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## Stabilization of an elevated heavy metal contaminated site

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### Abstract

Heavy metal contamination is a common problem that is encountered at many uncontrolled sites. Immobilization is seen as a promising technology for heavy metal remediation. Here, we report a remediation case study of an elevated and multi-metal contaminated site containing Cd, Cu, Ni, Pb, and Zn. In a laboratory test, when the soil was stabilized with reagent grade stabilizers ( $\text{CaHPO}_4$  and  $\text{CaCO}_3$ ), the toxicity characteristic leaching procedure (TCLP) extractable concentrations of Cd, Cu, Pb, and Zn were reduced by more than 87%. The greatest reduction was shown with Pb (99.8%). In the field,  $\text{Ca}(\text{H}_2\text{PO}_4)_2$  due to lower cost and higher solubility replaced  $\text{CaHPO}_4$ . The TCLP results of the field treatment showed that the extractable concentrations of Cd, Cu, Pb, and Zn were significantly reduced after 30 days of stabilization. The reduction ratios were 98% (Cd), 97% (Cu), 99% (Pb), and 96% (Zn). Although, the reduction ratio of Ni was only 65%, the average extractable concentration was still less than 4.0 mg/l. The percent reduction can, therefore, be considered reasonable. The significant reduction of extractable metal concentrations showed that the stabilizers, a combination of  $\text{Ca}(\text{H}_2\text{PO}_4)_2$  and  $\text{CaCO}_3$ , successfully immobilized heavy metals on the site. © 2001 Elsevier Science B.V. All rights reserved.

*Keywords:* Stabilization; Phosphate; Carbonate; TCLP; Heavy metals

### 1. Introduction

Heavy metal contaminated soils are encountered at many uncontrolled hazardous sites throughout the world. Contamination of heavy metals in the soil is a major concern because

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of their toxicity and threat to human life and environment. These heavy metals may adversely affect soil ecology, agricultural production, or product quality and water quality. Many methods have been used to stabilize heavy metal contaminated soils such as pH redox control and chemical processes that form carbonate, sulfide, or silicate precipitates, which reduce metal solubility [1–10]. Stabilization is seen as a cost-effective and promising remediation technology that may reduce the leachable potential of heavy metals. Recently, the potential of phosphate has been tested for in situ immobilization of Pb contaminated soil [11–25]. Only a few systematic cases have been reported [25,26]. In our previous work,  $\text{PO}_4^{3-}$  and  $\text{CO}_3^{2-}$  based salts reduced the leachability of five metals when extracted with a 0.1N HCl solution [27]. In addition, the calculated equilibrium results showed that  $\text{CO}_3^{2-}$  and  $\text{PO}_4^{3-}$  could significantly reduce  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  to form less soluble minerals. Here, we report a stabilization of a multi- and elevated-heavy metals contaminated site using a combination of  $\text{Ca}(\text{H}_2\text{PO}_4)_2$  and  $\text{CaCO}_3$  as stabilizers. A toxicity characteristic leaching procedure (TCLP) was conducted to ensure the stabilization effectiveness of the heavy metals, especially Cd and Pb.

The contaminated site is about 450 m<sup>2</sup> in the south of Taiwan. The site was a dumping site for a small scrap metal enterprise, which had been operated for more than 10 years. The valuable metals and materials were picked up for recycling and the residue was dumped on the site. The residue contained various kinds of metals and was exposed to rainfall, which produced leaching. Because many of these sites were spread around the island an emergency technology has to be developed to eliminate the leaching potential of heavy metals to groundwater.

In 1995, a routine investigation of the environmental media was conducted by the local environmental agency. The agency found that the soil was polluted by the heavy metals and the concentrations were significantly high. Concentration decreased sharply with depth; contamination reached 1.2 m below the surface. In addition, Pb and Cd concentrations exceeded regulatory limits. The greatest concern for soil pollution was by heavy metal cadmium and lead because they are very toxic; the regulatory limits were 1 mg/l (Cd) and 5 mg/l (Pb), conducted by TCLP. The local environmental agency declared site cleanup a priority. Many remediation technologies such as solidification and chelating-extraction were considered for cleanup. Unfortunately, financial restrictions limited these promising technologies. The estimated cost of solidification was about US\$ 750/m<sup>3</sup> and that of stabilization was US\$ 250/m<sup>3</sup> for the small site. Stabilization was the most feasible option due to its ease of operation and low cost.

