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Journal of Hazardous Materials B87 (2001) 289–300

Journal of Hazardous Materials

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Case study

Leaching of metals from soil contaminated by mining activities

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Received 10 February 2001; received in revised form 22 May 2001; accepted 24 May 2001

Abstract

Stabilization/solidification (s/s) is one of the most effective methods of dealing with heavy metal contaminated sites. The ability of lime and cement stabilization to immobilize Pb, Cu and Fe contained in a contaminated soil originating from an old mining and smelting area located along the Mediterranean Sea shore in northern Cyprus was investigated. The stabilization was evaluated by applying leaching tests. A series of tests were conducted to optimize the additive soil ratio for the best immobilization process. Additive/soil = 1/15 (m/m) ratio was found to be the optimum for both lime and cement. Application of the US EPA toxicity characteristic leaching procedure (TCLP) on the soil samples treated with lime at additive/soil = 1/15 (m/m) mixing ratios showed that Cu and Fe solubility was reduced at 94 and 90%, respectively. The results of cement treatment using the same ratio, reduced the solubility 48 and 71% for Cu and Fe, respectively. The Pb solubility was found to be below the regulatory limit of 5 mg/l so no additive treatment was needed. The optimum additive/soil amount (1/15) was selected for more detailed column studies, that were carried out in the acidic pH range. According to the results of column leaching tests, it was found that, the degree of heavy metal leaching is highly dependent on pH. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Remediation; Mining activity; Lead; Copper; Stabilization/immobilization

1. Introduction

Past mining and smelting of sulfide ore (pyrite–chalcopyrite–sphalerite) sites can represent important sources of metal pollutants for watercourses and soils [1–3]. In northern

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PII: S0304-3894(01)00277-1

Cyprus, there are environmental degradation examples caused by mining and associated smelting activities carried out for years, leading to large emission of metals such as Pb, Cu, Cd, Zn, Fe into the environment.

Remediation actions may involve excavation and removal of these contaminated soils. Even though, this seems like a logical solution, it is not feasible in many cases due to vast size of the contaminated area and the high costs involved [4]. It is known that a more cost effective alternative for soil remediation is in situ stabilization/solidification (s/s) of metals, in order to reduce the risk of the contaminants to enter the groundwater, surface water, or the atmospheric exposure pathways [5,6].

Stabilization/solidification is the technology that uses binding materials such as cement, lime, or organic polymers to transform contaminated soil containing toxic metals to more manageable forms and/or into a less toxic forms by physically and/or chemically immobilizing the contaminants [7]. In solidification, contaminated soil is incorporated into a monolithic solid with a reduced surface area over which leaching can occur. Solidification processes do not necessarily imply that any form of chemical reaction has occurred. The term stabilization on the other hand describes technologies that chemically alter toxic metals to produce less toxic or mobile forms. Many processes achieve immobilization by a combination of solidification and stabilization [8].

Being located along the Mediterranean Sea shore, leaching of Fe from the old smelting facility can become an important environmental issue, as are Cu and Pb leaching, because it is suggested that a maximum annual average value of 2 mg/l of total iron is tolerable by most fish and concentrations above that are toxic [9,10].

Therefore, the objective of the present study was to evaluate the efficiency and capacity of lime and cement as immobilization agents for heavy metals like Pb, Cu and Fe contained in contaminated soil samples of the old smelting facility located in northern Cyprus. The efficiency of the immobilization due to the additives was assessed by means of leaching tests.

2. Materials and methods

2.1. Environmental characterization of the samples

Soil samples were obtained at 20 different locations 0–15 cm depth of the old copper smelting facility site. Prior to the analysis, each of the collected samples was passed through 10 mm sieve to remove the rocks and other large materials not passing through the sieve. An amount of 1 kg of each sample was then weighed, transferred and mixed in a container to make a blend of 20 samples. The blended soil sample (20 kg) was mixed thoroughly to ensure uniformity and stored in a plastic barrel at room temperature for subsequent use in the experiments.

Initial copper, iron and lead contents, pH, water and organic matter contents of blended soil sample was determined. All of the experiments and digestions were carried out as triplicates.

