

REDUCTION OF Cd, Pb AND Ni LEACHING FROM CONTAMINATED SOILS BY IMMOBILIZATION

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Abstract

This paper discusses the results of Cd, Pb and Ni immobilization using cement. Soil contamination levels were in the range 500 mg/kg to 5,000 mg/kg, and cement ratios were in the range 3% to 18%. The process was highly effective in minimizing the leaching of tested heavy metals. The measured leaching reduction results were as follows: 76% to more than 96% for Pb; 30% to more than 99% for Cd; and 41% to more than 80% for Ni. Leaching was measured using the Toxicity Characteristic Leaching Procedure (TCLP). Treatment resulted in reducing the leaching of metals to below the TCLP hazardous concentration limits, specified by the United States Environmental Protection Agency, USEPA.

Introduction

Part of the current environmental engineering research at The University of Jordan, is focussed on investigating appropriate soil remediation technologies. Three new techniques, in terms of pollution control, are being evaluated: Soil washing, contaminants extraction, and contaminants immobilization. It is essential to benefit from the experience of developed countries in the area of pollution control and prevention, to cope with the expanding industrial activities in the area. What is urgent though, is the development of the appropriate regulatory framework and institutions to contribute to the success of environmental protection efforts. This paper discusses our most recent experimental results on Cd, Pb, and Ni immobilization in contaminated soils using cement.

In the United States, the development of contaminated site remediation technologies was accelerated in the last 15 years as a direct result of the enactment of a number of federal laws and amendments, including the Resources Conservation and Recovery Act (RCRA, 1976), the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA, 1980), the Hazardous and Solid Waste Amendments (HSWA, 1984), and the Superfund Amendments and Reauthorization Act (SARA, 1986). CERCLA required the establishment of cleanup standards and procedures for responding to releases of hazardous contaminants to the environment. To satisfy CERCLA requirements, a 1985 National Contingency Plan (U.S. NCP) outlined necessary levels of site cleanup

and mentioned solidification as an alternative remedial action⁽¹⁾. HSWA prohibited landfilling liquid hazardous wastes and banned the disposal of untreated hazardous wastes unless it can be proven that, as long as the waste remains hazardous, no migration of hazardous constituents can take place. HSWA called for the establishment of hazardous waste treatment standards based on the Best Demonstrated Available Technology (BDAT). SARA established an innovative technology program for the development of on-site treatment technologies that "permanently and significantly reduce the volume, toxicity or mobility of hazardous substances". Without such treatment, off-site disposal of hazardous wastes under SARA was considered to be "the least favoured alternative remedial action". A number of new and innovative soil remediation technologies are currently being investigated in the United States and Europe, and the accumulating body of knowledge is increasing the fundamental understanding of how such processes work. Sims⁽²⁾ provided a critical review of many new and emerging processes, including: soil washing, stabilization/solidification, soil vacuum extraction, bioremediation, glassification/vitrification, radio frequency heating, electrokinetics, and a number of other processes.

Solidification is the conversion of liquids into solids, and stabilization is a chemical reaction that renders the hazardous constituents less mobile⁽³⁾. The technology was developed to meet the regulatory requirement banning the disposal of liquids, and demanding that all hazardous wastes be treated in a manner that minimizes the likelihood of migration of hazardous constituents. Immobilization of

contaminants is contributed by both processes; stabilization and solidification. Contaminants in the final stabilized/solidified product are⁽⁴⁾ locked within unconnecting pore-holes, chemisorped, precipitated, chemically included, concentrated on surfaces, or attached by other mechanisms. Stabilization/solidification technology was demonstrated in small and full-scale projects and proved to be successful for the treatment of a wide range of contaminants⁽¹⁾. The process appears to offer a cheap and simple alternative soil remediation technology.