## 2. Experimental

### 2.1. Soil preparation and characterization

Before field treatment, the contaminated soil was sampled, characterized and tested with different stabilizers at our laboratory. Soil was taken from the site at two separate times. In the first series, soil was taken from six surface locations (0–10 cm) and was uniformly mixed. Laboratory tests were used to find the most effective reagents; analytical grade chemical reagents were used. In the second series, the site was divided into three different layers according to depth: a top layer (0–40 cm), a middle layer (40–80 cm), and a bottom

Table 1  
The characteristics of soils and heavy metal leaching concentration as evidenced by TCLP

	Top layer (0–10 cm)	Upper layer (0–40 cm)	Middle layer (40–80 cm)	Bottom layer (80–120 cm)
Composition (%)	>2 mm, 13.4; sand, 53.4; silt, 33.2			
Organic matter (%)	2.23	0.83	0.85	0.80
CEC <sup>a</sup> (meq/100 g)	9.86	12.8	12.1	14.9
pH	8.0	8.2	8.1	8.1
TCLP (mg/l) <sup>b</sup>				
Cd	4.52 ± 1.34	2.90 ± 0.20	0.14 ± 0.02	<0.5 µg/l
Cu	295 ± 48	172 ± 6	29.9 ± 1.8	15.0 ± 1.0
Ni	19.0 ± 5.5	2.3 ± 1.51	3.03 ± 0.45	1.82 ± 0.24
Pb	956 ± 132	629 ± 38	6.71 ± 0.30	2.89 ± 0.28
Zn	3153 ± 632	925 ± 190	236 ± 16	122 ± 3

<sup>a</sup> Cation exchange capacity obtained by the NH<sub>4</sub>OAc method.

<sup>b</sup> Sample tests were conducted in triplicate.

layer (80–120 cm). Soils were taken from four locations within the site. The preferred industrial grade reagents were applied to the soil to determine the optimal dosage for field treatment. The characterization of the soil followed standard procedures and results are listed in Table 1.

## 2.2. Materials and analytical methods

Distilled water was used throughout the testing. The laboratory temperature was maintained at 25 ± 2°C. Chemical compounds, HNO<sub>3</sub>, HCl, NaOH, CH<sub>3</sub>COOH, CaHPO<sub>4</sub>·2H<sub>2</sub>O, CaCO<sub>3</sub>, MgHPO<sub>4</sub>·3H<sub>2</sub>O, Na<sub>2</sub>HPO<sub>4</sub>·12H<sub>2</sub>O (Nacalai, Japan), and Ca(H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O (local fertilizer supplier) were used as received without further purification. Scaling down the amounts of soil and solution modified the standard TCLP test. Ten grams of soil were added to a 200 ml extraction solution and shaken for 18 h at 30 rpm (Cherng Huei RA-926, Taiwan). The TCLP extraction determination followed the standard procedure [28]. Generally, extraction solution B (pH 2.88) was used for the unaltered contaminated soil and extraction solution A (pH 4.93) was used for the calcium phosphate-based stabilized soil. After the end of the shaking, each extraction solution was withdrawn and passed through a 0.6 µm filter. Metal contents in the filtrate were analyzed with an atomic absorption (AA) Spectrophotometer (Hitachi Z-8000). Solution pH was measured with a Suntex-700 pH meter. All glassware was soaked in 6N HNO<sub>3</sub> for at least 6 h and rinsed with distilled water prior to use.

## 2.3. Stabilization treatment

Each laboratory stabilization test included 100 g soil, 50 ml H<sub>2</sub>O, and a predetermined weight ratio of phosphate- and carbonate-based salts to dry soil weight. All materials were uniformly mixed in a glass beaker. The stabilized soil was air dried for 14 days. Ten grams

Table 2  
Treatment processes (sequence 1–5) in the field

1	Excavation with backhoe
2	Screening/removal of large substances
3	(a) Mixing in a 6 m <sup>3</sup> tank containing 3.5 m <sup>3</sup> soil, predetermined stabilizers, and water (b) Mixing with backhoe about 10 min (c) An amount of 150 g soil of each mixture was withdrawn for TCLP analysis after 30 days (d) The stabilized soil was stockpiled near the site
4	TCLP testing was performed on the withdrawn soils after 30 days
5	When the withdrawn soils met TCLP regulatory limits the stockpile soils were back filled to the site to grade

Table 3  
The applied weight ratios (to dry soil) of Ca(H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O and CaCO<sub>3</sub> for the field treatment

