

REMEDIATION OF LEAD CONTAMINATED SOILS BY STABILIZATION/SOLIDIFICATION

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Abstract. Most available remediation technologies for treatment of heavy metal contaminated soils are very expensive and result in residues requiring further treatment. Stabilization/solidification (immobilization) techniques however, which are designed to decrease leaching potential of heavy metals from soil by addition of chemical additives, provide very cost-effective solutions for heavy metal contaminated soils. This study investigates the most efficient additive for immobilization of lead. To achieve this goal, several leaching experiments were conducted for mixtures of different additives (lime, activated carbon, clay, zeolite, sand and cement) with artificially Pb contaminated (spiked) soil samples in accordance with the Toxicity Characterization Leaching Procedure (TCLP) developed by U.S. EPA. Results showed that among the additives tried, activated carbon, clay, zeolite and sand are not very efficient for Pb immobilization. On the other hand, lime and cement are significantly effective in Pb immobilization with 88% efficiency at 1:21 lime:soil ratio and 99% efficiency at 1:15 cement:soil ratio, respectively.

Keywords: contaminated soil, heavy metals, immobilization, lead, metal leaching, soil pollution, soil remediation, stabilization/solidification, TCLP

1. Introduction

Polluted soil may be harmful to living organisms. Among various soil contaminants existing in contaminated sites, heavy metals are of great concern because of their increasing abundance in the hydrological cycle, their relatively high toxicity even at low concentrations and their chemical characteristics limiting the application of many remediation techniques. Once released into soil matrix, heavy metals have potential impact on environmental quality and on human health and a great risk for safe ground water and surface water supplies (Kim *et al.*, 1997). Runoff and leachate from heavy metal contaminated sites have led to increase metal concentrations in surface and groundwater. Moreover, high concentrations of heavy metals in soil may render soils nonproductive because of phytotoxicity and may cause bioaccumulation of heavy metals in animals and humans (Abdel-Sahab *et al.*, 1994).

There are two general approaches that could be applied to heavy metal contaminated sites; the one being removal/extraction of the heavy metal species from



the waste matrix, the other one being immobilization of such species rendering them inaccessible for dissolution into water bodies. Removing/extracting heavy metals from soil matrix is an energy intensive and time consuming process. On the other hand, reducing the mobility of heavy metal species by means of a chemical additive (stabilization/solidification technique) is a much more cost effective solution for heavy metal contaminated soils (Dermatas, 1994). It provides both reductions in waste toxicity and mobility as well as improvement in the engineering properties of the stabilized material, employing one or more of the mechanisms like macroencapsulation, microencapsulation, absorption, adsorption, precipitation and detoxification (La Grega *et al.*, 1994). Stabilization/solidification can be accomplished through treatment with chemical additives that limit the solubility of contaminants contained in the soil and capture the species within the soil (Yukselen *et al.*, 2000). Stabilization/solidification technique is a cost effective option for heavy metal contaminated soils, and is expected to be increasingly used.

Lead (Pb) is one of the most common contaminants found in soils contaminated as a result of agricultural activities, urban activities and industrial activities such as mining and smelting. It is toxic both to humans and animals, especially to young children and hence presents a serious environmental and health hazard (Ma *et al.*, 1995). Current remediation of Pb contaminated soils by stabilization/solidification (immobilization) technique is in the development stage. Historically researchers investigated the effectiveness of different additives on Pb immobilization. Among the different additives tried, lime-based stabilization/solidification technique showed high efficiency on Pb metal (Dermatas, 1994; Kim *et al.*, 1997). Moreover, Ma *et al.* (1995) reported that rock phosphate were very effective for immobilization of Pb in contaminated soils.

This study was conducted to investigate and compare the immobilization efficiencies of different additives on Pb metal and to find most effective additive:soil mixing ratio for additive showing best immobilization efficiency. For this purpose, Toxicity Characterization Leaching Procedure (TCLP) leaching test developed by U.S. EPA were conducted for different additive: Pb contaminated (spiked) soil mixtures.

