

A holistic approach to phosphate stabilization treatment of metal contaminated soil

M. Zupančič¹ and P. Bukovec²

¹ Faculty of Chemistry and Chemical Technology, University of Ljubljana, Aškerčeva 5, 1000 Ljubljana, SLOVENIA, marija.zupancic@fkkt.uni-lj.si

² Faculty of Chemistry and Chemical Technology, University of Ljubljana, Aškerčeva 5, 1000 Ljubljana, SLOVENIA, peter.bukovec@fkkt.uni-lj.si

Abstract. In our study we showed the importance of holistic approach to evaluation of chemical stabilization using phosphate amendments, where all aspects of chemical treatments were observed. An extensive evaluation of metal stabilization in contaminated soil and an evaluation of the leaching of phosphorus induced after treatment were performed. The soil from the former zinc smelter area in the Celje region, used in this study, was heavily polluted with Zn ($34\,400 \pm 1500 \text{ mg kg}^{-1}$), Pb ($20\,400 \pm 1500 \text{ mg kg}^{-1}$), As ($950 \pm 10 \text{ mg kg}^{-1}$), Cu ($549 \pm 7 \text{ mg kg}^{-1}$) and Cd ($158 \pm 4 \text{ mg kg}^{-1}$). The results of Toxicity Characteristic Leaching Procedure showed high mobility of Zn ($540 \pm 25 \text{ mg L}^{-1}$), Pb ($12.7 \pm 0.5 \text{ mg L}^{-1}$) and Cd ($2.9 \pm 0.1 \text{ mg L}^{-1}$). To immobilize metals in the soil, mixtures of soil with phosphate (variable molar ratio of hydroxyapatite and phosphoric acid) were prepared with a constant molar Pb:P ratio of 1:10. Hydroxyapatite as the only source of phosphate showed a high stabilization efficiency, above all for Pb with over 97 % of primary acetic acid leachable Pb immobilized. The addition of phosphoric acid as a source of phosphate resulted in an increase in leaching of phosphorus up to 50 mg L^{-1} in water extracts. Lime that was also added in some stabilization mixtures increased the stabilization efficiency of phosphate and also decreased the treatment-induced phosphate leaching. To evaluate the long-term stability of immobilization, leaching of metals and phosphorus was assessed in a column experiment with synthetic precipitation that in general showed steady decrease in leachability of metals and phosphorus with quite high cumulative Zn and Cd concentrations in leachates of soil sample and extremely high (30% of total added P concentration) cumulative P concentrations in leachates of mixture with highest amount of added phosphoric acid and no addition of lime.

Key words: Chemical stabilization, contaminated soil, lime, metal, phosphate, remediation

Introduction

Chemical stabilization of metal contaminated soil is sustainable and economically acceptable remediation technology. By chemical stabilization, mobile metal chemical species are transformed into less mobile ones, thus reducing the risk of heavy metal transport from contaminated soil to the ground and surface waters, and also decreasing the risk of the potential bioavailability/phytoavailability of metals. Contaminant immobilizing amendments decrease metal mobility by inducing various sorption processes: adsorption to mineral surfaces, formation of stable complexes, surface precipitation and ion exchange. Phosphate treatment was proven to be an efficient approach to immobilizing metals in contaminated soil and waste media (Bolan et al.,

2003; Miretzky and Fernandez-Cirelli, 2008; Park et al., 2011). Because of water resource eutrophication and the need for water protection strategies, estimation of diffuse phosphorus (P) leaching losses from soil is an important issue. Although many studies dealing with the phosphate treatment of metal-contaminated soil and wastes were reported, treatment-induced leaching of P has been largely overlooked.