In order to characterize the soil sample, conventional analytical techniques were applied, which include the following. pH measurements were conducted in soil solutions of

5 g soil: 96.5 ml deionized water as described in Code of Federal Regulations 40 (CFR 40) [11]. A Jenway 3040 pH meter was used for all pH measurements. Water content and organic content measurements were performed according to ASTM standards [12]. To determine the total lead, copper and iron contents of soil samples, 2 g of each sample was digested according to EPA SW 846, Method 3050 [13]. Each digestate was filtered through 0.8 μm glass fiber filter. Filtrates were analyzed for Pb, Cu and Fe with Unicam 919 atomic absorption spectrophotometer (AAS) by direct aspiration method.

2.2. Leaching experiments

The effectiveness of the additives on immobilization of metals was evaluated using the toxicity characterization leaching procedure (TCLP) developed by US EPA to determine the mobility of both organic and inorganic analytes present in liquid, solid and multiphase wastes [11]. A series of screening tests were carried out and, lime and cement were selected as the most suitable additives [14]. TCLP experiments were performed for the soil sample, lime/soil sample and cement/soil sample mixtures at ratios of 1/15, 1/20 and 1/25.

An appropriate extraction fluid for all mixtures was determined based on the pH of soil as described in TCLP, such that, if the pH of the soil is less than 5, extraction fluid 1 (5.7 ml glacial CH_3CH_2OOH and 64.3 ml 1N NaOH are diluted in 1 l reagent water) was used otherwise extraction fluid 2 (5.7 ml glacial CH_3CH_2OOH is diluted in 1 l reagent water) was used. An amount of 100 g of each mixture and 2 l chosen appropriate extraction fluid were put into 2 l plastic vessels and rotated for 18 h in a horizontal shaft mixer with a speed of 30 ± 2 rpm. At the end of 18 h extraction period, liquid in each vessel was separated from solid phase by vacuum filtration through 0.8 μm glass fiber filter paper. The pH of separated TCLP extracts were then measured and all extracts were acidified with 1N HNO_3 to pH less than 2 for long-term preservation. At the end, all acidified extracts were digested according to EPA, SW 846, Method 3010 [13] and Pb, Cu and Fe concentrations in digestates were determined with Unicam 919 atomic absorption spectrophotometer (AAS) by direct aspiration method.

2.3. Column experiments

Column tests were conducted to study the leaching behavior of metals in the soil additive system. An amount of 80 g of soil and additive/soil = 1/15 (m/m) mixtures, with additive evenly distributed throughout the soil, were packed into glass columns with 25 mm diameter and 600 mm height. The soil was added to the columns in 20 g portions and was placed between addition by shaking the columns. A fine textured synthetic cloth acted as a 6 μm filter for the leachate. The columns were operated under a constant head of 1.5 m and remained well drained throughout the experiments. HCl diluted from concentrated with pH 2 and 4, were used as leaching solutions. The glass columns were continuously washed for 48 h with each leaching solution (HCl pH 2; HCl pH 4). Pb, Cu and Fe in the leachate were determined on an hourly basis using AAS.

3. Results and discussion

3.1. Characterization of the samples

The chemical composition of the soil sample and regulatory limits of metals in the soil according to the Turkish Soil Pollution Control Regulations (TSPCR) [15] are included in Table 1 for comparison. According to the particle size analysis, the soil sample consists of silt 56%, clay 20%, sand 19% and organic matter 3% all with m/m.

As can be seen from Table 1, both Pb and Cu contents exceeds the limit values. The soil sample is Type III (extremely polluted soil) when considering Cu content and it is Type II (polluted soil) when considering Pb content. There is no limit value for Fe in TSPCR.

3.2. TCLP experiments

TCLP experiments were carried out for soil without additive (control), lime/soil and cement/soil mixtures at ratios of 1/15, 1/20 and 1/25. Since the results of TCLP experiment carried out for soil sample without additive (control) showed that very low concentration of Pb was available in the leachate (0.6 mg/l), no analysis were performed for Pb using the additives. The TCLP tests performed showed that the mobility of Pb in the soil was considerably limited. Heavy metals are retained by soil in three ways: by adsorption onto the surface of mineral particles, by adsorption on the organic matter, and by precipitation reactions. The mechanism of lead associated with soil is a mixture of some or all of the above processes, the predominant mode probably depending upon the composition and the pH of the soil sample.

Cu concentrations and pH values of TCLP extracts plotted against additive/soil mixing ratios for lime and cement are shown in Figs. 1 and 2. Lime addition at ratios of 1/15, 1/20 and 1/25 did not result a significant change in the pH of TCLP extract of the soil without additive. The best Cu immobilization efficiency of lime was observed at 1/15 mixing ratio. Comparing with the sample with no additive, 94% less Cu leached when lime used as an immobilization agent at a ratio of 1/15 (m/m). For other ratios, the leached Cu amounts from the soil increased gradually.