In regards to immobilization of metals using cement, the following information is currently available⁽⁴⁻¹⁰⁾: (i) Hg formed a soluble and volatile compound, HgO, in cement treated wastes; (ii) Cd was effectively immobilized, and the process was enhanced when sulfides were added forming insoluble CdS; (iii) Pb was effectively immobilized. Pb reacts with the silicates in the cement resulting in retarding the cement setting reactions. Pb immobilization was enhanced by the addition of phosphates; (iv) Chromate, arsenate, and arsenite were not effectively immobilized; (v) Ni and Cu were effectively immobilized, while Zn immobilization achieved intermediate results; and (vi) Ba formed BaSO₄ which weakened the solidified/stabilized product. The presence of Pb, organic matter, silt, and clay within the waste material increased the time needed for cement setting^(2,5). The use of portland cement was considered incompatible in the presence of borates, arsenates, or high concentrations of sulfates.

This study presents the leaching results obtained on treated soil samples originally contaminated with various concentrations of Pb(II), Cd(II), and Ni(II). The Toxicity Characteristic Leaching Procedure (TCLP) was used to determine the leaching of metals from contaminated and treated soils. The TCLP test is used as a criterion for defining hazardous and non-hazardous wastes^(1,11). The test is designed to identify wastes that, if improperly managed, are likely to leach hazardous constituents to the environment.

Materials and Methods

To ensure accuracy, blanks and duplicate leachate samples were analyzed for each run. All used glassware and sample vials were properly acid washed and rinsed. An organic silty soil was obtained from a nearby site and sieved using an ASTM No. 10 (2 mm) sieve. A summary of selected characteristics of the tested soil is presented in Table 1. The fraction passing the 2 mm sieve was oven dried and thoroughly mixed. Optimum water to cement ratios were determined at the maximum compressive strength, obtained on 5 cm standard cubes, prepared at selected water to cement ratios. The tested cement ratios were in the range 3% to 18%. Portions of the dried soil were contaminated with Cd ($\text{Cd}(\text{NO}_3)_2$), Pb ($\text{Pb}(\text{NO}_3)_2$) and Ni ($\text{Ni}(\text{NO}_3)_2$), at contamination levels of 500 mg/kg, 1,000 mg/kg, and 5,000 mg/kg. After contamination, the soil samples were oven dried, sieved through a 2 mm sieve, thoroughly mixed, and the concentration of metals

measured. All soil metal contamination levels were determined using the nitric acid digestion procedure, Method 302D⁽¹²⁾.

Table 1: Selected characteristics of the tested raw soil.

Soil Parameter	Parameter Value
Coarse Sand (%)	12.3
Fine Sand (%)	12.0
Silt (mostly) and Clay (%)	75.7
Moisture Content (%)	1.8
Volatile Content at 550 °C(%)	6.1
pH (1 wt. soil : 1 wt. water)	7.9

In preparing each test cube, an approximately 500 g portion of the contaminated soil was mixed with cement and water, then the mixture was placed in a standard 5 cm mold. The mold was then wrapped with thick plastic covering, which sealed the moisture inside the plastic, then covered with wet clothing. After approximately 24 hours of curing, the cubes were removed from the molds and replaced inside individual sealed plastic bags for curing. Two to four similar cubes were prepared for each test; one or two tested after seven days of curing, and the other one or two tested after 28 days of curing. Each cured cube was tested for compressive strength, and portions of the crushed cube (passing a 2 mm sieve) were tested for leaching using the TCLP test. Initial soil TCLP results were measured simultaneously with the 28 days treated and cured soil samples.

In the TCLP test, the solids were added to individual extractor bottles and extracted with a weight of extraction fluid equal to 20 times the weight of the solids. The TCLP⁽¹¹⁾ extraction fluid consisted of 5.7 mL glacial acetic acid and 64.3 mL of 1.0 N NaOH diluted to 1 L, with a pH of 4.93±0.05. The tightly closed extraction TCLP bottles were rotated in a rotary extractor at 30 rpm for 18 hours. After completion, the contents of the TCLP bottles were centrifuged for 15 minutes at 2000 rpm, and the concentration of metals in the liquid phase measured. The concentration of individual metals in all extraction solutions were measured using Flame Atomic Absorption, FAA.