In our study, heavily polluted soil from the former zinc smelter area in the Celje region, Slovenia, was used with the aim to find the equilibrium between all aspects (parameters) of phosphate based treatments of metal contaminated soil and to show the importance of such holistic approach. An extensive study on different stabilization mixtures, dealing with two phosphate sources and lime, was performed. All mixtures have the

Table 1. Mean TCLP concentrations (in mg kg^{-1} , $N=3$) of metals in soil and soil mixtures with different HA:H₃PO₄:CaO molar ratios and metal stabilization efficiency (in %) of mixtures, except for As where destabilization is presented as the n-times increase in leachability

mixture n(HA):n(H ₃ PO ₄):n(CaO)	Ni		Cu		Zn		As		Cd		Pb	
	TCLP conc. [mg L^{-1}]	stab. [%]										
Soil	0,11		0,33		437		0,02		2,9		13	
(1:0):0	0,09	17	0,11	65	226	48	1,4	90	1,3	55	0,3	97
(1:0.5):0	0,12	destab.	0,16	51	285	35	1,3	85	1,5	46	0,5	96
(1:1):0	0,13	destab.	0,18	46	277	37	1,3	85	1,3	53	0,4	97
(1:2):0	0,15	destab.	0,16	51	270	38	1,6	101	1,4	53	0,2	98
(1:1):1	0,07	34	0,07	78	152	65	1,0	62	1,2	58	1,1	91
(1:1):2	0,05	54	0,03	91	31	93	0,2	16	0,6	78	0,9	93
(1:1):3	0,04	63	0,02	94	10	98	0,1	5,5	0,3	90	0,3	98
(1:2):1	0,07	35	0,07	77	103	76	1,4	90	1,0	67	0,9	93
(1:2):2	0,05	53	0,03	90	45	90	0,4	28	0,9	69	0,7	95
(1:2):3	0,04	67	0,01	96	2	100	0,1	6,3	0,1	96	0,1	99

same amount of added total P, but varying amount of both phosphate additions. The mobility of metals and P was studied and evaluated in all parts of our study. The time-dependent leaching characteristic of metals and P for soil and all mixtures was evaluated by a column experiment.

Materials and Methods

The sub-samples of soil collected were combined into a representative composite sample and pre-treated according to SIST ISO 11464:1996 (dried in air, crushed and passed through the 2-mm sieve). The pH values of the soil sample and its mixtures were determined in a 0.01 M CaCl₂ suspension (liquid to soil ratio 5:1). To determine the total metal concentration in soil samples, approximately 0.5 g of air-dried soil sample was digested in 5 mL of aqua regia (SIST ISO 11466:1996) at 473 K for 4 hours. To immobilize metals in soil, soil mixtures with phosphate additions (constant molar Pb:P ratio of 1:10 in all mixtures) were prepared. The phosphate additions were prepared from two phosphate sources with quite different solubility characteristics, H₃PO₄ and hydroxyapatite (HA), with varying compositions. To regulate the pH, lime was also used in the stabilization mixtures (stated as molar ratio to total phosphate). The mobility of metals in soil and prepared mixtures was evaluated according to the Toxicity Characteristic Leaching Procedure – TCLP (USEPA, SW-846: Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, Analytical Method 1311: Toxicity Characteristic Leaching Procedure). Twenty mL of 0.11 M acetic acid were added to 1.000±0.005 g of air-dried soil samples. Samples were shaken for 20 hours at 150 rpm, centrifuged, decanted and filtered through the membrane filter of 0.45 µm pore size. Treatment-induced leaching of P was evaluated by the phosphate concentration in water extracts (S/L = 1:10) of soil mixtures.

The time-dependent leaching characteristics of metals and phosphate for all mixtures were evaluated with a column experiment. The columns (PE, $\Phi = 25$ mm, $h = 130$ mm) were filled with 65.000±0.005 g of soil or mixture ($N=3$ for all samples). The leaching of mixtures with average annual amount of synthetic precipitation (pH 4.2) of 1300 mm was simulated. An amount of precipitation was divided into 40 portions that were poured into columns every two days. The first ten leachings were performed with one portion of precipitation followed with fifteen leaching with double portions of leachate. The concentration of metals and P in all prepared samples were analysed by ICP-MS.