Table 1
The physical and chemical properties of the blended soil with limit values of TSPCR

Elements	Soil	TSPCR		
		Type I	Type II	Type III
Pb (mg/kg)	153	100	150	600
Cu (mg/kg)	510	50	100	500
Fe (%)	15.3	–	–	–
S (%)	14.63	–	–	–
Organic matter (%)	2.65	–	–	–
Water content (%)	15.57	–	–	–
pH	2.73	–	–	–

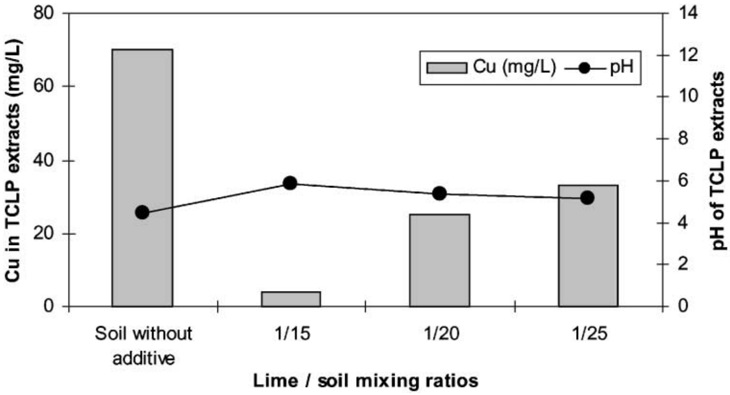

Fig. 1. Leaching tests for Cu using lime as additive.

Similar to the lime/soil mixtures, cement addition at ratios of 1/15, 1/20 and 1/25 did not change the pH of TCLP extracts significantly. The best Cu immobilization efficiency was observed at 1/15 mixing ratio with a 48% decrease in Cu amount leached from soil/cement mixture when compared with the control sample. This was significantly lower than the 94% decrease obtained by lime addition at the same ratio. Thus, it can be concluded that lime is more efficient than cement for the immobilization of Cu for the soil samples tested.

Copper is amphoteric and has the least solubility at pH value of about 9. Solubility of copper hydroxide increases significantly for pH values less than 6 [16]. Thus, the mechanism responsible for the great increase in leached copper in 1/20 and 1/25 additive soil mixtures is due to the greater solubility of copper as copper hydroxide.

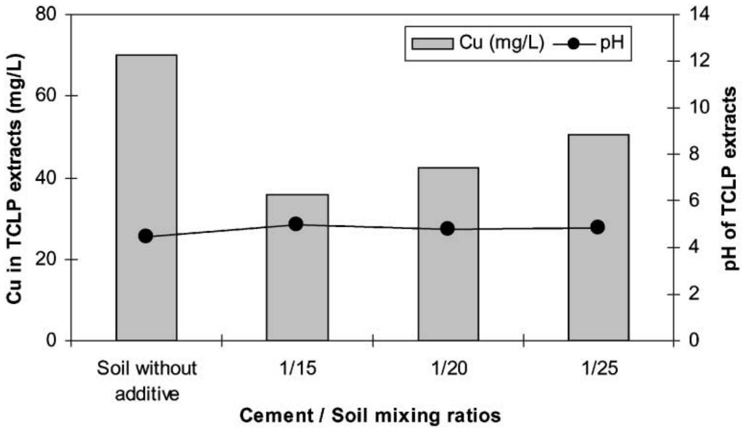

Fig. 2. Leaching tests for Cu using cement as additive.

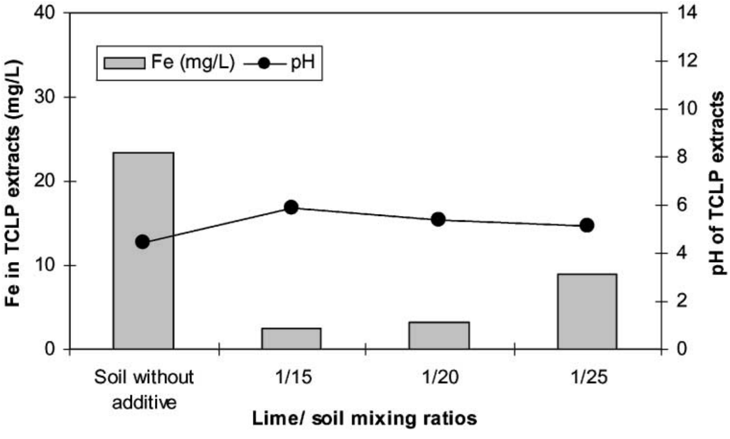

Fig. 3. Leaching tests for Fe using lime as additive.

