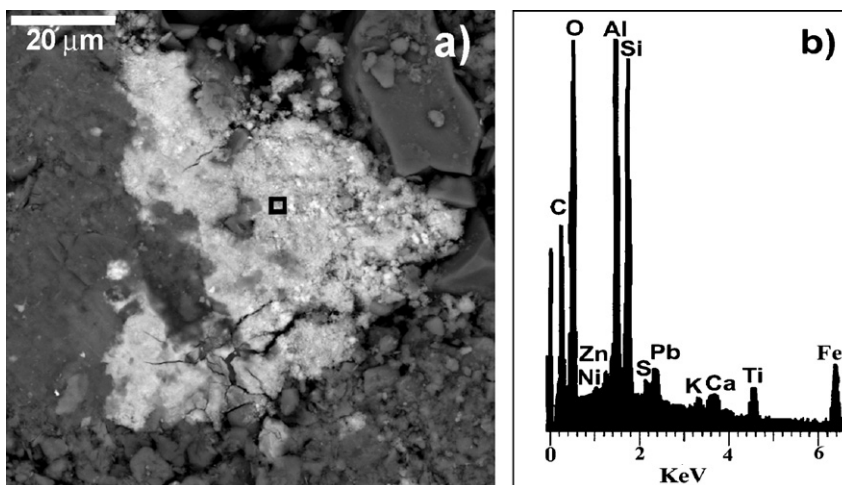


Fig. 4. (a) SEM-BSE image of Fe/Ti oxide phases in the (RG+ACB)₂-treated soil samples and (b) EDS X-ray spectrum of the zone marked with square showing the presence of Pb, Zn and Ni.

Table 6
pH_w values (*n* = 3) for the soil-by-products mixtures after incubation.

	Rate 1 ^a	Rate 2
Control ^b		4.75 ^c
PG ^d	5.05	4.97
RG	4.98	4.67
SF	6.93	7.58
ACB	6.28	6.92
PG+SF	6.17	6.58
RG+SF	5.89	6.45
PG+ACB	5.87	6.26
RG+ACB	5.48	6.01
SF+ACB	7.40	7.39
PG+SF+ACB	6.62	7.20
RG+SF+ACB	6.10	6.98

^a Rate 1 = 0.5%; rate 2 = 1%.

^b Soil contaminated without by-products.

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

^d All standard deviations are ≤0.10.

finding (Fig. 4). Lead's affinity for the hydroxyl groups in both Fe and Ti oxides due to the large tendency of Pb to hydrolyze is well documented [11,37]. Also, Coston et al. [38] showed lead's preference to form complexes onto iron hydroxyl sites as compared to that on aluminol sites. Instead, these authors showed that the reverse tendency was true for Zn. The presence of S in the composition of these Fe/Ti rich phases may indicate an alteration of the surface properties of these compounds giving rise to the adsorption of Zn and, to a lesser extent, Ni through the formation of metal-sulfate ternary complexes [11].

In addition, the presence of the ACB by-product in the amendment, with a high liming power, produced an increase of the pH of the soil in up to one unit with respect to the control. At pH 6.1, geochemical modelling using Visual MINTEQA2 [35] predicted the precipitation of Pb(OH)₂ and Ni(OH)₂ while Zn(OH)₂ only precipitates when pH is higher than 6.5. Lastly, the addition of sulfate anions could also promote the precipitation of anglesite (PbSO₄) and larnakite (PbOSO₄) minerals as predicted by geochemical modelling. However, XRD analyses of the amended samples did not prove the presence of any of these compounds (data not shown).

4. Conclusions

The present study evaluates the potential use of four industrial by-products (phosphogypsum (PG), red gypsum (RG), sugar foam

(SF), and ashes from the combustion of biomass (ACB)), applied at two different rates in single and combined amendments to reduce the mobility and availability of Pb, Zn and Ni in a metal-spiked acid soil. Although most of treatments induced a significant decrease of metal leachability, both SF and a mixture of RG and ACB (RG+ACB) applied at high rate, were selected as first choices to reduce potential mobility and availability of the three metals. SEM-BSE analysis of the SF₂-treated samples confirmed the formation of non-crystalline Al-hydroxy polymers containing the three metals and associated with phyllosilicates and organic matter particles. Long-term stability of these new solid phases should be performed in order to assess the feasibility of this treatment for in situ remediation of contaminated soils. The joint addition of RG and ACB at rate 2 also produced a significant reduction of the leachability indexes of the three metals. In this case, SEM-BSE observations showed that Pb and Zn as well as traces of Ni were found associated to Fe/Ti oxide phases in whose elemental composition, a significant concentration of S was encountered, indicating that metal-sulfate ternary complexes, in addition to direct coordination with hydroxyl groups of the Fe/Ti compounds, could be the main metal sorption mechanisms in the treated soils.

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