Layer	Ca(H <sub>2</sub> PO <sub>4</sub> ) <sub>2</sub> ·H <sub>2</sub> O (%)	CaCO <sub>3</sub> (%)
Upper	6.25	6.25
Middle	2.1	2.1
Bottom	0.5	0.5

of soil were taken for each TCLP test. CaCO<sub>3</sub> and Ca(H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O were used as field treatment stabilizers. CaHPO<sub>4</sub> was replaced by Ca(H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub> because: (1) the PO<sub>4</sub><sup>3-</sup> content of Ca(H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O (76%) was higher than CaHPO<sub>4</sub>·2H<sub>2</sub>O (56%); (2) the solubility of Ca(H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O is higher than CaHPO<sub>4</sub>·2H<sub>2</sub>O (Ca(H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O = Ca<sup>2+</sup> + 2H<sub>2</sub>PO<sub>4</sub><sup>-</sup> + H<sub>2</sub>O, log *K* = -1.15) [29] and (CaHPO<sub>4</sub>·2H<sub>2</sub>O = Ca<sup>2+</sup> + HPO<sub>4</sub><sup>2-</sup> + 2H<sub>2</sub>O, log *K* = -6.6) [30]; and, (3) the Ca(H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O is a common agriculture fertilizer in Taiwan that costs less than CaHPO<sub>4</sub>·2H<sub>2</sub>O. The on site stabilization procedure is shown in Table 2. On the site, the treatment process was divided into three different layers, as judged by the heavy metal content and different amounts of minerals. Chowdhury et al. [26] reported a lead contamination site. Phosphate was used as a remediation agent. The contents of phosphate are distinguished by lead concentrations. 2.5% phosphate was added to the site containing less than 5000 mg/l of lead. For the soil containing more than 5000 mg/l of lead, 5% phosphate was added to the site as stabilization agent. The Ca(H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub> and CaCO<sub>3</sub> to soil weight ratio is listed in Table 3.

After 30 days of stabilization, when the soil passed the TCLP test, it was placed back on the site. Then the surface of the site was layered with concrete. A drainage system was rebuilt to prevent further rainfall leaching. In addition, the groundwater table was 3 m below the surface, so it would not flush the metals out of the soil.

### 3. Results and discussion

#### 3.1. Laboratory test

Table 1 shows the soil characteristics. The surface soil was predominantly sand and silt. The TCLP leachable metal concentrations were much higher than normal. Pb and Cd

concentrations were higher than regulatory limitations (Pb = 5 mg/l, Cd = 1 mg/l); the Pb concentration (956 mg/l), particularly was about 200-fold higher than the regulatory limit. Although, there were no regulatory limits for Zn, Cu, and Ni at the time of investigation, the Zn (3135 mg/l) and Cu (295 mg/l) leachable soil concentrations were considered too high and needed to be reduced. Previous tests [27] showed that when those soils were stabilized with 5% Na<sub>2</sub>CO<sub>3</sub>, and then extracted with 0.1N HCl, metal concentrations were significantly reduced. However, the TCLP metal extractable concentrations were 3.2 mg/l (Cd), 136 mg/l (Cu), 8.6 mg/l (Ni), 589 mg/l (Pb), and 1576 mg/l (Zn). Both Pb and Cd still exceeded regulatory limits and the leachable soil concentrations of Zn and Cu were still considered too high. When 10% CaHPO<sub>4</sub> was added as a stabilizer, TCLP results showed that Pb and Cd concentrations were below regulatory limits. The use of other stabilizers did not give the same results. The results matched those reported by Berti and Cunningham [11]. Three sites of Pb-contaminated soil contained Pb concentration from 1200 to 3500 mg/kg soil. The leachable soil Pb concentrations were below 5 mg/l by TCLP after soils were treated with 0.5% P as KH<sub>2</sub>PO<sub>4</sub>. Other materials, such as CaSO<sub>4</sub>, CaCO<sub>3</sub> were not as effective as P for reducing leachable Pb at a rate up to 10%. Therefore, laboratory stabilization procedures were expanded to find the optimum, effective quantity of CaHPO<sub>4</sub> or combinations of CaHPO<sub>4</sub> with other salts. Analytical grade reagents were used. After the optimum stabilizer concentrations were found, different soil layers were tested with industrial grade reagents to derive the most cost-effective combination of reagents and stabilizer. The selected combinations were then applied to the site.