Figs. 3 and 4 show the effect of lime and cement addition at different additive/soil mixing ratios on the leaching characteristics of Fe. Lime addition at ratios of 1/15, 1/20 and 1/25 did not result a significant change in the initial TCLP pH of soil without additive. The best Fe immobilization efficiency of lime was observed at 1/15 mixing ratio with an 89.5% decrease when compared with the control. Similar trend as lime's was observed in the TCLP pH when cement was used as additive. Almost 71% of leachable Fe in the control sample was immobilized by 1/15 cement/soil mixture.

The efficiency of cement on Fe immobilization is pH dependent but it can work efficiently at lower pH values than lime. It is known that hydration of cement forms a crystalline structure. This results in a rock-like, monolithic, hardened mass [16]. Thus, besides formation of insoluble iron hydroxides, microencapsulation and entrapment in the crystal structures

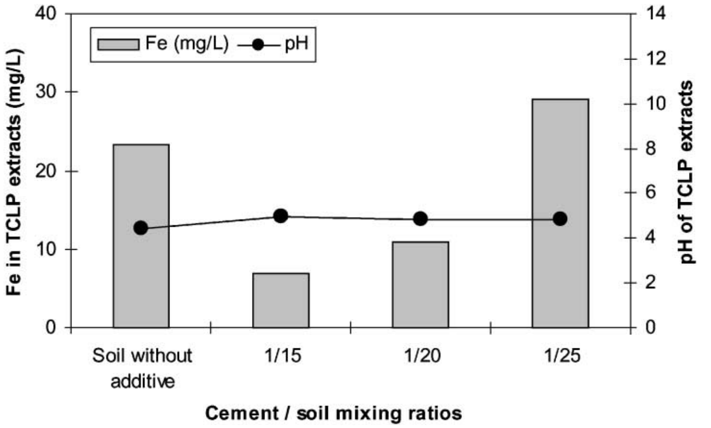

Fig. 4. Leaching tests for Fe using cement as additive.

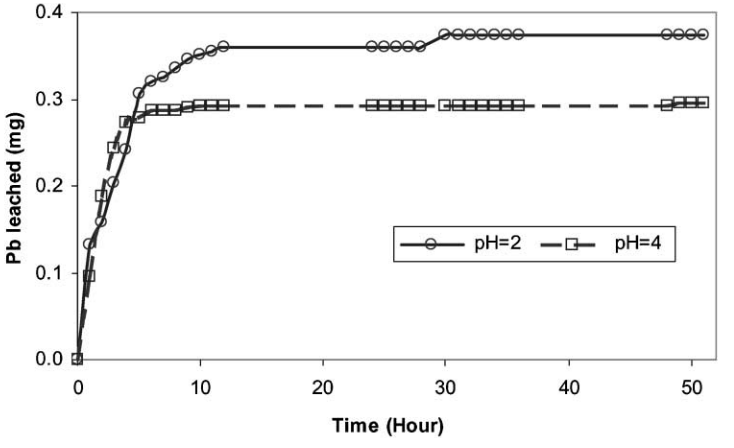

Fig. 5. The cumulative Pb leached using different solutions.

of cementitious compounds formed as a result of pozzolanic reactions are also effective in decrease of Fe mobility due to cement addition.

3.3. Column experiments

Column studies more closely simulate field conditions than TCLP experiments. Moreover, they provide detailed information about the mobility of contaminant with respect to time. Thus, further analysis of the site was carried out by column experiments and Pb, Cu and Fe concentrations were determined. To simulate the worse case of acid rain leaching, the best stabilized specimen based on the TCLP from each additive was selected for column experiments and applied with acidic solutions.

3.3.1. Lead

The cumulative amount of Pb released as a function of time using different leaching solutions (without any additive) are shown in Fig. 5. With every leaching solution that was applied, less than 5% of lead initially present in the soil leached out. The maximum concentration was observed within the first hour of operation when pH 2 solution was applied. The small amount of release from the control is due to the low mobility of Pb when incorporated in the soil. Since Pb concentrations in leachate from soil without any additive were significantly low (below the TCLP Pb limit of 5 mg/l according to the 40 CFR, Chapter 1), Pb column experiments were not carried out for the samples with additives.