2. Materials and Methods

2.1. CHARACTERIZATION OF SOIL SAMPLES

The clean (unpolluted) soil samples were obtained from different locations in Goztepe, Istanbul. The soils were passed through a 10 mm sieve. Rocks and other large materials not passing through the sieve were removed. The samples were then thoroughly mixed to ensure uniformity and stored in plastic barrels at room temperature for subsequent use in the experiments. Prior to artificial contamination, pH, water content and initial Pb content of each clean soil sample were determined.

TABLE I
Characterization of clean and spiked soil samples

Measured parameter	Soil I		Soil II		Soil III	
	Clean	Spiked	Clean	Spiked	Clean	Spiked
pH	7.69	5.68	7.61	5.71	8.30	6.91
Water content (%)	6.12	1.50	6.11	1.16	0.94	1.14
Pb amount (g Pb kg ⁻¹ soil)	0.004	7.77	0.004	8.04	2.43	12.4

pH measurements were conducted in soil solutions of 5 g soil: 96.5 mL de-ionized water as described in Code of Federal Regulations (CFR 40, 1990). A Jenway 3040 pH meter was used for all pH measurements. Water content measurements were performed according to ASTM standards (Bardet, 1997). To determine the total lead content of soil samples, 2 g of each sample was digested according to EPA SW 846, Method 3050 (EPA, 1986). Each digestate was filtered through 0.8 μ m glass fiber filter. Filtrates were analyzed for Pb with Unicam 919 Atomic Absorption Spectrophotometer (AAS) by direct aspiration method. The same measurements were determined for each soil sample after Pb contamination.

The results of experiments conducted to characterize both clean and Pb contaminated (spiked) soil samples are given in Table I.

2.2. CONTAMINATION PROCEDURE

Experiments were carried out by using 3 artificially Pb contaminated soil samples (spiked samples). Clean water samples with known pH, water content and Pb amount were treated using 0.016 M Pb(NO₃)₂ solution. To contaminate clean soil samples, 500 g (on dry basis) of each soil sample was transferred to a 2 L plastic vessel and 1.5 L of 0.016 M Pb(NO₃)₂ solution corresponding to approximately 5 g of Pb (10 g of Pb per kg of dry soil) was added to each sample. The samples were mixed for 48 hr in a horizontal shaft mixer with a speed of 30 \pm 2 rpm. At the end of 48 hr mixing period, soils were separated from liquid phase and were dried at 105 °C overnight. The dried soils were then ground manually and passed through 10 mm sieve.

2.3. CHEMICAL ADDITIVES

In the experiments, lime, powdered activated carbon, clay, zeolite, sand and cement were used as additives.

2.4. LEACHING EXPERIMENTS

The effectiveness of the additives on immobilization of lead metal was evaluated using the Toxicity Characterization Leaching Procedure (TCLP) developed by U.S. EPA to determine the mobility of both organic and inorganic analytes present in liquid, solid and multiphase wastes (CFR 40, 1990).

Initially, lime, activated carbon, clay, cement, zeolite and sand were mixed separately with spiked soil I at 1:5, 1:10, 1:20, 1:40, 1:50, 1:75, and 1:100 additive:soil ratios respectively. Then, the appropriate extraction fluid for all mixtures was determined based on the pH of spiked soil I as described in TCLP. 100 g of each mixture and 2 L chosen appropriate extraction fluid were put into 2 L plastic vessels and rotated for 18 hr in a horizontal shaft mixer with a speed of 30 ± 2 rpm. At the end of 18 hr extraction period, liquid in each vessel was separated from solid phase by vacuum filtration through $0.8 \mu\text{m}$ glass fiber filter paper. The pH of separated TCLP extracts were then measured and all extracts were acidified with 1 N 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 (EPA, 1986) and Pb concentrations in digestates were determined with Unicam 919 Atomic Absorption Spectrophotometer (AAS) by direct aspiration method.

