Immobilization of Cu, Pb and Zn in mine-contaminated soils using reactive materials

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ABSTRACT

Immobilization processes were used to chemically stabilize soil contaminated with Cu, Pb and Zn from mine tailings and industrial impoundments. We examined the effectiveness of ordinary Portland cement (OPC), phosphoric acid and MgO at immobilizing Cu, Pb and Zn in soil contaminated by either mine tailings or industrial and mine wastes.

The effectiveness was evaluated using column leaching experiments and geochemical modelling, in which we assessed possible mechanisms for metal immobilization using PHREEQC and Medusa numerical codes.

Experimental results showed that Cu was mobilized in all the experiments, whereas Pb immobilization with H_3PO_4 may have been related to the precipitation of chloropyromorphite. Thus, the Pb concentrations of leachates of pure mining and industrial contaminated soils (32–410 μg/l and 430–1000 μg/l, respectively) were reduced to 1–60 and 3–360 μg/l, respectively, in the phosphoric acid experiment. The mobilization of Pb at high alkaline conditions, when $Pb(OH)_4^-$ is the most stable species, may be the main obstacle to the use of OPC and MgO in the immobilization of this metal.

In the mining- and industry-contaminated soil, Zn was retained by OPC but removed by MgO. The experiments with OPC showed the Zn decrease in the leachates of mining soil from 226–1960 μg/l to 92–121 μg/l. In the industrial contaminated soil, the Zn decrease in the leachates was most elevated, showing >2500 μg/l in the leachates of contaminated soil and 76–173 μg/l in the OPC experiment.

Finally, when H_3PO_4 was added, Zn was mobilized.

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1. Introduction

The release of metals to the environment in old mining areas is generally associated with the abandonment of mine wastes. These are mainly composed of tailings (wastes from the ore concentration processes) and impoundments, which contain waste rock and low grade ore. Soil and groundwater contamination with metals is a major environmental hazard [1]. Although Cu and Zn are not a human health concern, they may have phytotoxic effects. In contrast, Pb was ranked second on the CERCLA (Comprehensive Environmental Response, Compensation and Liability Act) Priority List of Hazardous Substances in 1999 and 2001 [2].

The remediation of soils contaminated with metals may involve the following processes: concentration reduction of bioavailable metals in soil and/or waste and contaminant isolation to prevent the interaction of such metals with the environment. For such processes to be successful, we must consider the metal speciation and metal concentration and the influence on metal mobility of the pH, redox conditions, dissolved organic matter (DOM), particle size, microbial activity and bioavailability. Commonly used in situ immobilization methods include base neutralization with lime, dolomite and industrial by-products of an alkaline nature, such as combustion ash, magnesium oxide and hydroxides [3–7].

Portland cement materials have been used successfully in soils contaminated with Pb, in which they immobilized the metal highly efficiently [8–12]. Thus, the use of cement may immobilize Pb in contaminated soils with 99% efficiency at a 1:15 cement:soil ratio [8] through the formation and microencapsulation of insoluble lead hydroxides. However, the use of ordinary Portland cement (OPC) under highly alkaline conditions may produce high concentrations of leached Pb, because the solubility of amphoteric metals, such as Pb varies with pH, showing an optimum pH value near 10, which may indicate that the pH of OPC is not ideal for precipitating some metals. This phenomenon could be a limiting factor for the use of this material in stabilization/solidification [12].

Sewage sludge has also been used to address metal pollution problems. Studies have been based on an analysis of the nutrient supply to various plants, in order to develop ground cover on

Table 1
Main physical characteristics of soils used in the column experiments.

Sample	d_e	ε	pH	C	ρ	FC (%)
MS	0.26	0.56	7.22	5100	1210	23
MIND	0.51	0.52	6.34	6400	1380	22

MS: mining soil; MIND: industrial soil; d_e: equivalent diameter (mm) obtained by sieve analysis; ε: porosity obtained by water displacement in a test tube; C: electrical conductivity (μS/cm); ρ: bulk density (kg/m^3); and FC: field capacity obtained by numerical code SOILPAR 2.00 [32] and textural data.

waste and contaminated soils [13–16]. The leaching of metals in relation to acid mine waters and mine tailings, by using sewage sludge and organic amendments has been analyzed and the retention of these metals has been assessed [17–19]. Some examples suggest that metals such as Cu, Fe, Mn, Pb and Zn may be removed by sorption, siderite and hydroxide precipitation and sulphide precipitation after sulphate reduction in anaerobic conditions [16,17]. However, the addition of organic-carbon material such as sewage sludge or composted wastes to sulphide tailings may promote the mobilization of metals due to the reductive dissolution processes of Fe oxyhydroxides [20–22].

Several laboratory studies show that Pb is retained through the use of sewage sludge [16] and composted sludge in proportions of up to 15% by weight of the reactive material [23]. In addition, experimental tests have shown that the use of digested sludge on contaminated soil from smelting facilities reduces the bioavailability and mobility in water of metals such as Cd, Pb and Zn.

Contaminated soils can also be treated by phosphate rock and phosphorus materials [24]. For example, water-soluble phosphates and phosphoric acid have been used to eliminate Pb [25–28]. The use of phosphate amendments at sites contaminated by past battery recycling activities showed the transformation of 60% of total soil Pb from the non-residual fraction to the residual fraction. However, the leaching of extractable Pb concentrations was higher than the critical control level [26]. In fact, phosphoric acid should be used with caution, as it decreases the soil pH and can lead to mobilization of remaining metals present in the soil. However, the "in situ" application of phosphoric acid to soils with >0.2% of Pb reduced the bioaccessibility of Pb in the soil and the amount of Pb leached in column experiments [27,28].

The purpose of this study was to evaluate the effectiveness of three reactive materials (OPC, phosphoric acid and MgO) at immobilizing Cu, Pb and Zn in mining-contaminated soils. We used percolation column experiments, which simulate field conditions more accurately than the USEPA toxicity characteristic leaching procedure (TCLP) [10].

2. Materials and methods

2.1. Sampling and characterization

The reference soils used in this study were collected from the upper 2 m of an abandoned mining area and a current industrial battery recycling site, developed over old mine tailings in NE Spain. Mine tailings were generated from gravimetric concentration processes and industrial wastes were dumped with the most recent mine wastes over an alluvial plain of approximately 3 ha.

Soil and waste in the study area were characterized during two sampling campaigns conducted in January 2009. The mining and industrial wastes were sampled by excavation equipment (up to 2 m deep) and by manual sampling (up to 0.3 m deep). Also, some physical characteristics of soil were evaluated: pore size distribution, porosity, pH, electrical conductivity and bulk density (Table 1).

The identification and analysis of the mineral phases in the samples was performed in the laboratories of the Autonomous University of Barcelona (UAB). We used X-ray diffraction (XRD) and scanning electron microscopy coupled with an identification sys-

tem (SEM-EDS). In addition to quantitative analysis, SEM-EDS can reveal the distribution of chemical elements in mineral phases.