3.3.2. Copper

Cumulative amount of Cu leached from blend soil samples without any additive, 1/15 lime/blend soil and 1/15 cement/blend soil mixtures using the leaching solutions are plotted as a function of time in Figs. 6 and 7.

When pH 2 leaching solution was applied to the blend soil without additive, approximately 75% the available of initially present copper of 40.8 mg leached during first 3 h and this

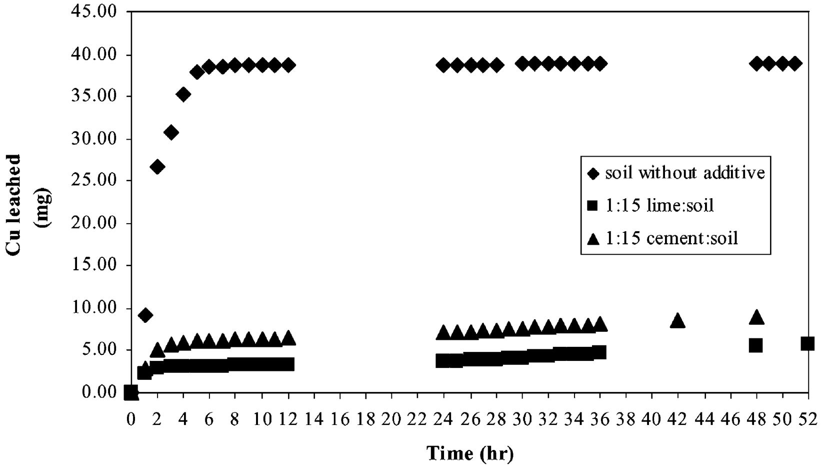

Fig. 6. The cumulative amount of Cu leached when pH 2 leaching solution is applied.

value reached to 94% at the end of sixth hour. After sixth hour, only a slight change in cumulative amount of Cu leached was observed and at the end of the test, about 95% of the initially present Cu had leached. In the case of 1/15 lime/soil mixture, only 15% of initially present Cu amount leached. Similar to the 1/15 lime/soil mixture, increase in cumulative leached Cu amount of 1/15 cement/soil mixture was gradual but very low with respect to that of soil without additive. Only, about 24% of initially present Cu of 38.3 mg leached at the end of the test. These results showed that leaching of Cu metal is very high (95%) under pH 2 condition and addition of lime and cement at 1/15 ratios reduces leaching from 95 to 15, and 24%, respectively. Moreover, comparison of findings of lime/soil and

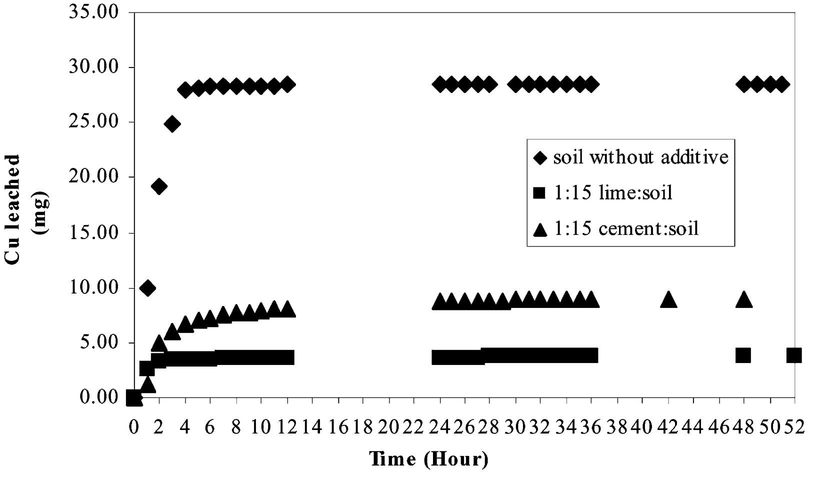

Fig. 7. The cumulative amount of Cu leached when pH 4 leaching solution is applied.

Table 2
Summary of the results of the column experiments for Cu

Sample	Initially available Cu amount (%)	
	Leaching solution with pH 2	Leaching solution with pH 4
Without additive	95	70
Lime/soil = 1/15	15	10
Cement/soil = 1/15	24	24

cement/soil mixtures showed very similar results with TCLP experiments for Cu metal and that lime has higher immobilization efficiency than cement at ratio of 1/15 under pH 2 condition.