Results and Discussion

Total metal determination showed that the soil was heavily polluted with Zn ($34\,400 \pm 1500$ mg kg^{-1}), Pb ($20\,400 \pm 1500$ mg kg^{-1}), As (950 ± 10 mg kg^{-1}), Cu (549 ± 7 mg kg^{-1}) and Cd (158 ± 4 mg kg^{-1}). The results of TCLP showed high mobility of Zn (540 ± 25 mg L^{-1}), Pb (12.7 ± 0.5 mg L^{-1}) and Cd (2.9 ± 0.1 mg L^{-1}).

Table 1 presents the mean TCLP concentrations of metals in soil and in soil mixtures (in mg kg^{-1}) for different HA:H₃PO₄:CaO molar ratios and the metal stabilization efficiencies of mixtures, except for As, where destabilization is presented as the n-times increase in leachability. Addition of HA significantly decreased the mobility of metals, especially of Cu, Zn, Cd and Pb (65 %, 48 %, 55 % and 97 %, respectively, of the primary TCLP leachable concentration), increased the mobility of As, increased the water leachable phosphate concentration and decreased pH of the mixture (Table 2). An addition of phosphoric acid decreased the stabilization efficiency observed on addition of HA (probably due to a decrease in pH of the mixtures as a consequence of the addition of phosphoric acid). At higher amounts of added phosphoric acid, the

stabilization efficiency overcame the impact of lower pH. A great increase in mobility of As was observed after the addition of phosphoric acid, but the highest As TCLP concentration of 1.56 mg L⁻¹ was still far below the stated TCLP value of 5 mg L⁻¹. Arsenic is present in the environment mainly as oxyanions, and similarities between phosphate and arsenate obviously resulted in the leaching of As as a consequence of phosphate addition. Both oxyanions compete for the same adsorption sites and the results suggest that the retardation factor for arsenate is lower than for phosphate. An increase in the stabilization efficiency of Co, Ni and Zn was observed after the addition of lime with high decrease in water leachable P concentrations and increase of pH of soil mixtures.

Leaching of soil with synthetic precipitation showed an increase in leachability of Pb, Cd and Ni at the beginning of the experiment up to 1.6 mg L⁻¹, 2.5 mg L⁻¹ and 0.2 mg L⁻¹, respectively, followed with sharply decrease after addition of 230 mm of precipitation. Concentrations of As, P and Cu in soil leachates were less than 0.002 mg L⁻¹, 0.05 mg L⁻¹ and 0.02 mg L⁻¹, respectively, during all irrigation period. Cumulative concentration of Zn, Pb, Cd and Ni in leachates of soil sample represents 5.0 %, 0.044 %, 6.4 % and 6.3 %, respectively, of total metal concentration.

At first four mixtures, where no lime was added, sharp decrease in leachability of all elements was observed at the beginning of irrigation, followed by a slow decrease till the end of the experiment. The concentrations of elements in leachates of mixtures with added lime were much lower compared to the first four mixtures.

Table 2. Concentrations of water leachable phosphorus in water extracts in mg L⁻¹ ± standard deviation (N=3) and pH of soil and of soil mixtures.

mixture <i>n</i> (HA): <i>n</i> (H ₃ PO ₄): <i>n</i> (CaO)	P conc. [mg L ⁻¹]	pH
Soil	<0.05	6.43
(1:0):0	5.3±0.9	5.45
(1:0.5):0	11±2	5.05
(1:1):0	22±3	4.86
(1:2):0	50±10	4.81
(1:1):1	0.7±0.2	7.61
(1:1):2	0.26±0.06	8.3
(1:1):3	0.06±0.02	12.2
(1:2):1	2.9±0.9	7.24
(1:2):2	0.09±0.03	8.67
(1:2):3	<0.05	9.54

Sharp increase of leachability of Pb and Cd was observed up to leaching with 300 mm of precipitations, followed by a sharp decrease till the end of irrigation. These trends were observed specially at mixture *n*(HA):*n*(H₃PO₄):*n*(CaO) = (1:1):3 for Pb (up to 0.1 mg