Once the materials had been dried and ground, their geochemical composition was analyzed using instrumental neutron activation analysis (INAA) in Actlabs (Ontario, Canada). The following elements were found: Au, Ag, As, Ba, Br, Ca, Co, Cr, Cs, Fe, Hf, Hg, Ir, Mo, Na, Ni, Rb, Sb, Sc, Se, Sn, Sr, Ta, Th, U, W, Zn, La, Ce, Nd, Sm, Eu, Tb, Yb and Lu. In addition, the following composition was determined by acid digestion and subsequent inductively coupled plasma atomic emission spectrometry (ICP-AES): Ag, Cd, Cu, Mn, Mo, Ni, Pb, Zn, Al, Be, Bi, Ca, K, Mg, P, Sr, Ti, V, Y and S.

2.2. Soil amendments

OPC was applied to the soils at a 10:1 weight ratio (soil:OPC) and the soils were mixed with low-mineralized water in a 6:1 ratio (soil:water). Field capacity of soils, obtained from textural data, was evaluated in 0.23 and 0.22, for mining and industrial soil, respectively (Table 1).

Phosphate was added to soil samples as phosphoric acid (H_3PO_4) at a dose of 20 g P/kg soil. Then, an small quantity of NaCl was added to the soils (220:1) to promote the precipitation of chloropyromorphite, and 0.5 l of low-mineralized water was mixed with the sample (5:1, soil:water ratio).

The amount of MgO amendment was calculated on the basis of similar experiments [7] and was applied to the soils in a weight ratio of 5:1 (soil:MgO). In addition, 183 ml of low-mineralized water was added per kg of soil and MgO mixture. Soil samples and amendments were incubated for 7 days before the leaching experiments.

2.3. Leaching experiments

We carried out two types of experiments to explore the possible immobilization of metals and metalloids: leaching of soil contaminated by mine wastes and soil contaminated by industrial and mine wastes; and leaching of two reference soils amended by three reactive materials (OPC, phosphoric acid and MgO). The column leaching method was similar to PrEN 14405, which is the European standard percolation test, although in our case water flow was located at the top of the column.

The experiments were carried out for 420 min and 7 samples were taken from the leachates at the end of the column. In addition, in situ electrical conductivity, Eh and pH were measured. The leachate, which was previously filtered to 45 μm, was acidified to pH < 2 and sent for analysis. In addition, several samples from each experiment were sent for analysis without acidification, to determine the major anions. The fluids were analyzed by ICP-MS Actlabs (Ontario, Canada) using standard techniques to determine the dominant anions and the following elements: Li, Na, Mg, Al, Si, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ge, As, Se, Br, Rb, Sr, Y, Zr, Ag, Cd, Sn, Sb, Te, I, Cs, Ba, Hg, Pb and REE. These determinations were contrasted with the reference sample NIST 1640 and were conducted in the laboratories mentioned above.

In the column experiments, we used a column that was designed and built in the Fluid Mechanics Laboratory of ETSEIAT (UPC). The column was basically a cylinder with the following dimensions: 750 mm length, 150 mm outer diameter and 5 mm thickness. At

Fig. 1. Leaching column used in the laboratory experiments.

the bottom of the column and attached to it was a plastic funnel that was 222 mm long with an internal diameter of 186 mm. Inside this was a fibreglass plate with holes in it, which acted as a support column. Methacrylate was coated on a mesh that acted as a filter and retained the porous medium (Fig. 1). The entire device was mounted on a metal structure to hold the column in a vertical position at a regular height above the surface. The column was subjected to the metal structure by two clamps, one at the top that directly held the spine and one at the bottom that was isolated from it by a 20×20 mm piece of rubber, ensuring that the system was fixed securely during the experiments. The fluid was introduced into the column using a rain simulator connected to

a metering pump, which provided a maximum flow of 10 l/h and could be adjusted from 1% to 100% of low-mineralized water. This simulated the possible effects of rainfall on the waste [16].

3. Results and discussion

Main physical parameters of soils used in the column experiments showed a bulk density of 1210 kg/m^3 and 1380 kg/m^3 for mining and industrial soil, respectively, a porosity of 0.56 and 0.52 and a field capacity of 0.23 and 0.22 (Table 1). The pH values range between 7.22 for mining soil and 6.34 for industrial soil, and the electric conductivity was of 5100 μS/cm and 6400 μS/cm, respectively.

3.1. Mineralogy and geochemistry

The two reference soils were mainly composed of quartz, calcite, barite, cerussite and muscovite. The mining soil also contained hydrozincite and jarosite, and the industrial land soil contained some albite and dickite (Table 2).

As expected, the soils treated with amendments had a similar composition. All of them contained quartz and barite. Calcite was also found in almost all soils. However, there were some significant differences. Kaolinite was formed in waste soils treated with phosphoric acid (Table 2). Treatment with magnesium oxide produced the precipitation of periclase and rare minerals, such as szomolnokite in the mining soils and todorokite in the industry-contaminated soils. OPC treatment hardly affected the soil mineralogy.

Table 3 shows the element concentrations in the contaminated soils. For comparison, the table also includes analyses of the composition of the OPC and that of ore samples from nearby mines

Table 2
Identified main mineral phases in the contaminated soils.

Mineral phase	Formula
Mining soil	
Quartz	SiO_2
Cerussite	$PbCO_3$
Calcite	$CaCO_3$
Barite	$BaSO_4$
Jarosite	$KFe_3(SO_4)_2(OH)_6$
Hydrozincite	$FZn_5(CO_3)_2(OH)_6$
Muscovite–kaolinite	$KAl_2(Al,Si)_4O_{10}(OH,F)_2$
Rustumite	$Ca_{10}(Si_2O_7)_2(SiO_4)Cl_2(OH)_2$
Industrial and mining contaminated soil	
Quartz	SiO_2
Cerussite	$PbCO_3$
Calcite	$CaCO_3$
Albite	$Na_{0.986}(Al_{1.005}Si_{2.995}O_8)$
Barite	$BaSO_4$
Muscovite–kaolinite	$KAl_2(Al,Si)_4O_{10}(OH,F)_2Al_4(Si_4O_{10})(OH)_8$
Dickite	$Al_2(Si_2O_5)(OH)_4$

	Untreated	Treated with phosphoric acid	Treated with magnesium oxide	Treated with OPC
Mining dump	Quartz	Quartz	Quartz	Quartz
	Calcite	Calcite	Barite	Calcite
	Barite	Barite	Dickite–nacrite	Barite
	Cerussite	Cerussite	Szomolnokite	Muscovite
	Muscovite	Muscovite	Periclase	Albite
	Jarosite	Kaolinite		
	Hydrozincite			
Mining and industrial dump	Quartz	Quartz	Quartz	Quartz
	Calcite	Barite	Barite	Calcite
	Barite	Albite	Albite	Barite
	Cerussite	Kaolinite/illite	Periclase	Muscovite
	Muscovite		Dickite	Dickite
	Albite		Todorokite	
	Dickite			

Table 3
Concentrations of metals and metalloids in contaminated soils, ore samples and OPC. Values in mg kg^{-1}.

Element	Cu	Pb	Zn	As	Sb	Ba
Detection limit	1	3	1	0.5	0.1	50
Mining Soil	>10000	>5000	38600	218	143	35000
Industrial and mining soil	6030	>5000	14800	121	220	55000
Carlota mine	42	>5000	26	9	4	1600
Serrat Blanc mine	21	39	21	11	2.8	330000
Osor mine	88	>5000	34000	164	208	2190
OPC	13	123	18	4	1.1	200
CAL*	1000	540	1000	30	30	1000

CAL(*): The Catalonian soil intervention values (industrial use) in mg kg^{-1}.