To double check the results obtained, spiked soil II was also mixed separately with clay, zeolite and sand at mixing ratios used for additives: spiked soil I mixtures. Moreover, spiked soil III was mixed with 2 additives showing best immobilization efficiency on spiked soil I – lime and cement – at increased number of mixing ratios used for spiked soil I. Procedures applied to additives: spiked soil I mixtures were also applied to these mixtures.

3. Results and Discussions

The effects of lime, activated carbon, clay, cement, zeolite and sand on mobility of Pb metal in spiked soil I are shown in Figures 1–6, respectively.

Addition of lime (Figure 1) up to 1:20 additive: soil mixing ratio resulted in increase of TCLP extracts pH from 4.89 to the range of 12.5–13. When compared with the initial amount of leachate (174 mg L^{-1}) a decrease of 82–93% was observed. It is known that lead hydroxide is least soluble at pH value of about 9.5 and its solubility increases significantly for pH values greater than 11. Thus, the mechanism responsible for the great decrease in leached lead amount in the pH range of 12.5–13 is not only the precipitation of lead as lead hydroxide but also entrapment in crystal structures of the cementitious compounds formed as a result of pozzolanic reactions. Beginning from 1:40 additive:soil mixing ratio, a significant increase in leached lead amount was observed due to decrease in pH of TCLP extracts to the levels of 5–6. The leached lead amount at these ratios almost reached the value that was observed without lime addition.

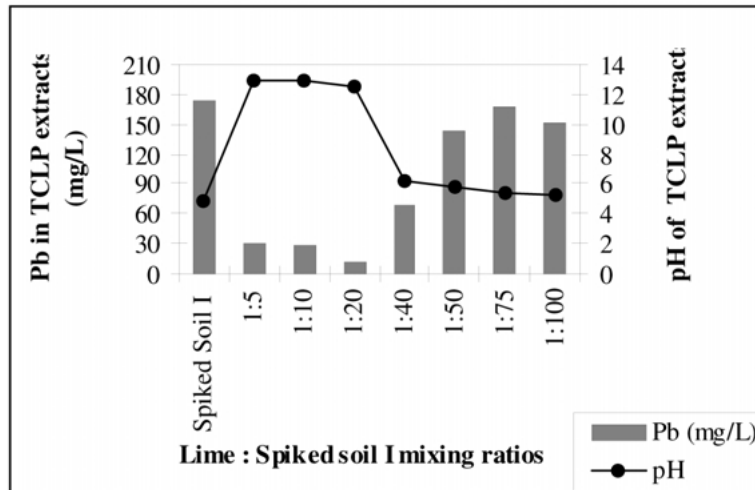


Figure 1. Leaching experiment results of Lime:Spiked soil I mixtures.

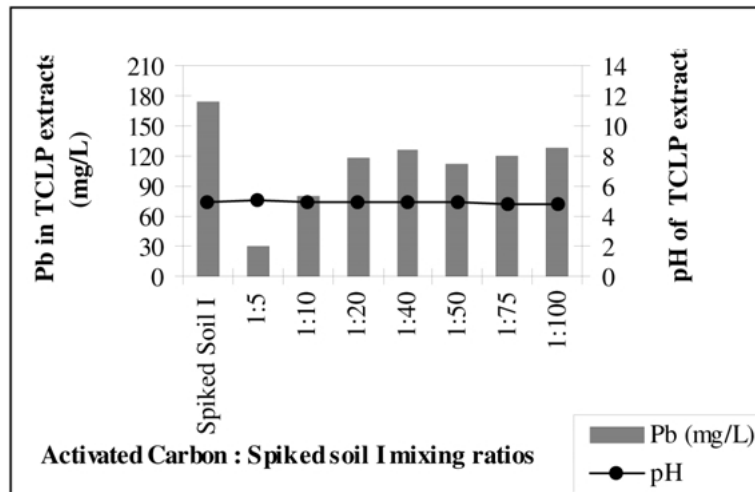


Figure 2. Leaching experiment results of Activated Carbon:Spiked soil I mixtures.