The first row of Table 4 shows TCLP leachable concentrations of Cd, Cu, Ni, Pb, and Zn after stabilization with 10% of CaHPO<sub>4</sub> on days 7 and 14. Generally, the leachable concentrations on the 14th day were lower than on 7th day, except for Ni, which did not show significant change. This indicated that the stabilization reaction was effective for more than seven days.

Table 4  
TCLP leaching concentrations of Cd, Cu, Ni, Pb, and Zn as stabilized with CaHPO<sub>4</sub>, Na<sub>2</sub>HPO<sub>4</sub>, and MgHPO<sub>4</sub>

	Time (day)	Cd (mg/l)	Cu (mg/l)	Ni (mg/l)	Pb (mg/l)	Zn (mg/l)	Final pH
10% CaHPO <sub>4</sub>	7	0.89 ± 0.11 <sup>a</sup>	79.1 ± 14.7	8.89 ± 1.30	3.94 ± 0.50	460 ± 108	
	14	0.52 ± 0.08	37.2 ± 2.58	9.14 ± 0.84	1.46 ± 0.31	344 ± 29	7.1
7.5% Na <sub>2</sub> HPO <sub>4</sub>	7	1.28 ± 0.02	78.5 ± 1.1	9.0 ± 1.02	34.6 ± 2.44	1260 ± 360	
	14	1.08 ± 0.02	54.5 ± 1.5	5.63 ± 0.29	21.9 ± 0.87	900 ± 210	9.9
10% Na <sub>2</sub> HPO <sub>4</sub>	7	0.82 ± 0.05	56.0 ± 1.25	7.17 ± 0.14	8.1 ± 3.02	1000 ± 280	
	14	0.71 ± 0.02	43.6 ± 0.53	4.80 ± 0.72	3.6 ± 0.64	570 ± 40	10.1
15% Na <sub>2</sub> HPO <sub>4</sub>	7	0.47 ± 0.02	42.7 ± 3.21	7.15 ± 1.23	1.4 ± 0.06	520 ± 60	
	14	0.34 ± 0.02	30.3 ± 1.29	4.35 ± 0.18	0.44 ± 0.2	350 ± 20	10.2
5% MgHPO <sub>4</sub>	7	1.67 ± 0.06	58.7 ± 4.6	9.33 ± 0.83	49.2 ± 2.1	1050 ± 9	
	14	1.45 ± 0.05	50.2 ± 1.16	6.8 ± 0.82	23.7 ± 1.45	850 ± 72	7.9
10% MgHPO <sub>4</sub>	7	0.85 ± 0.04	36.8 ± 4.5	9.39 ± 0.88	71.3 ± 11.3	650 ± 14	
	14	0.80 ± 0.06	35.6 ± 3.2	6.5 ± 0.9	11.4 ± 4.13	490 ± 26	7.7

<sup>a</sup> Sample tests were conducted in triplicate.

The mean Cd leachable concentrations were reduced from 4.52 to 0.89 and 0.52 mg/l (80 and 88% reduction) after 7 and 14 days of stabilization. Cu leachable concentrations were reduced from 295 to 79.1 and 37.2 mg/l (73 and 87% reduction). At the 7th and 14th days, the mean Ni leachable concentrations were reduced to 8.9 and 9.1, respectively, from 19.0 mg/l (52% reduction). Pb leachable concentrations were reduced from 956 to 3.9 and 1.5 mg/l (>99.5% reduction). This shows that phosphate is particularly promising in immobilizing Pb contaminated soil. Zn leachable concentrations were reduced from 3153 to 460 and 344 mg/l (85 and 89% reduction). Many researchers have examined the stabilization of metals in contaminated soils. Chowdhury et al. [26] reported a 22,388 mg Pb/kg contaminated soil treated with 5% phosphate-based additive. Pb leaching concentration was reduced from 180 to 3.6 mg/l. Basing on a geochemical modeling, Ruby et al. [15] reported that the addition of phosphate amendment to Pb-bearing soil resulted in aqueous lead solubility of 0.1  $\mu\text{g/l}$  in soil. Ma et al. [17] reported that phosphate rocks reduced water-soluble Pb from a contaminated soil by 56.8–100%. Ma [20] reported that hydroxyapatite ( $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ ) effectively immobilized (>71%) of the aqueous Pb in four sites of  $\text{PbHAsO}_4$  contaminated soil. Chlopecka and Adriano [18] reported that the ameliorants of lime and apatite ( $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ ) decreased the leaching concentration of Zn in a contaminated soil. Berti and Cunningham [11] investigated three sites of Pb contaminated soil from 1200 to 3500 mg/kg. The leachable soil Pb was significantly reduced in all cases from as high as 30 mg Pb/l to below the regulatory limit of 5 mg/l after treatment of 0.5% of P to the soil. Chen et al. [21] reported that a Pb, Cd, and Zn contaminated soil was stabilized with apatite. The removals were about 0.729 mmol of Pb, 0.489–1.317 mmol of Cd, and 0.596–2.187 mmol of Zn/g of apatite. Eighmy et al. [23] added 1.2 mol of  $\text{H}_3\text{PO}_4$  to 1 kg dry scrubble residue and the leachable concentrations of heavy metal reductions were Cd (38%), Cu (58%), Pb (98%), and Zn (28%). Zhang et al. [22] reported that a Pb contaminated soil was added apatite and the soluble Pb concentration was 96% reduced in suspension. Hettiarachchi et al. [24] added 5 g of P to five sites of Pb contaminated soil ranging from 4463 to 42,592 mg/kg soil. The reductions in bioavailable Pb ranged from 15 to 41%. These results showed that phosphate-based additive was able to form less soluble minerals with heavy metals in aqueous soil and can reduce leachable concentration of heavy metals, particularly Pb.