L⁻¹) and at mixtures *n*(HA):*n*(H₃PO₄):*n*(CaO) = (1:1):1 and *n*(HA): *n*(H₃PO₄):*n*(CaO) = (1:2):1 for Cd (up to 0.015 mg L⁻¹). An addition of HA decreased the cumulative Cd and Pb concentration on 0.87 % and on 7·10⁻⁴ %, respectively, of total metal concentration. With addition of HA cumulative Zn leachate concentration reached 0.8 % of total Zn concentration. An addition of H₃PO₄ increase the cumulative P leachate concentration from 69 mg kg⁻¹ (2.3 % of total added P concentration) in mixture with added HA on 963 mg kg⁻¹ (30.7 % of total added P concentration) in mixture with the highest amount of added H₃PO₄ (mixture *n*(HA):*n*(H₃PO₄):*n*(CaO)= (1:2):0). In mixtures with added lime cumulative leachate P concentration drastically decreased down to 0.083 % of total added P amount. Steady increase in leachability of P was observed for both mixtures with lowest amount of added lime (*n*(HA):*n*(H₃PO₄):*n*(CaO) = (1:1):1 and *n*(HA):*n*(H₃PO₄):*n*(CaO) = (1:2):1) up to 1.2 mg L⁻¹ (cumulative leachate P concentration of 0.29 % and 0.24 %, respectively, of total added P).

The mixture *n*(HA):*n*(H₃PO₄):*n*(CaO) = (1:2):3 with pH 9.45 showed the lowest metal and P mobility in first part of our study (Table 1 and Table 2). Results of the column experiment showed that during all irrigation period the concentrations of Zn, Cd, Ni and Co in leachates of this mixture were below limit of detection, whereas the cumulative amount of leached Cu, As, Pb and P was 0.42 mg kg⁻¹, 0.059 mg kg⁻¹, 0.045 mg kg⁻¹ and 2.4 mg kg⁻¹, respectively.

pH of leachates varied from 4.9 at mixture *n*(HA):*n*(H₃PO₄):*n*(CaO) = (1:2):0 to 8.4 at mixture *n*(HA):*n*(H₃PO₄):*n*(CaO) = (1:1):3 with no significant changes during all irrigation period.

Conclusion

The ultimate goal of each soil remediation should be the full restoration of the capability of soil to fulfil its environmental role. Therefore, detailed attention should be paid to the equilibrium between the benefits of metal-stabilization efficiency on the one hand, and the treatment-induced leaching of stabilization agents on the other. Furthermore, the long-term stability of metal immobilization should be evaluated for each metal stabilization study. Although the use of phosphate amendments for the stabilization of metal-contaminated soil and waste materials has been widely studied, studies of the leaching of P itself as a consequence of phosphate treatment are generally overlooked.

The results of our study clearly show the importance of holistic approach to phosphate based metal stabilization studies where all aspects of chemical treatments should be observed and evaluated.

Acknowledgements

This research study was financially supported by the Ministry of Higher Education, Science and Technology (P1-0134) of the Republic of Slovenia.

