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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.

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

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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 system (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