To find cost-effective phosphate-based salts,  $\text{Na}_2\text{HPO}_4$  and  $\text{MgHPO}_4$  were used to stabilize the contaminated soil. The metal leachable concentrations, with varying ratios of  $\text{Na}_2\text{HPO}_4$  and  $\text{MgHPO}_4$ , are listed in Table 4. The results indicated both phosphate salts could reduce the metal leachable potential after 14 days of stabilization but identical ratios were not as effective as  $\text{CaHPO}_4$ . For example, the extracted Pb and Zn leachable concentrations stabilized with 10%  $\text{Na}_2\text{HPO}_4$  and  $\text{MgHPO}_4$  were higher than that stabilized with 10%  $\text{CaHPO}_4$ . The final pH of the stabilized soil was 7.1 with  $\text{CaHPO}_4$ , 7.7–7.9 with  $\text{MgHPO}_4$ , and 9.9–10.2 with  $\text{Na}_2\text{HPO}_4$ . The pH of the  $\text{Na}_2\text{HPO}_4$  stabilized soil was considered to be too high.

The compound  $\text{CaCO}_3$  is less expensive than  $\text{CaHPO}_4$  and previous studies have shown that carbonate effectively immobilizes Cd.  $\text{CaHPO}_4$  and  $\text{CaCO}_3$  were combined and tested to immobilize the metals in the soil. Table 5 shows the leachable metal concentrations following  $\text{CaHPO}_4/\text{CaCO}_3$  stabilization. The concentrations were effectively reduced with 5%  $\text{CaHPO}_4$  and 10%  $\text{CaCO}_3$ ; the Cd and Pb leachable concentrations were lower than

Table 5  
TCLP leaching concentrations of Cd, Cu, Ni, Pb, and Zn as stabilized with CaHPO<sub>4</sub> and CaCO<sub>3</sub>

	Time (day)	Cd (mg/l)	Cu (mg/l)	Ni (mg/l)	Pb (mg/l)	Zn (mg/l)	Final pH
5% CaHPO <sub>4</sub> + 10% CaCO <sub>3</sub>	7	0.83 ± 0.01 <sup>a</sup>	51.4 ± 2.3	7.2 ± 0.3	4.3 ± 1.0	601 ± 35	
	14	0.68 ± 0.05	44.8 ± 11.2	6.7 ± 0.6	4.1 ± 0.4	524 ± 79	7.4
6% CaHPO <sub>4</sub> + 10% CaCO <sub>3</sub>	7	0.75 ± 0.02	56.5 ± 2.5	9.1 ± 1.2	5.4 ± 0.1	602 ± 243	
	14	0.57 ± 0.01	42.9 ± 3.7	6.3 ± 0.9	2.5 ± 0.2	406 ± 60	7.4
7% CaHPO <sub>4</sub> + 10% CaCO <sub>3</sub>	7	0.64 ± 0.14	53.4 ± 19.3	7.1 ± 1.3	2.4 ± 0.8	418 ± 63	
	14	0.44 ± 0.01	40.6 ± 5.1	6.6 ± 1.3	1.4 ± 0.1	329 ± 68	7.4
8% CaHPO <sub>4</sub> + 10% CaCO <sub>3</sub>	7	0.64 ± 0.05	47.1 ± 8.9	7.8 ± 2.8	2.1 ± 0.2	707 ± 514	
	14	0.34 ± 0.01	37.0 ± 2.4	6.6 ± 0.4	0.6 ± 0.2	278 ± 64	7.4
6% CaHPO <sub>4</sub> + 9% CaCO <sub>3</sub>	7	0.82 ± 0.05	57.6 ± 11.1	8.4 ± 3.2	5.0 ± 0.1	553 ± 18	
	14	0.60 ± 0.04	50.2 ± 5.7	7.8 ± 0.8	2.6 ± 0.3	551 ± 51	7.4
7.5% CaHPO <sub>4</sub> + 7.5% CaCO <sub>3</sub>	7	0.70 ± 0.05	46.9 ± 4.9	7.3 ± 0.5	2.5 ± 0.2	423 ± 28	
	14	0.44 ± 0.03	42.3 ± 3.1	7.1 ± 0.9	1.2 ± 0.2	402 ± 57	7.4
5% CaHPO <sub>4</sub> + 5% CaCO <sub>3</sub>	7	0.97 ± 0.11	58.6 ± 2.1	7.9 ± 1.3	7.6 ± 1.5	808 ± 90	
	14	0.77 ± 0.06	55.0 ± 3.8	7.8 ± 0.3	4.8 ± 0.4	739 ± 67	7.4