(the Carlota, Serrat Blanc and Osor mines), which are typical of the ore processed in the area. The geochemical data show that the two types of contaminated soils have similar compositions, with significant amounts of As, Ag, Ba, Cd, Cu, Ni, Pb, Sb and Zn. Some metals (Cu, Pb, Zn, As, Ba and Sb) have concentrations above the Catalan standard levels for soils contaminated by industry (Table 3).

The presence of significant amounts of As in soils may be due to the processing of ore from the Osor mine and dumped batteries from current industrial activity. The industry-contaminated soil had slightly less As (121 mg kg^{-1}) than the mining-contaminated soil (218 mg kg^{-1}). There was also a clear difference in Zn content, which stood at up to 3.8% of the mining soil sample, but only 1.4% of the industrial soil.

Portland cement contained significant concentrations of Pb (123 mg kg^{-1}), but not of the other metals. Therefore, before cement is selected for metal immobilization, its composition should be analyzed. The magnesium oxide used in the soil amendments was supplied by Magnesitas de Navarra S.A. [7].

3.2. Leaching tests

The same method was used in all of the leaching tests. In each trial, approximately 11 cm of reference and/or treated soil was used with 5 cm of polystyrene (Fig. 1). The flow rate of circulating low-mineralized water (Table 4) was 1.4 l/h in all tests.

The solution pH of leachates was 7.99–8.36 during the "pure" mining-contaminated soil column experiment (Fig. 2a). However, in the treated soil experiments, the pH increased to 11.43–11.52 (in the OPC experiment) and 12.01–12.61 (in the MgO experiment). In the phosphoric acid experiment, the pH of leachates decreased to 3.85–5.93, which contributed to the mobilization of all metals except Pb, Ba and Se.

The solution pH of leachates during the "pure" industrial contaminated soil leaching experiment was 6.93–7.29 (Fig. 2b). Nevertheless, in soils treated with OPC and MgO, the pH increased to 10.85–11.03 and 12.35–12.61, respectively. In the leaching test with phosphoric acid, the pH decreased to 3.40–5.34, favouring the mobilization in small proportions of all metals except Pb, Ba, Cd and Se.
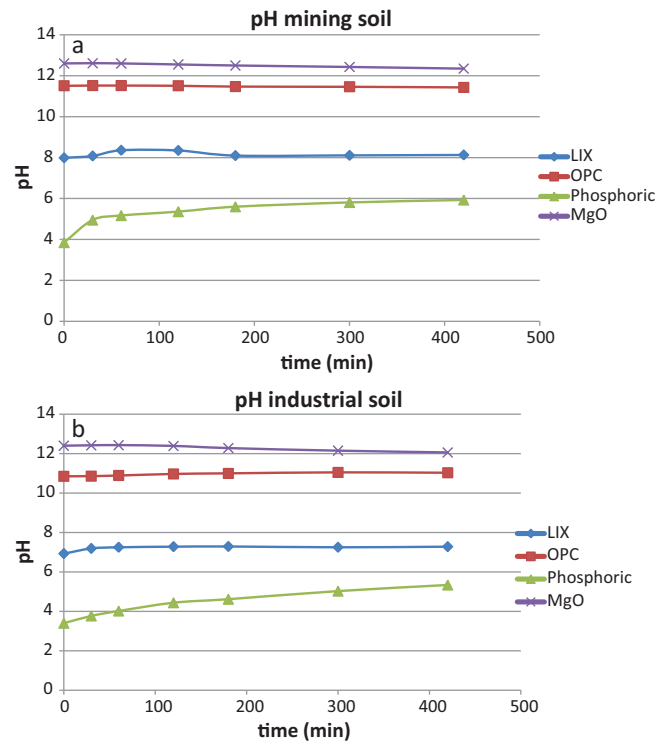

Fig. 2. a: Evolution of pH in the leaching experiments with mining soil. b: Evolution of pH in the leaching experiments with mining and industrial soil. LIX: low-mineralized water leaching experiment with "pure" contaminated soils; OPC: low-mineralized water leaching experiment with OPC; Phosphoric: low-mineralized water leaching experiment with phosphoric acid; and MgO: low-mineralized water leaching experiment with MgO.

During the experiment, the Eh values were negative for the mining-contaminated soil and slightly positive for the mining- and industry-contaminated soil. However, after treatment with OPC and MgO, all the leachates showed negative redox potential values.

All three reactive materials led to the mobilization of Cu in mining-contaminated soil (Fig. 3a) (Tables 5–8). Cu was partially removed at the end of the assay when OPC was used to treat the

Table 4
Main characteristics of low-mineralized water used in the leaching experiments.

Parameter	HCO₃(−)	SO₄	Cl	NO₃	NO₂	PO₄	F	Br	Mg	Ca	Na	K	Si
Unit	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l
Detection limit	1	0.03	0.03	0.05	0.03	0.06	0.01	0.03	0.1	0.1	0.1	0.03	0.2
Method	TITR	IC	IC	IC	IC	IC	IC	IC	ICP-OES	ICP-OES	ICP-OES	ICP-MS	ICP-MS
	98	11	5.6	1.99	0.01	0.03	1	0	4.3	27.4	12.2	1.2	8.5

Parameter		Cu		Zn		As		Sb		Pb
Unit		μg/l		μg/l		μg/l		μg/l		μg/l
Detection limit		0.2		0.5		0.03		0.01		0.01
Method		ICP-MS		ICP-MS		ICP-MS		ICP-MS		ICP-MS
		3.3		2.2		1.02		0.25		0.20

Table 5
Temporal evolution of metal contents in leachates from mining contaminated soils and industrial contaminated soils. The leachates were successively obtained since first leachate (0 min) until the last leachate (420 min), corresponding to 9.3 pore volumes. M: mining soil, I: mining and industrial contaminated soils. M-1/I-1: 0 min, M-2/I-2: 30 min, M-3/I-3: 60 min, M-4/I-4: 120 min, M-5/I-5: 180 min, M-6/I-6: 300 min, M-7/I-7: 420 min. Values in μg/l.

Analyte symbol	Zn	Pb	As	Sb	Cu
Unit	μg/l	μg/l	μg/l	μg/l	μg/l
Detection limit	0.5	0.01	0.03	0.01	0.2
Analysis method	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS
M-1	487	32	5.2	27.5	42
M-1A	1960	410	14.1	30.2	683
M-2	389	79	6.1	22.8	64
M-3	233	41	4.6	18	21
M-4	298	44	4.6	14.6	30
M-5	303	46	3.7	12.3	21
M-6	247	51	3.4	11.1	20
M-7	226	53	3.6	10.4	19
I-1	>2500	449	5.4	21	218
I-1A	>2500	1000	5.3	22.5	312
I-2	>2500	430	2	14.2	169
I-3	>2500	535	1.5	13.8	174
I-4	>2500	588	1.2	13	181
I-5	>2500	605	1	11.7	173
I-6	>2500	625	1.1	11.2	171
I-7	>2500	684	1.2	9.3	110
MCL*	1200	150	60	100	600

(*)MCL: maximum contaminated level of leachates (percolation test) of solid wastes, in order to deposit in landfills (inert solid wastes).