References

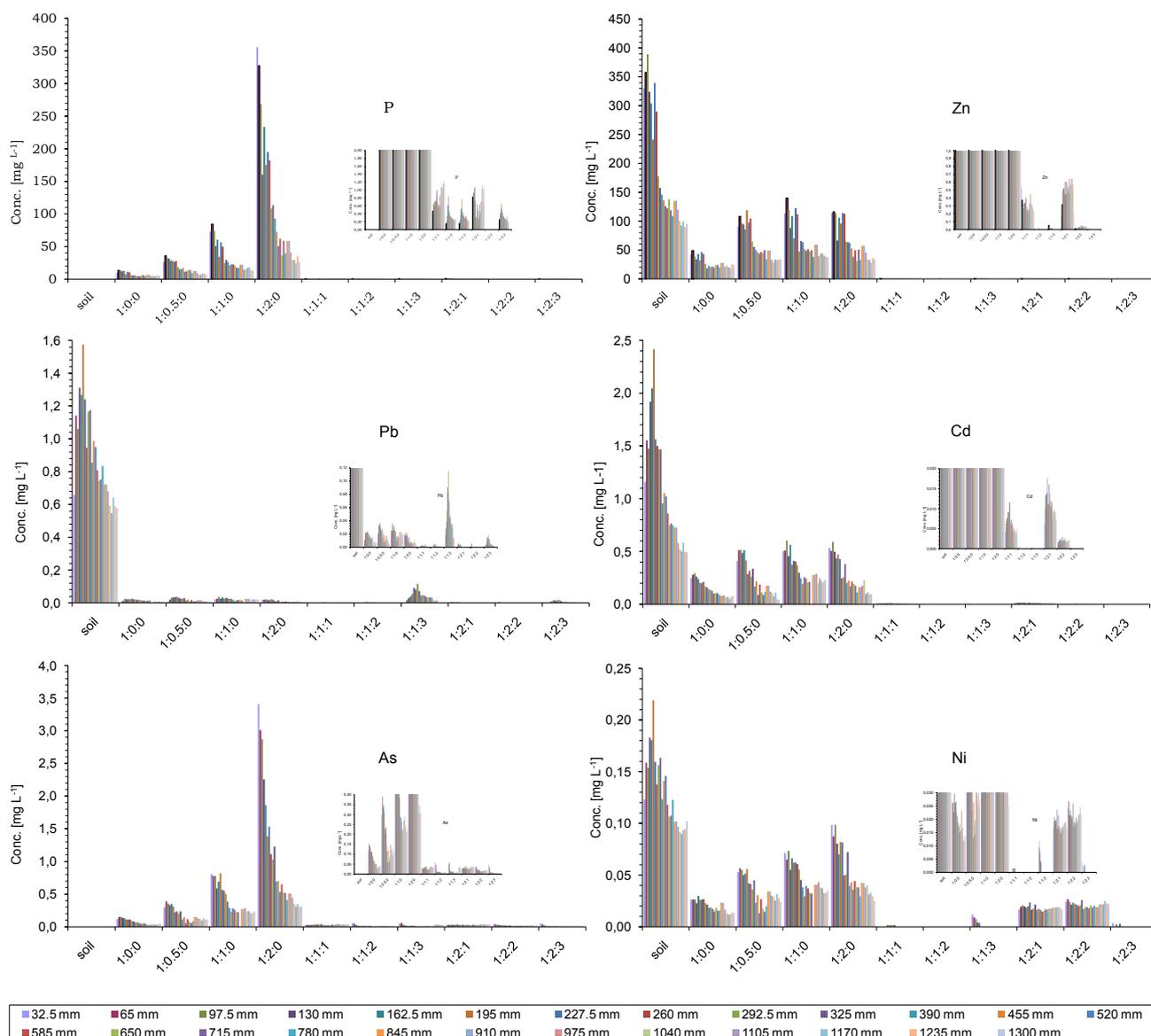


Fig. 1. Metal concentrations (mean, N=3) in leachates collected after leaching of mixtures with annual amount of synthetic precipitation (pH 4.2)

References

Miretzky P, Fernandez-Cirelli A. Phosphates for Pb immobilization in soils: a review. *Environ Chem Lett* 2008; 6:121-133.
 Park JH, Bolan NS, Megharaj M, Naidu R. Comparative value of phosphate sources on the immobilization of

lead, and leaching of lead and phosphorus in lead contaminated soils. *Sci Total Environ* 2011; 409, 853-860.
 Bolan NS, Adriano DC, Naidu R. Role of phosphorus in (im)mobilization and bioavailability of heavy metals in the soil-slant system. *Rev Environ Contam Toxicol* 2003; 177: 1-44.