<sup>a</sup> Sample tests were conducted in triplicate.

regulatory limits. The most effective combination dose was 8% CaHPO<sub>4</sub>/10% CaCO<sub>3</sub>. Generally, increasing the CaHPO<sub>4</sub> dosage reduced the more leachable metal concentrations after 14 days of stabilization. The soil pH remained at about 7.4. Therefore, the CaHPO<sub>4</sub>/CaCO<sub>3</sub> combination was employed to stabilize the contaminated soil. The cost was less than when using only CaHPO<sub>4</sub>, and the soil pH change was moderate.

### 3.2. Field test

Three layers of soil were sampled a second time with industrial grade reagents. The effective reagent dosages, which reduced the leachable concentrations of the heavy metals, are listed in Table 3. The remediation work followed the procedures listed in Table 2. The stabilization process was carried out in a 6 m<sup>3</sup> tank; about 3.5 m<sup>3</sup> soil was placed into the tank, the predetermined amount of salts and water were added, and the material was mixed vigorously for 10 min with a backhoe. After the soil had been treated, it was removed with the backhoe and stockpiled near the site. A 150 g aliquot was withdrawn from each tank mixture and TCLP analyzed in the laboratory after 30 days. After the TCLP heavy metal leachable concentrations had met regulatory limits the stockpiled soil was taken back to the site to grade. Figs. 1–5 show a bar chart with an error bar (S.D.) for five metal leachable concentrations from the top, middle and bottom layers of the site after 30 days stabilization with CaCO<sub>3</sub> and Ca(H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub>.

Fig. 1 shows the Cd leachable concentrations from the three layers after 30 days. The results show that all 138 leachable concentrations were far less than 1 mg/l. In the top layer, the Cd mean leachable concentration was 0.051 mg/l, which was a 98% reduction when

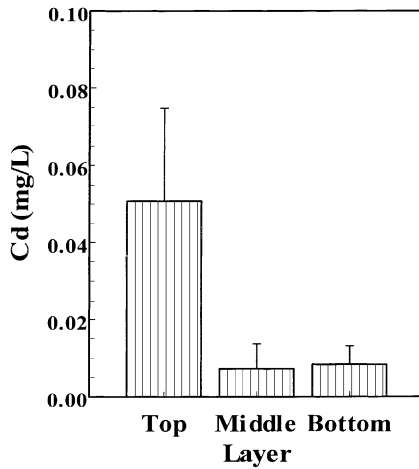


Fig. 1. TCLP leaching concentration of Cd as stabilized with  $\text{Ca}(\text{H}_2\text{PO}_4)_2$  and  $\text{CaCO}_3$ . The leachable concentration  $[\text{Cd}]_0$  of the untreated sample of the top layer is 2.9 mg/l, samples  $n = 51$ , the average leachable concentration  $[\text{Cd}]_{\text{av}} = 0.051$  mg/l, and S.D. = 0.024 mg/l. The middle layer:  $n = 41$ ,  $[\text{Cd}]_0 = 0.14$  mg/l,  $[\text{Cd}]_{\text{av}} = 0.0072$  mg/l, and S.D. = 0.0064 mg/l. The bottom layer:  $n = 24$ ,  $[\text{Cd}]_{\text{av}} = 0.0084$  mg/l, and S.D. = 0.0041 mg/l.

compared with the untreated sample 2.9 mg/l. All mean leachable Cd concentrations from the middle and bottom layers were less than 0.01 mg/l. Some samples were less than the instrument detection limit of 0.5  $\mu\text{g/l}$ .