Table 6
Temporal evolution of metal contents in leachates of OPC experiments. The leachates were successively obtained since first leachate (0 min) until the last leachate (420 min), corresponding to 9.3 pore volumes. OCM: mining soil, CI: mining and industrial contaminated soils. OCM-1/CI-1: 0 min, OCM-2/CI-2: 30 min, OCM-3/CI-3: 60 min, OCM-4/CI-4: 120 min, OCM-5/CI-5: 180 min, OCM-6/CI-6: 300 min, OCM-7/CI-7: 420 min. Values in μg/l.

Analyte symbol	Zn	Pb	As	Sb	Cu
Unit	μg/l	μg/l	μg/l	μg/l	μg/l
Detection limit	0.5	0.01	0.03	0.01	0.2
Analysis method	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS
OCM-1	116	97	30.7	28.3	>2000
OCM-2	99	98	29.1	30.5	1460
OCM-3	121	95	27	37.1	702
OCM-4	111	95	25.2	41.6	321
OCM-5	92	97	24.5	45.3	215
OCM-6	117	99	25.2	48.9	155
OCM-7	96	94	27	51.7	127
CI-1	173	140	33.7	32.7	1900
CI-2	111	133	15.3	28.2	746
CI-3	109	135	12.1	29.5	465
CI-4	157	146	8.1	37.9	223
CI-5	76	154	6.6	51.5	142
CI-6	93	162	6.1	71.1	94
CI-7	81	164	5.3	87.4	76

Table 7
Temporal evolution of metal contents in leachates of phosphoric acid experiments. The leachates were successively obtained since first leachate (0 min) until the last leachate (420 min), corresponding to 9.3 pore volumes. PM: mining soil, PSI: mining and industrial contaminated soils. PM-1/PSI-1: 0 min, PM-2/PSI-2: 30 min, PM-3/PSI-3: 60 min, PM-4/PSI-4: 120 min, PM-5/PSI-5: 180 min, PM-6/PSI-6: 300 min, PM-7/PSI-7: 420 min. Values in μg/l.

Analyte symbol	Zn	Pb	As	Sb	Cu
Unit	μg/l	μg/l	μg/l	μg/l	μg/l
Detection limit	0.5	0.01	0.03	0.01	0.2
Analysis method	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS
PM-1	>25000	60	2530	45	7240
PM-2	>2500	16	1760	43.3	>2000
PM-3	>2500	7	1270	45.7	>2000
PM-4	>2500	5	912	50.5	1510
PM-5	>2500	11	726	57.6	1200
PM-6	>2500	3	491	56.7	836
PM-7	>2500	1	391	63.9	675
PSI-1	>25000	360	5850	232	>20000
PSI-2	>2500	71	1980	55.3	>2000
PSI-3	>2500	36.5	1300	39.2	>2000
PSI-4	>2500	16	645	31.2	>2000
PSI-5	>2500	19	508	33.5	>2000
PSI-6	>2500	4	331	40	>2000
PSI-7	>2500	3	229	46.4	>2000

Table 8

Temporal evolution of metal contents in leachates of MgO experiments. The leachates were successively obtained since first leachate (0 min) until the last leachate (420 min), corresponding to 9.3 pore volumes. MGM: mining soil, MGI: mining and industrial contaminated soils. MGM-1/MGI-1: 0 min, MGM-2/MGI-2: 30 min, MGM-3/MGI-3: 60 min, MG-4/MGI-4: 120 min, MGM-5/MGI-5: 180 min, MGM-6/MGI-6: 300 min, MGM-7/MGI-7: 420 min. Values in µg/l.

Analyte symbol	Zn	Pb	As	Sb	Cu
Unit	µg/l	µg/l	µg/l	µg/l	µg/l
Detection limit	0.5	0.01	0.03	0.01	0.2
Analysis method	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS
MGM-1	>2500	>2000	6.7	7.7	>2000
MGM-2	>2500	>2000	6.3	9.7	>2000
MGM-3	>2500	>2000	5.3	6.7	1500
MGM-4	>2500	>2000	4.6	5.5	1100
MGM-5	>2500	>2000	4.3	5.8	795
MGM-6	>2500	>2000	4.2	5.8	538
MGM-7	>2500	>2000	4.6	6.7	406
MGI-1	1570	>2000	19.1	2.4	>2000
MGI-2	1800	>2000	20.7	3.4	>2000
MGI-3	1750	>2000	9.75	2.75	1380
MGI-4	1550	>2000	5.8	2.6	616
MGI-5	976	>2000	3.5	2.1	371
MGI-6	665	>2000	3.5	2.9	269
MGI-7	513	>2000	3.3	4	243

mining- and industry-contaminated soil (Fig. 3b). At neutral to alkaline pH (>7), Cu oxides are stable. However, Cu was clearly mobilized in the experimental conditions. Some authors found that the addition of H_3PO_4 increased Cu and Zn solubility [1].

The leaching of Pb showed that OPC and MgO treatments mobilized this metal (Tables 6 and 8). In contrast, despite the increase in soil acidity, the addition of H_3PO_4 reduced the mobility of Pb in the

two soils (Table 7). The use of OPC also led to the removal of Pb in the mining- and industry-contaminated soil (Fig. 4b), as in similar experiments [8,10,11]. However, the use of MgO always favoured Pb mobilization, possibly because of the increase in pH above 12, which may have promoted the release of the metal [12]. The results of Zn leaching in the mining- and industry-contaminated soil (Fig. 5a and b) showed that Zn was retained when OPC was used as a reactive material (Table 6), removed when MgO was added (Fig. 5b, Table 8) and mobilized when H_3PO_4 was added (Table 7). However, in similar experiments, Zn was immobilized when P-amendments were added [29].
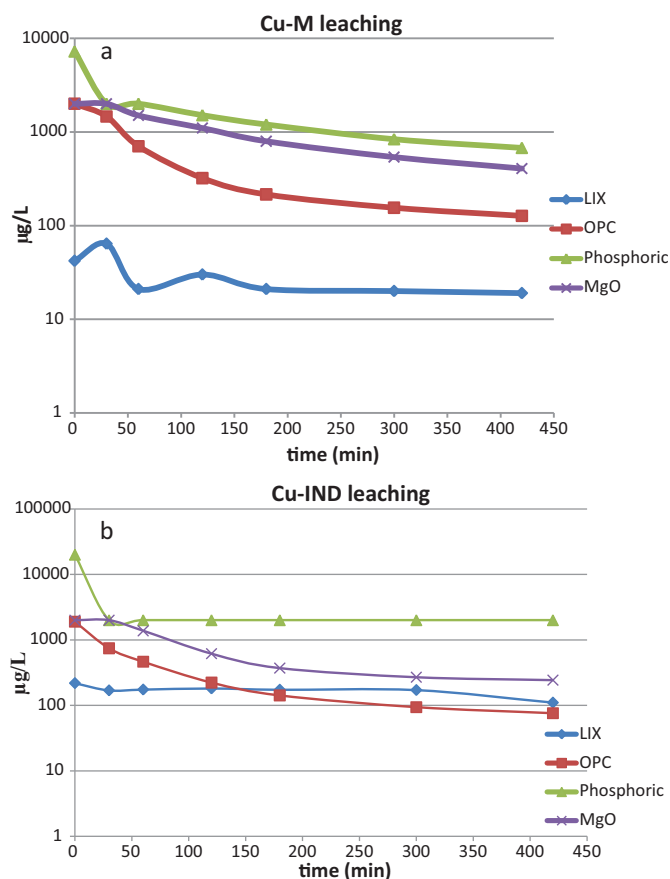