As a result of activated carbon addition to spiked soil I (Figure 2), except for 1:5 ratio, no significant change in leached Pb amount as well as pH of TCLP extracts were observed with respect to those observed without activated carbon addition. 82% decrease in leached Pb amount observed in case of 1:5 additive: soil mixture may be explained by adsorption of Pb metal on activated carbon. Although this amount of decrease seems significantly high, applying such an additive:soil mixing ratio in practice is not economical.

Similar to the activated carbon addition, clay addition to spiked soil I (Figure 3) resulted in almost no change in leached Pb amount and pH of TCLP extracts with

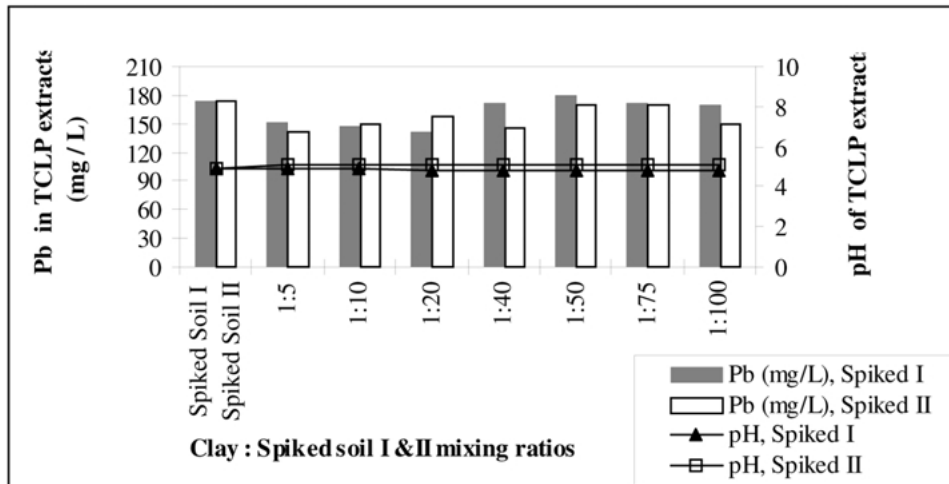


Figure 3. Leaching experiment results of Clay:Spiked soil I and Clay:Spiked soil II mixtures.

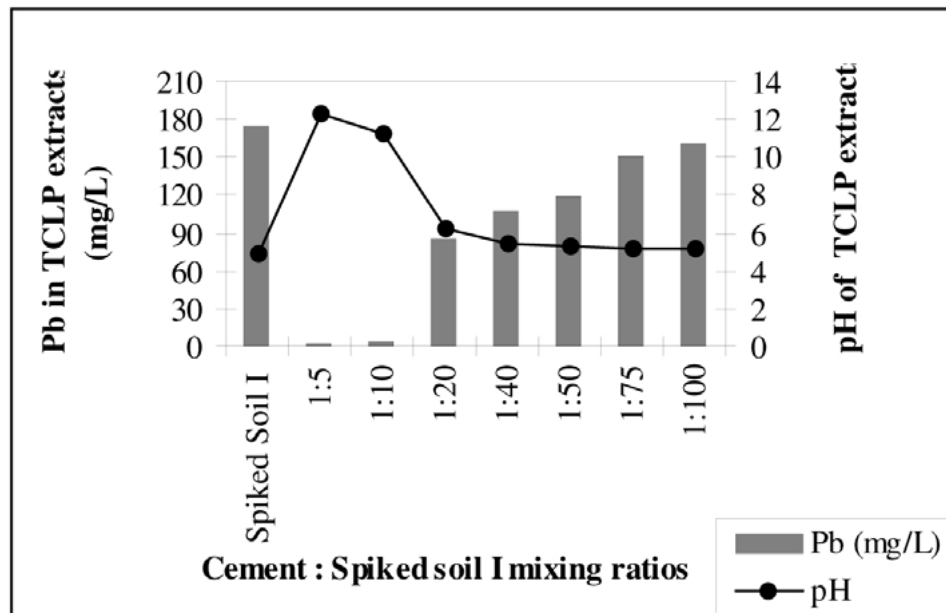


Figure 4. Leaching experiment results of Cement:Spiked soil I mixtures.