Fig. 2 shows the Cu leachable concentrations. All 138 leachable concentrations were far less than 10 mg/l. The top layer Cu mean (51 samples) leachable concentration was

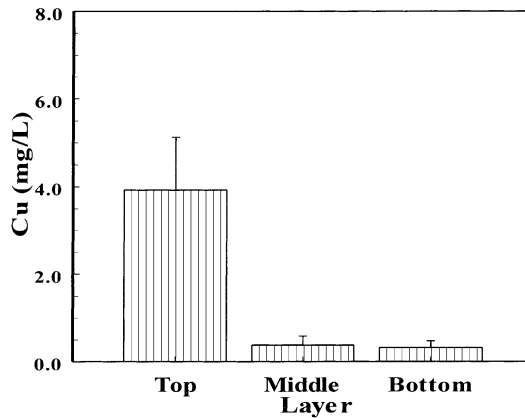


Fig. 2. TCLP leaching concentration of Cu as stabilized with  $\text{Ca}(\text{H}_2\text{PO}_4)_2$  and  $\text{CaCO}_3$ . The leachable concentration  $[\text{Cu}]_0$  of the untreated sample of the top layer is 172 mg/l, samples  $n = 51$ , the average leachable concentration  $[\text{Cu}]_{\text{av}} = 3.92$  mg/l, and S.D. = 1.21 mg/l. The middle layer:  $n = 40$ ,  $[\text{Cu}]_0 = 29.9$  mg/l,  $[\text{Cu}]_{\text{av}} = 0.376$  mg/l, and S.D. = 0.21 mg/l. The bottom layer:  $n = 37$ ,  $[\text{Cu}]_0 = 15.0$  mg/l,  $[\text{Cu}]_{\text{av}} = 0.33$  mg/l, and S.D. = 0.15 mg/l.



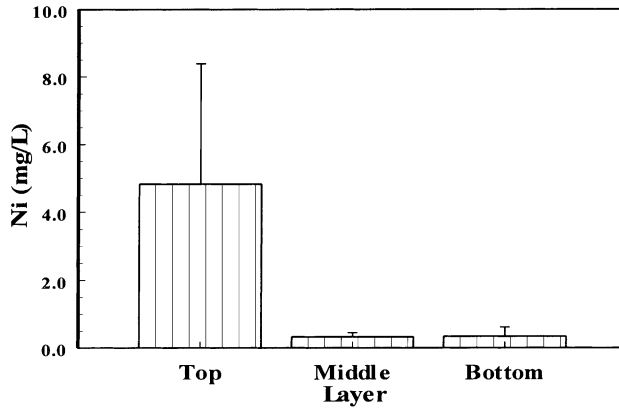


Fig. 3. TCLP leaching concentration of Ni as stabilized with  $\text{Ca}(\text{H}_2\text{PO}_4)_2$  and  $\text{CaCO}_3$ . The leachable concentration  $[\text{Ni}]_0$  of the untreated sample of the top layer is 12.3 mg/l, samples  $n = 51$ , the average leachable concentration  $[\text{Ni}]_{\text{av}} = 4.83$  mg/l, and S.D. = 3.56 mg/l. The middle layer:  $n = 44$ ,  $[\text{Ni}]_0 = 3.03$  mg/l,  $[\text{Ni}]_{\text{av}} = 0.33$  mg/l, and S.D. = 0.12 mg/l. The bottom layer:  $n = 43$ ,  $[\text{Ni}]_0 = 1.82$  mg/l,  $[\text{Ni}]_{\text{av}} = 0.34$  mg/l, and S.D. = 0.28 mg/l.

reduced to 3.9 mg/l from the untreated sample 172 mg/l (>97% reduction). The mean Cu concentration for both the middle and bottom layers was less than 0.4 mg/l (>97% reduction).

Fig. 3 shows the Ni leachable concentrations. For the top layer Ni mean (51 samples) the leachable concentration was reduced to 4.0 mg/l from the untreated 12.3 mg/l (>67% reduction). The mean Ni concentration for the middle and bottom layers was less than 0.4 mg/l (>80% reduction).