Fig. 3. a: Evolution of Cu in the leaching experiments with mining soil. Values in µg/l. b: Evolution of Cu in the leaching experiments with mining and industrial soil. Values in µg/l. LIX: low-mineralized water leaching experiment with "pure" contaminated soils; OPC: low-mineralized water leaching experiment with OPC; Phosphoric: low-mineralized water leaching experiment with phosphoric acid; and MgO: low-mineralized water leaching experiment with MgO.
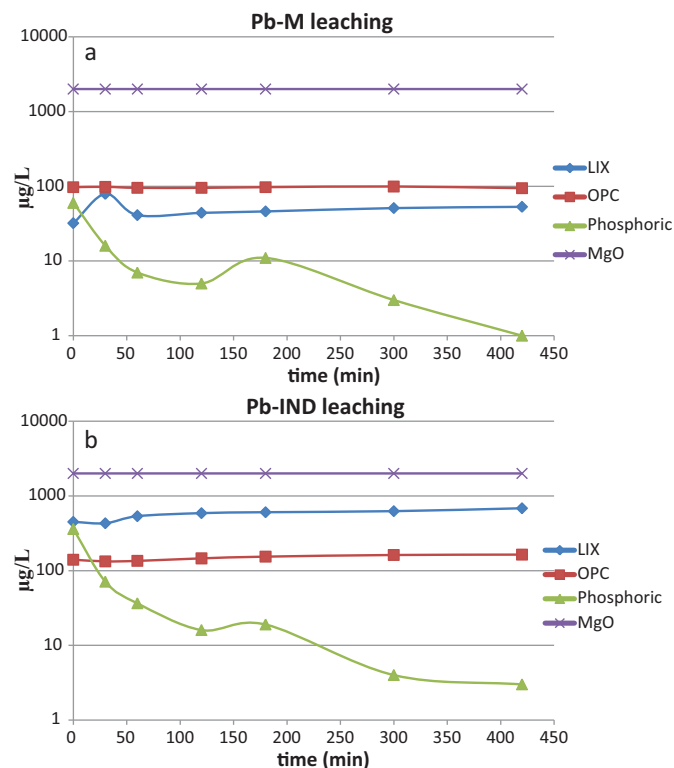

Fig. 4. a: Evolution of Pb in the leaching experiments with mining soil. Values in µg/l. b: Evolution of Pb in the leaching experiments with mining and industrial soil. Values in µg/l. LIX: low-mineralized water leaching experiment with "pure" contaminated soils; OPC: low-mineralized water leaching experiment with OPC; Phosphoric: low-mineralized water leaching experiment with phosphoric acid; and MgO: low-mineralized water leaching experiment with MgO.
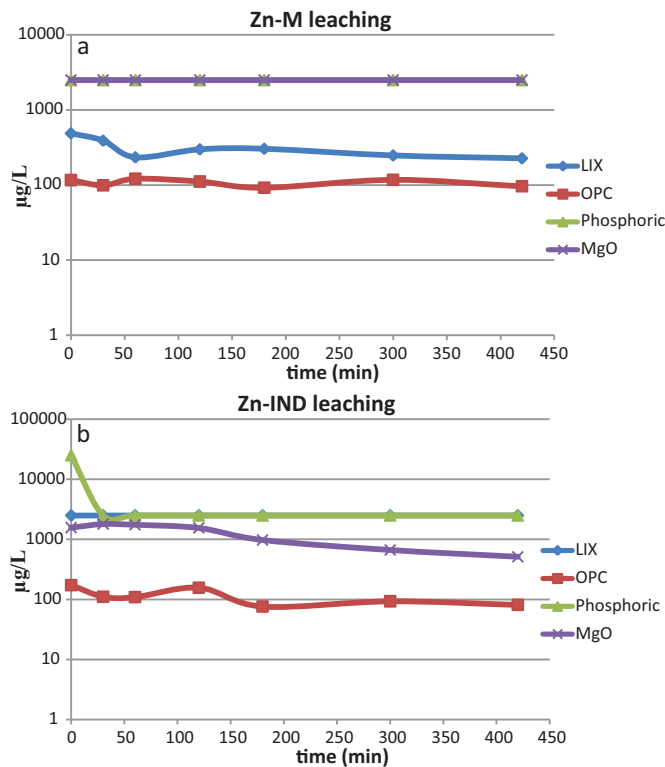
Fig. 5. a: Evolution of Zn in the leaching experiments with mining soil. Values in μg/l. b: Evolution of Zn in the leaching experiments with mining and industrial soil. Values in μg/l. LIX: low-mineralized water leaching experiment with "pure" contaminated soils; OPC: low-mineralized water leaching experiment with OPC; Phosphoric: low-mineralized water leaching experiment with phosphoric acid; and MgO: low-mineralized water leaching experiment with MgO.

The correlation studies between pH and metal concentration in the leachates showed a high correlation coefficient between pH and Pb ($R^2 = 0.88$) in the OPC experiment with industrial soil, and a significant coefficient between pH and Cu ($R^2 = 0.63$), while the correlation in the mining soil experiment was very low. In the experiments with phosphoric acid, pH correlates with Cu ($R^2 = 0.91$) and Pb ($R^2 = 0.87$) in the mining soil experiment, and also correlates with Cu, Pb and Zn in the industrial soil experiment. The correlation between pH and Cu in the MgO experiments was significant in the mining and industrial soil experiments, and greater for Zn in the industrial soil assay ($R^2 = 0.95$), whereas Pb showed a very low correlation, due to high concentrations detected.

Fig. 6. Eh–pH diagram for the system Cu–SO_4^{2-}–Cl^- at 25 °C. Total $SO_4^{2-} = 0.06$ M, total $Cl^- = 0.44$ M and total $Cu^{2+} = 0.01$ M. Ionic strength = 1 M. Builded by MEDUSA code (Puigdomenech [30]). (c): Solid phase, $E_{SHE/V}$: Eh (V).

3.3. Geochemical modelling

Hydrogeochemical analyses of leachates were conducted to evaluate the speciation of dissolved constituents and to calculate the saturation state of the effluents (Tables 9 and 10). The PHREEQC (version 2.10.03) numerical code was used for the calculations. In addition, some pH–Eh diagrams were drawn up using the MEDUSA hydrogeochemical code [30].

The study of aqueous Cu speciation showed that the predominant species in treated leachates were $Cu(OH)_2$, $CuCl_2^-$ and Cu^+ (Table 9), which may indicate the mobilization of Cu if these species are stable in the pH–Eh conditions of the experiments. In addition, the pH–Eh diagram of Cu (Fig. 6) for these conditions shows that $CuCl_2^-$ is the most stable species under low pH and oxidant conditions. This may explain the mobility of Cu in the H_3PO_4 leaching experiment. $Cu(OH)_2^-$ is the most stable species under high pH and slightly reducing conditions, coinciding with the Eh–pH values of OPC and MgO experiments. Furthermore, leachates were saturated with respect to $Cu(OH)_2$ (Table 10), except in the MgO experiments, despite the fact that Cu was mobilized with the use of these materials.