respect to initial values detected for spiked soil I without any additive. Since metals attach to negatively charged clay particles (EPA, 1991), increase in Pb immobilization is expected due to clay addition. It is known however that adsorption behaviour of heavy metals is greatly depend on pH of solution (Dermatas, 1994) and lead is adsorbed on clay surfaces at pH values greater than 6 (EPA, 1992). Thus, the fact

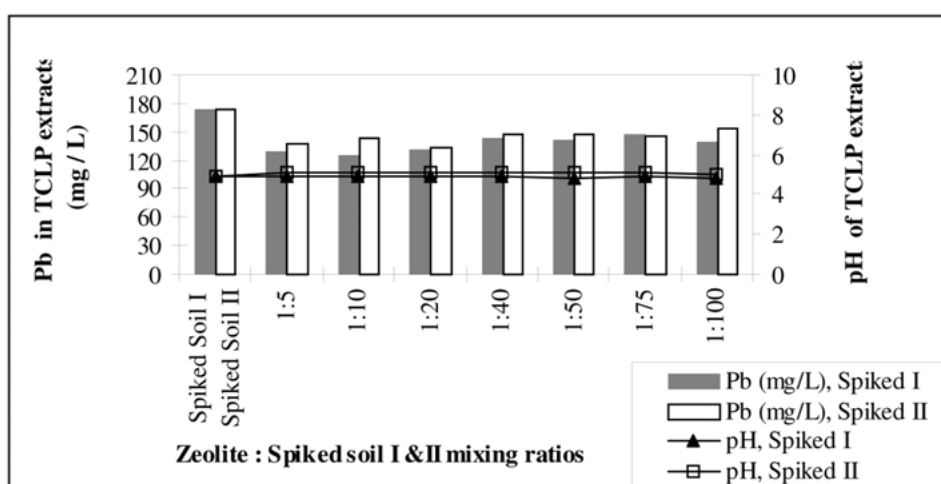


Figure 5. Leaching experiment results of Zeolite:Spiked soil I and Zeolite:Spiked soil II mixtures.

that the same mobility of Pb was observed for clay: spiked soil I mixtures can be related to the pH of TCLP extracts, which were around 5 at all mixing ratios.

Addition of cement (Figure 4) up to 1:10 additive:soil ratio resulted in increase of TCLP extracts pH from 4.89 to the range of 11–12 and 98% decrease in leached Pb amount was observed. This 98% decrease at 1:10 mixing ratio is higher than the 93% decrease observed in case of 1:20 lime: spiked soil I mixture. These results showed that, similar to the lime, the efficiency of cement on Pb immobilization is pH dependent but it can work efficiently at lower pH values than lime. As a result of the high pH provided by cement addition, Pb metal retained in the form of insoluble hydroxide. Moreover, it is known that hydration of cement forms a crystalline structure. This results in a rock-like, monolithic, hardened mass (La Grega *et al.*, 1994). Thus, besides formation of insoluble lead hydroxides microencapsulation is also effective in decrease of Pb mobility due to cement addition. Beginning from 1:20 additive:soil mixing ratio, an increase in leached lead amount was observed due to decrease in pH of TCLP extracts to the levels of 5–6.

On the other hand, no significant decrease in mobility of Pb with respect to the initial value of 174 mg L^{-1} was observed when zeolite and sand were mixed with soil I (Figures 5 and 6).

Since almost no change was observed in mobility of Pb metal due to addition of clay, zeolite and sand to spiked soil I, leaching experiments were conducted using these additives and spiked soil II to ensure that these additives have no significant effect on immobilization of lead. The results of these experiments through which the same mixing ratios of additive: spiked soil I mixtures were used are shown in Figures 3, 5 and 6. As it can be seen from these figures, almost the same results with those of spiked soil I were obtained for each additive and hence no significant efficiency of these additives on lead metal was proved.