Fig. 4 shows the leachable Pb concentrations at the top layer. All 51 sample leachable concentrations were less than 2 mg/l. For the top layer, Pb mean leachable

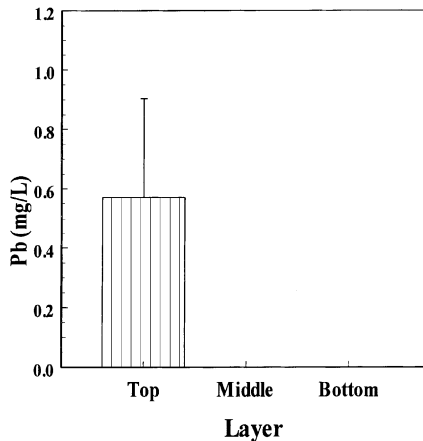


Fig. 4. TCLP leaching concentration of Pb as stabilized with  $\text{Ca}(\text{H}_2\text{PO}_4)_2$  and  $\text{CaCO}_3$ . The leachable concentration  $[\text{Pb}]_0$  of the untreated sample of the top layer is 629 mg/l, samples  $n = 51$ , the average leachable concentration  $[\text{Pb}]_{\text{av}} = 0.57$  mg/l, and standard deviation is S.D. = 0.33 mg/l.

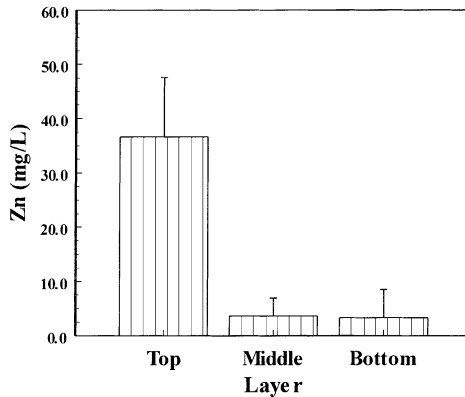


Fig. 5. TCLP leaching concentration of Zn as stabilized with  $\text{Ca}(\text{H}_2\text{PO}_4)_2$  and  $\text{CaCO}_3$ . The leachable concentration  $[\text{Zn}]_0$  of the untreated sample of the top layer is 925 mg/l, samples  $n = 51$ , the average leachable concentration  $[\text{Zn}]_{\text{av}} = 36.6$  mg/l, and S.D. = 11.0 mg/l. The middle layer:  $n = 44$ ,  $[\text{Zn}]_0 = 236$  mg/l,  $[\text{Zn}]_{\text{av}} = 3.61$  mg/l, and S.D. = 3.32 mg/l. The bottom layer:  $n = 43$ ,  $[\text{Zn}]_0 = 122$  mg/l,  $[\text{Zn}]_{\text{av}} = 3.30$  mg/l, and S.D. = 5.23 mg/l.

concentrations were reduced to a mean 0.57 mg/l from the untreated 629 mg/l (>99% reduction). All leachable concentrations from the middle and the bottom layers were less than the instrument detection limit of 0.05 mg/l. This was consistent with the laboratory results that showed phosphate-based salts could significantly reduce Pb leachable concentrations. The  $\text{Ca}(\text{H}_2\text{PO}_4)_2$  and  $\text{CaCO}_3$  combination showed great potential for field immobilization of Pb.

Fig. 5 shows the leachable Zn concentrations. All 138 leachable concentrations were less than 100 mg/l; the top layer (51 samples) mean Zn concentrations were reduced to 36.6 from 925 mg/l (96% reduction). The mean Zn concentrations for the middle and the bottom layer samples were less than 4 mg/l (>97% reduction).

#### 4. Conclusion

The results of the laboratory treatment showed that extractable heavy metal concentrations were reduced when the elevated multi-metals contaminated soil was stabilized with phosphate salts. The extractable concentrations of Cd and Pb were lower than regulatory limits. When the  $\text{CaHPO}_4/\text{CaCO}_3$  combination was used as a stabilizer, it decreased the extractable heavy metal concentrations as evidenced by the TCLP test. In the field, the TCLP results of leachable metal concentrations showed that stabilization with  $\text{Ca}(\text{H}_2\text{PO}_4)_2/\text{CaCO}_3$  successfully immobilized the heavy metals in the site. The leachable concentrations of Cd, Cu, Pb, and Zn had a greater than 95% reduction, particularly, Pb with a 99% reduction. Although, the Ni leachable concentration only had a >65% reduction, after 30 days the 4.0 mg/l of leachable concentration was not considered too high.

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