The removal of Pb after H_3PO_4 addition may be related to the precipitation of chloropyromorphite. Thus, under the Eh–pH conditions of the phosphoric acid experiment, this mineral phase was
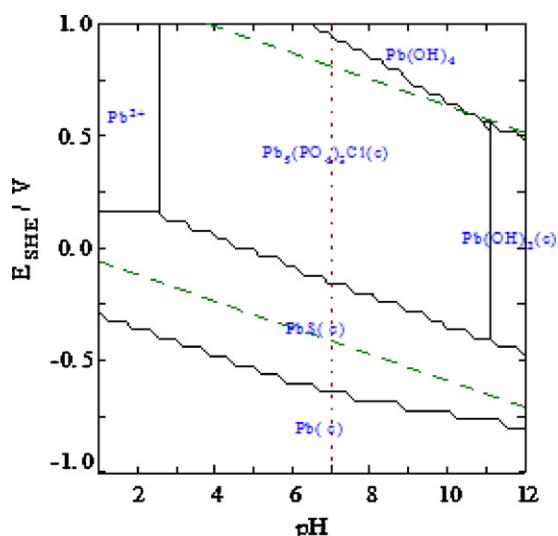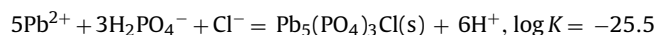
Table 9
Distribution of species for leachates. Data calculated using PHREEQC and database Minteq. Values in molality.

Species	M-1A	I-1A	OCM-1	CI-1	PM-1	PSI-1	MGM-1	MGI-1
Cu								
Cu^+	8.52×10^{-6}	3.25×10^{-6}	7.67×10^{-8}	7.24×10^{-8}	1.09×10^{-7}	2.31×10^{-7}	1.09×10^{-8}	4.18×10^{-8}
$CuCl_2^-$	1.46×10^{-6}	1.56×10^{-6}	1.79×10^{-8}	1.28×10^{-7}	9.62×10^{-5}	2.47×10^{-4}	1.67×10^{-9}	1.83×10^{-8}
$Cu(OH)_2$	7.02×10^{-7}	3.70×10^{-8}	3.06×10^{-5}	2.94×10^{-5}	4.11×10^{-13}	2.43×10^{-13}	2.36×10^{-5}	2.80×10^{-5}
$CuCO_3$	5.17×10^{-8}	1.80×10^{-8}	5.36×10^{-12}	7.87×10^{-12}	1.51×10^{-10}	2.92×10^{-9}	6.42×10^{-13}	1.99×10^{-12}
Pb								
$PbCO_3$	1.71×10^{-6}	1.62×10^{-6}	9.85×10^{-11}	3.28×10^{-10}	5.83×10^{-11}	7.99×10^{-10}	6.50×10^{-12}	6.56×10^{-11}
$PbOH^+$	8.04×10^{-8}	8.03×10^{-8}	5.72×10^{-10}	2.65×10^{-9}	8.17×10^{-12}	1.12×10^{-11}	3.03×10^{-11}	2.59×10^{-10}
$PbSO_4$	7.13×10^{-8}	1.77×10^{-6}	8.80×10^{-14}	2.59×10^{-12}	3.60×10^{-8}	2.18×10^{-7}	2.55×10^{-17}	1.06×10^{-14}
Pb^{2+}	6.64×10^{-8}	9.13×10^{-7}	1.33×10^{-13}	1.50×10^{-12}	1.27×10^{-7}	5.83×10^{-7}	9.02×10^{-16}	1.78×10^{-14}
$Pb(OH)_4^{-2}$	–	–	2.91×10^{-7}	2.17×10^{-7}	–	–	8.70×10^{-6}	7.85×10^{-6}
Zn								
Zn^{2+}	1.52×10^{-5}	1.89×10^{-5}	9.69×10^{-13}	9.84×10^{-12}	3.21×10^{-4}	2.89×10^{-4}	4.44×10^{-14}	3.39×10^{-13}
$ZnSO_4$	6.74×10^{-6}	1.55×10^{-5}	2.62×10^{-13}	7.09×10^{-12}	3.87×10^{-5}	4.49×10^{-5}	5.21×10^{-16}	8.57×10^{-14}
$ZnCO_3$	4.69×10^{-6}	4.13×10^{-7}	8.48×10^{-12}	2.61×10^{-11}	1.81×10^{-9}	4.73×10^{-9}	3.80×10^{-12}	1.50×10^{-11}
$Zn(SO_4)_2^{-2}$	3.73×10^{-7}	3.56×10^{-6}	7.39×10^{-15}	9.32×10^{-13}	1.33×10^{-6}	3.01×10^{-6}	6.93×10^{-19}	2.87×10^{-15}
$Zn(OH)_3^-$	–	–	9.19×10^{-7}	7.01×10^{-6}	–	–	2.20×10^{-5}	1.56×10^{-5}

Fig. 7. Eh–pH diagram for the system Pb–SO_4^{2-}–Cl^-–PO_4^{3-} at 25 °C. Total SO_4^{2-} = 0.06 M, total Cl^- = 0.01 M, total PO_4^{3-} = 0.01 M and total Pb^{2+} = 0.01 M. Ionic strength = 1 M. Builded by MEDUSA code (Puigdomenech [30]). (c): Solid phase, $E_{SHE/V}$: Eh (V).

the most stable species (Fig. 7). This suggests that Pb is controlled by chloropyromorphite. Moreover, the leachates (except in the OPC and MgO experiments) were clearly saturated with respect to this mineral phase (Table 10). Therefore, Pb removal may be associated with the following reaction:

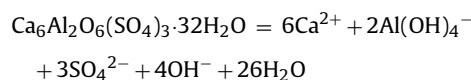$$5Pb^{2+} + 3H_2PO_4^- + Cl^- = Pb_5(PO_4)_3Cl(s) + 6H^+, \log K = -25.5$$

In contrast, under high pH (>12) and reducing conditions, such as in the experiment with MgO, Pb was highly mobile. Lead is known to form stable aqueous complexes with OH^-, Cl^-, CO_3^{2-}, SO_4^{2-} and HS^-, besides, in general, complexation with chloride and sulphate is most important at near-neutral to moderate alkaline conditions, whereas OH^- species dominate at high pH. Thus, PHREEQC showed that most abundant species in OPC and MgO experiments was $Pb(OH)_4^-$, with concentrations of 2.1–2.9×10^{-7} mol in OPC experiments and 7.7–8.7×10^{-6} mol in MgO experiments (Table 9).

The Pb mobilization at high alkaline conditions was, also, detected by De Angelis et al. [12], which showed that the high alkalinity of cement creates favourable conditions to the elevated
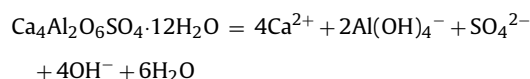
release of Pb. Moreover, although the possible "doping" of cementitious components by lead may also to favour the Pb mobilization [12], the Pb hydroxyl species formation, seems the most likely mechanism of lead mobilization at elevated pH conditions. In this way, the MgO experiments which reached pH values of 12.0–12.6, were associated with the higher concentrations of Pb leached (>2 mg/l), while the OPC experiments with pH values of 10.8–11.5, generated lower concentrations of Pb leached.