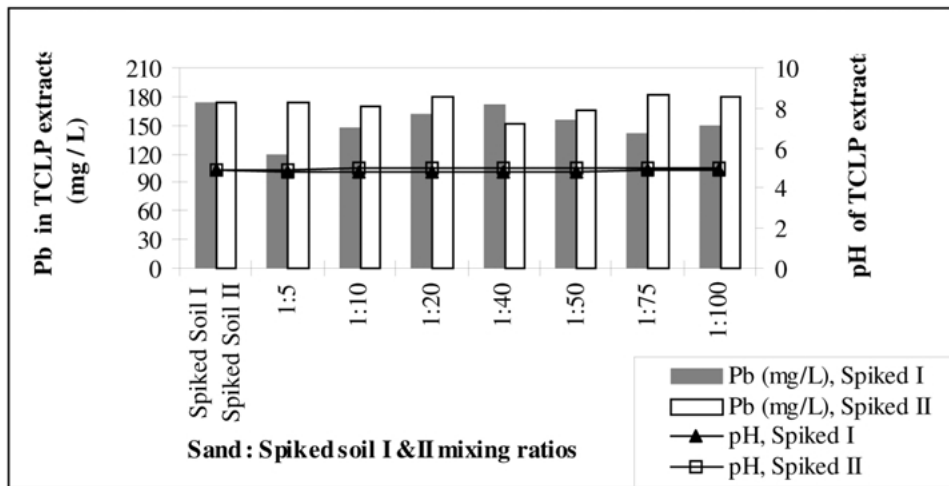


Figure 6. Leaching experiment results of Sand:Spiked soil I and Sand:Spiked soil II mixtures.

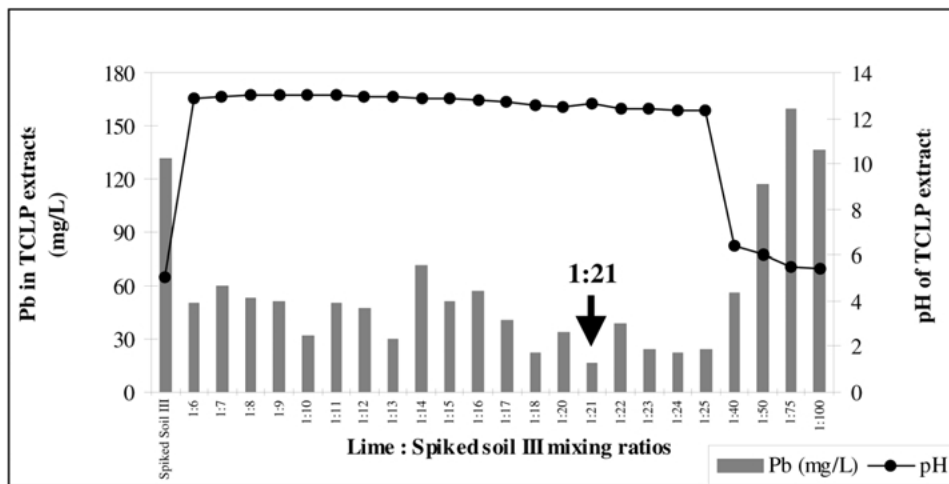


Figure 7. Leaching experiment results of Lime:Spiked soil III mixtures.