When pH 4 leaching solution was applied to blend soil without additive, about 61% of leachable Cu of 40.8 mg in the control sample was leached during first 3 h and this value reached to about 70% at the end of sixth hour. Afterwards, almost no change in cumulative amount of Cu leached was observed. In case of 1/15 lime/soil mixture, a slight increase in cumulative amount of Cu leached was observed until 32nd hour and at this stage about 10% of initially present Cu of 38.3 mg leached. From then on, no change in cumulative amount of Cu leached was observed. For 1/15 cement/soil mixture, a gradual and slight increase in cumulative amount of Cu leached was observed till the end of the test. At the end of the test, only about 24% of initially present Cu amount leached. Addition of lime and cement to this soil with 1/15 ratios results in decrease of 70% leaching to 10 and 24%, respectively. Similar to the results of pH 2 condition and results of TCLP experiments, lime showed higher immobilization efficiency than cement at ratio of 1/15 under pH 4 condition.

The highest concentrations of Cu were detected at the 1 h for all samples. Although concentrations from control samples remained at higher values for a longer duration, a sudden drop was observed in samples with additives during the same time interval. Comparison of leaching Cu concentrations of 1/15 lime/soil and 1/15 cement/soil mixtures showed that leaching Cu concentrations from 1/15 cement/soil mixture were higher than those from 1/15 lime/soil mixtures at all times. Furthermore, results of pH 2 and 4 solutions showed that at almost all time intervals less leachable Cu was immobilized with pH 2 solutions. The Cu concentration in the leachates from soils with additives were significantly less than those from the control soils. This reduction in Cu release from the soil additive mixtures could have been due to precipitation in response to the pH rise, and adsorption of Cu onto the additive particles. Table 2 summarizes the results of column experiments for Cu.

3.3.3. Iron

Cumulative amounts of Fe leached from three samples, blend soil without any additive, 1/15 lime/blend soil mixtures and 1/15 cement/blend soil mixtures plotted against time are shown in Figs. 8 and 9.

When pH 2 solution was applied to the blend soil without additive, about 7% of leachable Fe of 12.3 g leached in 2 h, later on a slight increase was observed and at the end of the test, about 10% of initially present Fe amount leached. In case of 1/15 lime/soil mixture,

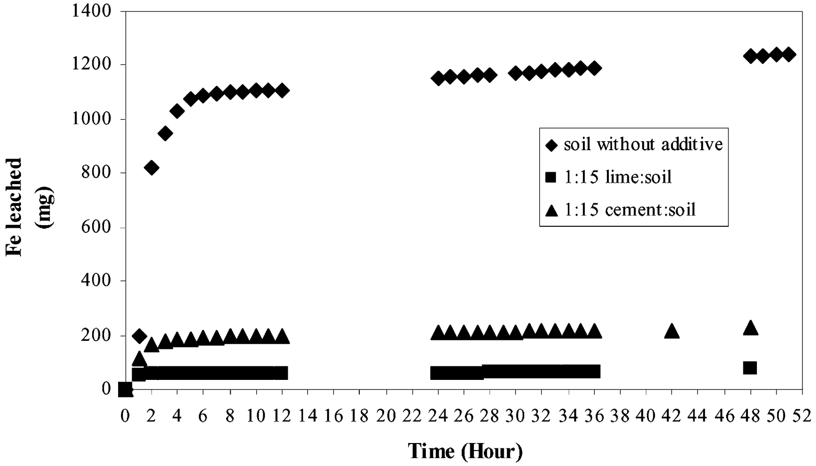

Fig. 8. The cumulative amount of Fe leached when pH 2 leaching solution is applied.

no significant change in cumulative amount of Fe leached was observed till the end of the test. At the end of the test, about 0.7% of leachable Fe of 11.5 g leached. For the 1/15 cement/soil mixture, increase in cumulative Fe amount leached was slightly greater than that of 1/15 lime/soil mixture. At the end of the test, about 2% of initially present Fe amount of 11.5 g leached. These results showed that leaching of Fe metal is low under pH 2 condition. Addition of lime and cement at 1/15 ratio reduces this leaching from 10 to 0.7, and 2%, respectively. Moreover, comparison of results of 1/15 lime/soil and 1/15 cement/soil mixtures showed that lime has higher immobilization efficiency on Fe metal with respect to cement.