In the study of Pb and Zn removal by OPC, we added the chemical reactions of the main cement hydrates to the PHREEQC numerical code:
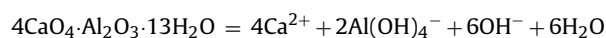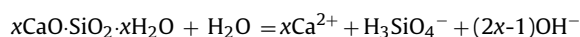
Ettringite

$$Ca_6Al_2O_6(SO_4)_3 \cdot 32H_2O = 6Ca^{2+} + 2Al(OH)_4^-$$
$$+ 3SO_4^{2-} + 4OH^- + 26H_2O$$

Monosulphate

$$Ca_4Al_2O_6SO_4 \cdot 12H_2O = 4Ca^{2+} + 2Al(OH)_4^- + SO_4^{2-}$$
$$+ 4OH^- + 6H_2O$$

Calcium aluminate hydrate (C_4AH_{13})

$$4CaO_4 \cdot Al_2O_3 \cdot 13H_2O = 4Ca^{2+} + 2Al(OH)_4^- + 6OH^- + 6H_2O$$

Microcrystalline hydrate (CSH)

$$xCaO \cdot SiO_2 \cdot xH_2O + H_2O = xCa^{2+} + H_3SiO_4^- + (2x\text{-}1)OH^-$$

x = Ca/Si ratio

The solubility properties and $\log K$ were obtained from [31]. Gypsum, portlandite and brucite have well defined solubility in PHREEQC. Thus, the mixing of OPC and water at environmental temperature promotes the formation of a stabilizing agent composed of CSH gel (50–60%), portlandite (20–25%), ettringite (15–20%) and other minority phases. In some cases, the removal of Pb and similar metals can be achieved by sorption on CSH, substitution on the CSH lattice, and precipitation or co-precipitation with some of the hydrated phases. However, a study of the saturation of OPC leachates with respect to these minerals (Table 10) only detected the saturation of brucite and the near saturation of ettringite. Furthermore, OPC leachates are saturated with respect

Table 10
Calculated saturation index for leachates using PHREEQC and database Minteq.

Minerals	M-1A	I-1A	OCM-1	CI-1	PM-1	PS-1	MGM-1	MGI-1
Cu and Fe minerals								
$Cu(OH)_2$	−1.35	−2.87	0.29	0.23	−7.57	−7.77	0.23	0.34
Ferrihydrite	−0.09	−3.14	−0.60	−0.33	−8.74	−10.24	−1.24	−1.11
Goethite	4.07	1.03	3.56	3.79	−4.57	−6.04	2.97	3.14
Jarosite	−3.26	−9.05	−15.79	−13.43	−17.71	−20.71	−23.26	−18.73
Pb minerals								
Anglesite	−2.07	−0.67	−7.98	−6.50	−2.36	−1.57	−11.52	−8.91
Cerussite	0.20	0.18	−4.04	−3.50	−4.26	−3.11	−5.23	−4.24
$Pb(OH)_2$	0.17	−0.91	1.55	1.85	−8.01	−8.34	1.23	1.85
Chloropyromorphite	12.88	15.98	−11.36	−6.09	4.44	7.66	−19.60	−15.02
Zn minerals								
Zincite	−0.57	−2.68	−0.69	−0.44	−7.69	−8.71	−0.15	0.08
Zincosite	−10.83	−10.46	−18.24	−16.86	−10.06	−9.96	−20.88	−18.62
Other minerals								
Calcite	0.02	−0.87	1.41	1.40	−4.11	−3.25	2.51	2.60
Ettringite	–	–	−1.62	−0.19	–	–	–	–
Monosulphate	–	–	−5.14	−5.58	–	–	–	–
C_4AH_{13}	–	–	−9.60	−11.24	–	–	–	–
CSH	–	–	−1.21	−1.22	–	–	–	–
Portlandite	−10.04	−11.99	−3.02	−3.30	−17.88	−18.48	−1.02	−1.27
Brucite	−4.63	−6.39	0.21	0.16	−12.03	−13.01	2.30	0.60
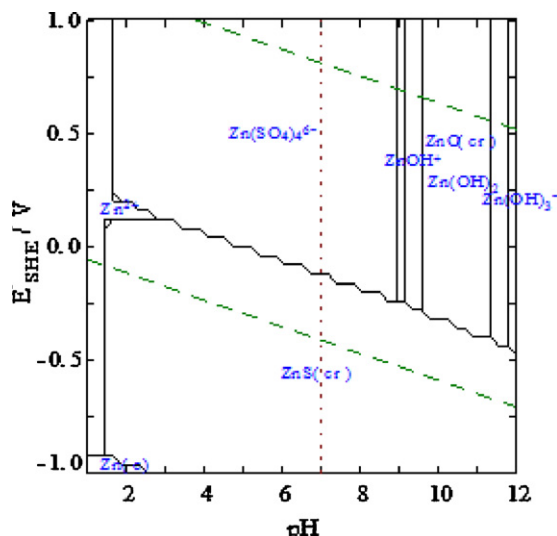
Fig. 8. Eh–pH diagram for the system Zn–SO$_4^{2-}$–Cl$^-$ at 25 °C. Total SO$_4^{2-}$ = 0.06 M, total Cl$^-$ = 0.44 M and total Zn^{2+} = 0.01 M. Ionic strength = 1 M. Builded by MEDUSA code (Puigdomenech [30]). (c): Solid phase, $E_{SHE/V}$: Eh (V).

to Pb(OH)$_2$, which may suggest that this mineral phase controls Pb. Since leachates showed high concentrations of available sulphate and the pH reached in the OPC experiments was 10–11, Pb and Zn mobilization at moderate alkaline conditions may be controlled by these mineral phases.

According to the pH–Eh diagram (Fig. 8), Zn should be a mobile element under low and medium pH and oxidizing conditions such as those of the phosphoric acid tests, and under high pH (pH > 12) and slightly reducing conditions such as those of the MgO tests. However, Zn should be less mobile in alkaline and low redox environments, due to the possible precipitation of zinc oxides and hydroxides. Similarly, under reducing conditions and in a high-S system, sphalerite precipitation would also reduce Zn mobility (Fig. 8).

The geochemical speciation of Zn leachates indicates that Zn may be not retained in the treated samples (Table 9). This metal may be mobilized as Zn(OH)$_3^-$ in the OPC- and MgO-treated samples, although it was immobilized by OPC in the column experiments. In addition, it may be mobilized as Zn^{2+} and ZnSO$_4^0$ in the tests with phosphoric acid, which was not obvious from the pH–Eh diagram (Fig. 8) calculated from the limited Medusa database. The PHREEQC calculations indicated that all leachates were subsaturated with respect to all the Zn-solid phases available in the database (Table 10).

4. Conclusions

In the mining-contaminated soil, Cu was mobilized with the three reactive materials used. However, when OPC was used to treat the mining- and industry-contaminated soil, Cu was partially removed at the end of the assay.

The Pb concentrations of leachates of pure mining and industrial contaminated soils (32–410 μg/l and 430–1000 μg/l, respectively) were reduced to 1–60 and 3–360 μg/l, respectively, in the phosphoric acid experiment. The mobilization of Pb at high alkaline conditions, when Pb(OH)$_4^-$ is the most stable species, may be the main obstacle to the use of OPC and MgO in the immobilization of this metal.