Finally two sets of leaching experiments were performed to identify the most optimum mixing ratio of two additives, lime and cement, determined as additives showing best immobilization efficiency on Pb metal through leaching experiments conducted for spiked soil I. In these experiments, lime and cement were mixed with spiked soil III at increased number of mixing ratios used for spiked soil I. Addition of lime (Figure 7) up to 1:18 additive:soil ratio resulted in increase of TCLP extracts pH from 5.06 to nearly 13 and greater than 80% decrease in mobility of Pb was observed with respect to initial value of 131.88 mg L^{-1} detected for spiked soil III without any additive. The least mobility of Pb was observed at 1:21 additive: soil ratio as 88%. The pH of TCLP extract detected at this ratio

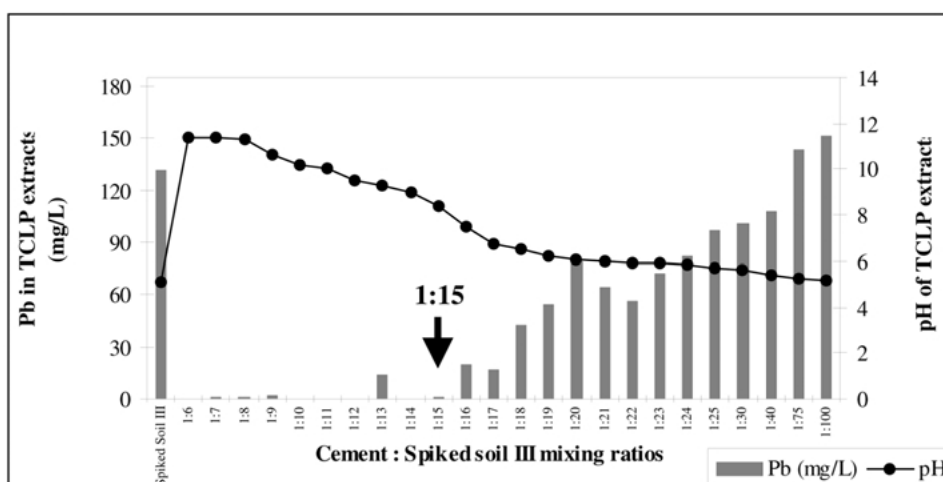


Figure 8. Leaching experiment results of Cement:Spiked soil III mixtures.

was around 12.6 which is approximately the pH of a saturated $\text{Ca}(\text{OH})_2$ solution (Dermatas and Meng, 1996). Similar to the results of lime:spiked soil I mixtures, starting from 1:40 additive:soil ratio, pH of TCLP extracts dropped sharply to the range of 5.5–6 and leached Pb amount from these mixtures began to increase. As a result of cement addition (Figure 8), 99% of decrease in mobility of Pb was observed for the mixtures within the range of 1:5–1:15 having TCLP pH values in the range of 8–12. Gradual decrease in pH of TCLP extracts was detected as the cement amount in mixtures decreased. Since the mobility of Pb metal began to increase for mixing ratios greater than 1:15, this additive:soil mixing ratio having TCLP pH value of 8.3 was determined as optimum ratio for cement.

4. Conclusions

The following conclusions were obtained from this study:

- Although a significant decrease (82%) on mobility of Pb was observed through activated carbon addition at 1:5 additive:soil ratio, application of this mixing ratio will not be economical in practice and volume of treated soil matrix will increase as a result of huge amount of activated carbon addition. Thus, activated carbon was determined as inefficient additive for immobilization of Pb.
- Since no decrease in Pb mobility was observed due to clay, zeolite and sand addition, it was concluded that these additives have no effect on Pb immobilization. If the pH of soil is somehow increased above 6 however, clay can be effective due to adsorption of Pb on clay surfaces.

- Lime was determined as very effective additive for lead immobilization through precipitation of lead hydroxides formed and entrapment of them in cementitious compounds resulted from pozzolonic reactions occurring with lime addition. The optimum mixing ratio of lime:soil was found as 1:21 ratio showing 88% immobilization efficiency on Pb at pH 12.6.
- Cement showed very high efficiency on immobilization of Pb through formation of insoluble lead hydroxides and microencapsulation of them in resultant hardened mass. The determined 1:15 cement:soil ratio provided significantly higher Pb immobilization efficiency (99%) at pH 8.3 than that was provided by optimum lime:soil ratio under 12.6.

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