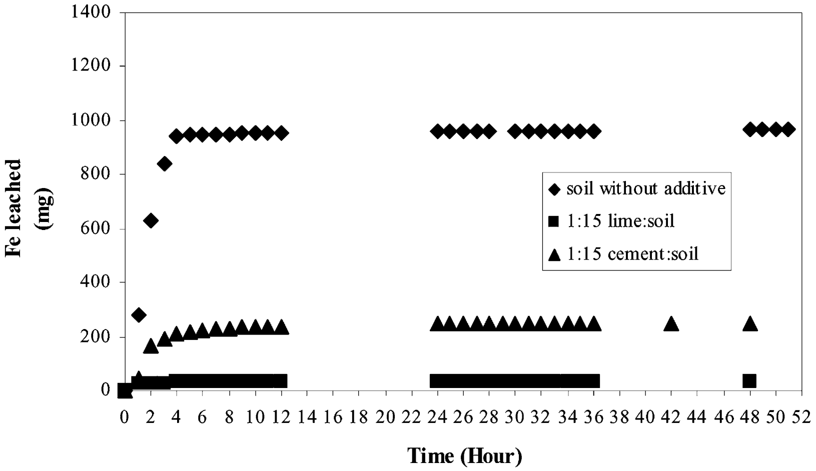

Fig. 9. The cumulative amount of Fe leached when pH 4 leaching solution is applied.

Table 3
Summary of the results of the column experiments for Fe

Sample	Initially available Fe amount	
	Leaching solution with pH 2	Leaching solution with pH 4
Without additive	10	8
Lime/soil = 1/15	0.7	0.3
Cement/soil = 1/15	2	2

When pH 4 solution was applied to blend soil without additive, about 8% of initially present Fe of 12.3 g leached. In case of 1/15 lime/soil mixture, almost no change in cumulative leached Fe amount was observed and at the end of the test, only about 0.3% of initially present Fe of 11.5 g leached. For 1/15 cement/soil mixture, a gradual slight increase in cumulative amount of Fe leached was observed until 24 h and after this stage no change was detected. At the end of the test, about 2% of initially present Fe was leached. These results showed that 8% leaching of Fe metal under pH 4 is slightly lower than the 10% leaching detected under pH 2. Moreover, addition of lime and cement to this soil at ratios 1/15 reduces this leaching from 8 to 0.3, and 2%, respectively. Thus, similar to the pH 2 condition, lime showed higher immobilization efficiency on Fe metal than cement under pH 4 condition. Table 3 summarizes the results of column experiments for Fe.

Lower concentrations of Pb, Cu and Fe were extracted by washing fluids from the additive treated soils than from the untreated soils. This indicates that metal retention due to additives was not mainly because of the adsorption of metals onto either soil or additive particles. Although not fully characterized, the retention of metals appears to be partially due to pH increase and partially, due to the metal hydroxides created.

The leaching tests performed showed that the solubility of metals in the additive mixture was considerably limited and the order of decreasing metal leachability was Cu > Fe > Pb.

4. Conclusions

In this study, lime and cement were evaluated as an immobilization agent for the remediation of heavy metal polluted soils of an old smelting facility from northern Cyprus. The following conclusions can be made:

1. The addition of lime and cement to contaminated soils containing Cu, Pb and Fe reduced the leachability of the contained metals.
2. Additive/soil = 1/15 mixture was found to be the optimum for the samples studied.
3. At a ratio of 1/15 lime/soil mixture (m/m), the TCLP solubility of Cu and Fe decreased by 94 and 90%, respectively.
4. At a ratio of 1/15 cement/soil, the TCLP solubility of Cu and Fe decreased by 48 and 71%, respectively.
5. The Pb solubility was found to be below the regulatory limit of 5 mg/l.
6. Column tests also confirmed the finding of the TCLP tests and showed that degree of heavy metal leaching is highly pH dependent.

Although the mechanism of metal immobilization is not fully understood, the results from the current study indicate that lime stabilization has the potential to be an effective means of remediating the heavy metal contaminated soils studied.

Acknowledgements

The study is a part of project FE-1998/15, which is financially supported by the Marmara University Research Fund. This support is gratefully acknowledged. The authors would also like to thank Cenk Terzioglu, Selvihan Balcioglu and Hakan Altun for assistance with the experiments.

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