The removal of Pb after H$_3$PO$_4$ addition may be related to the precipitation of chloropyromorphite. Thus, under the Eh–pH conditions of the phosphoric acid experiment, this mineral phase was the most stable species, which suggests that chloropyromorphite

controls Pb. In contrast, under high pH (>12) and reducing conditions, such as in the MgO experiment, Pb was highly mobile. In general, the solubility of amphoteric metals such as Pb varies with pH, and the optimum pH range to precipitation is about 10, thus the OPC used in the experiments may be in the frontier to Pb immobilization, since the pH conditions of the OPC experiments were 10.8–11.5.

In the mining- and industry-contaminated soil, Zn was retained by OPC and removed by MgO. Zn was mobilized after H$_3$PO$_4$ addition, despite the results of other similar experiments.

References

[1] X. Cao, A. Wahbi, L. Ma, B. Li, Y. Yang, Immobilization of Zn, Cu, and Pb in contaminated soils using phosphate rock and phosphoric acid, J. Hazard. Mater. 164 (2009) 555–564.
[2] R.G. Ford, R.T. Wilkin, R.W. Puls, Monitored Natural Attenuation of Inorganic Contaminants in Ground Water, vol. 2, U.S. Environmental Protection Agency, Ada, Oklahoma, 2007.
[3] Environmental Pollution Agency, Review of scientific literature on the use of stabilisation/solidification for the treatment of contaminated soil, solid waste and sludges, Science Report SC980003/SR2, Bristol UK, 2004.
[4] A. Dybowska, M. Farago, E. Valsami-Jones, I. Thornton, Remediation strategies for historical mining and smelting sites, Sci. Prog. 89 (2006) 71–138.
[5] A. Navarro, J.M. Chimenos, E. Pérez, F. Espiell, Evaluación del comportamiento de una barrera reactiva mediante ensayos en columna, VII Simposio de Hidrogeología, Murcia, Hidrogeología y Recursos Hidráulicos 24 (2001) 327–339.
[6] A. Navarro, J.M. Chimenos, D. Muntaner, Caracterización de materiales reactivos para el control de metales pesados en aguas subterráneas, Hidropres 39 (2003) 64–74.
[7] A. Navarro, J.M. Chimenos, D. Muntaner, I. Fernández, Permeable reactive barriers for the removal of heavy metals: lab-scale experiments with low-grade magnesium oxide, Ground Water Monit. Remed. 26 (2006) 142–152.
[8] B. Alpaslan, M. Yukselen, Remediation of lead contaminated soils by stabilization/solidification, Water Air Soil Pollut. 133 (2002) 253–263.
[9] G. Thevenin, J. Pera, Interactions between lead and different binders, Cem. Concr. Res. 29 (1999) 1605–1610.
[10] M.A. Yukselen, B. Alpaslan, Leaching of metals from soil contaminated by mining activities, J. Hazard. Mater. B87 (2001) 289–300.
[11] C. Park, Hydration and solidification of hazardous wastes containing heavy metals using modified cementitious materials, Cem. Concr. Res. 30 (2000) 429–435.
[12] G. De Angelis, F. Medici, M.R. Montereali, L. Pietrelli, Reuse of residues from lead batteries recycle: a feasibility study, Waste Manage. 22 (2002) 925–930.
[13] J.R. Pichtel, W.A. Jick, P. Sutton, Comparison of amendments and management practises for long-term reclamation of abandoned mine lands, J. Environ. Qual. 23 (1994) 766–772.
[14] P. Theodoratus, A. Moirou, A. Xenidis, I. Paspialanis, The use of sewage sludge for the stabilization of soil contaminated by mining activities, J. Harzard. Mater. B77 (2000) 177–191.
[15] L. Simon, Stabilization of metals in acidic mine spoil with amendments and red fescue (*Festuca rubra* L.) growth, Environ. Geochem. Health 27 (2005) 289–300.
[16] A. Navarro, F. Martínez, Effects of sewage sludge application on heavy metal leaching from mine tailings impoundments, Biores. Technol. 99 (2008) 7521–7530.
[17] A.H.M. Hulshof, D.W. Blowes, W.D. Gould, Evaluation of in situ layers for treatment of acid mine drainage: a field comparison, Water Res. 40 (2006) 1816–1826.
[18] G.J. Zagury, V.I. Kulnieks, C.M. Neculita, Characterization and reactivity assessment of organic substrates for sulphate-reducing bacteria in acid mine drainage treatment, Chemosphere 64 (2006) 944–954.
[19] L.S. Forsberg, S. Ledin, Effects of sewage sludge on pH and plant availability of metals in oxidising sulphide mine tailings, Sci. Total Environ. 353 (2006) 21–35.
[20] I. Ribet, C.J. Ptacek, D.W. Blowes, J.L. Jambor, The potential for metal release by reductive dissolution of weathered mine tailings, J. Contam. Hydrol. 17 (1995) 239–273.
[21] C.A. Cravotta, Effect of sewage sludge on formation of acidic ground water at a reclaimed coal mine, Ground Water 35 (1998) 9–19.
[22] P. Schwab, D. Zhu, M.K. Banks, Heavy metal leaching from mine tailings as affected by organic amendments, Biores. Technol. 98 (2007) 2935–2941.
[23] I.T. Urasa, S.F. Macha, Investigation into heavy metal uptake by waste water sludges, Water Air Soil Pollut. 109 (1997) 207–218.
[24] P. Miretzky, A. Fernández-Cirelli, Phosphates for Pb immobilization in soils: a review, Environ. Chem. Lett. 6 (2008) 121–133.

[25] J. Yang, D. Mosby, Field assessment of treatment efficacy by three methods of phosphoric acid application in lead-contaminated urban soil, Sci. Total Environ. 366 (2006) 136–142.

[26] R. Melamed, X. Cao, M. Chen, L.Q. Ma, Field assessment of lead immobilization in a contaminated soil after phosphate application, Sci. Total Environ. 305 (2003) 117–127.

[27] J. Yang, D. Mosby, S.W. Casteel, R.W. Blanchar, In vitro lead bioaccessibility and phosphate leaching as affected by surface application of phosphoric acid in lead-contaminated soil, Arch. Environ. Contam. Toxicol. 43 (2002) 399–405.

[28] J. Yang, D. Mosby, S.W. Casteel, R.W. Blanchar, Lead immobilization using phosphoric acid in a smelter-contaminated urban soil, Environ. Sci. Technol. 35 (2001) 3553–3559.

[29] N.T. Basta, S.L. McGowen, Evaluation of chemical immobilization treatments for reducing heavy metal transport in a smelter-contaminated soil, Environ. Pollut. 127 (2004) 73–82.

[30] I. Puigdomenech, Make Equilibrium using Sophisticated Algorithms (MEDUSA) Program, Inorganic Chemistry Department, Royal Institute of Technology, 100 44, Stockholm, Sweden, 2004, http://web.telia.com/.

[31] J.Y. Park, B. Batchelor, Prediction of chemical speciation in stabilized/solidified wastes using a general chemical equilibrium model. Part I. Chemical representation of cementitious binders, Cem. Concr. Res. 29 (1999) 361–368.

[32] M. Acutis, M. Donatelli, SOILPAR 2.00: software to estimate soil hydrological parameters and functions, Eur. J. Agron. 18 (2003) 373–377.