Results and Discussion

The addition of cement and water to the contaminated soil samples during treatment resulted in diluting the contaminant. Accordingly, the measured reductions in the concentrations of leachable metals in the TCLP extracts were partly due to dilution. The regulatory limits are based on the concentration of contaminants in the TCLP liquid extract, regardless of the quantity of added cement. However, to better evaluate the degree of immobilization achieved using cement, it was necessary to normalize the data to account for the dilution effects. Because all samples were oven dried before the TCLP test, it was assumed, for the purposes of this evaluation, that the dilution effects were mainly due to cement

addition. Accordingly, the soil ratio in all treated samples was estimated according to Equation 1, and the corrected leachable metal concentrations were calculated according to Equation 2. A factor of 20 appears in Equation 2 to convert the TCLP measurement units from mg/L to mg/kg, as discussed in the previous section.

$$SR=(100-CR)/100 \quad \dots\dots\dots (1)$$

$$TCLP (mg/kg)=20 \text{ TCLP (mg/L)}/SR \quad \dots\dots\dots (2)$$

(where: SR=Soil Ratio in treated and dried samples; CR=Cement Ratio (%) used for treatment). The upper hazardous concentration limit for cadmium in the TCLP extract is 1 mg/L. The leaching results for untreated soil samples exceeded the TCLP limit, and were as follows: 8.6 mg/L for the contamination level 490 mg/kg; 14.0 m/L for the contamination level 1,130 mg/kg; and 138 mg/L for the contamination level 4,880 mg/kg. As presented in Table 2, none of the treated soil samples, at all three levels of Cd contamination, achieved the TCLP regulatory limit after 7 days of curing. However, after 28 days of curing, 11 of the 18 treated soil samples achieved the TCLP limit. Clearly, the continued cement reactions resulted in significant reduction in the mobility of cadmium. The data in Table 2 indicate that after 7 days of curing, reductions in Cd leaching were in the range 30% to 88%. As curing time increased from 7 days to 28 days, leaching was reduced further by more than 44% to 94%. The overall leaching reductions achieved after 28 days of curing were in the range 40% to more than 99%. The contribution of dilution to the achieved leaching reduction results is estimated to be in the range 3% to 18%. The results indicate that the quantity of cement needed to achieve the

TCLP limit increased as the contamination level increased. In addition, the concentration of Cd in the tested TCLP extracts decreased as the quantity of binder increased. However, if the dilution effects were taken into account, then the achieved Cd leaching reductions become smaller, particularly after 7 days of curing. Immobilization of cadmium was viewed⁽¹³⁾ to be a direct result of the formation of insoluble Cd(OH)₂ early in the cement setting process, serving as a nuclei for the formation of calcium-silicate-hydrate crystals.

Table 2: Immobilization of Cd using cement.

Cement Ratio (%)	Contamination Level = 490 mg/kg				Contamination Level = 1,130 mg/kg				Contamination level = 4,880 mg/kg			
	(A)	(B)	(C)	(D)	(A)	(B)	(C)	(D)	(A)	(B)	(C)	(D)
0	8.6	8.6	172	172	14.0	14.0	280	280	138	138	2760	2760
3	6.2	1.8	128	37	8.1	3.7	167	76	57.0	22.0	1175	454
6	5.8	<1.0	123	<21	5.2	1.3	111	28	23.0	11.1	489	236
9	4.1	<1.0	90	<22	4.5	<1.0	99	<22	22.0	3.6	483	79
12	2.2	<1.0	50	<23	4.0	<1.0	91	<23	22.0	1.7	500	37
15	2.2	<1.0	52	<24	3.7	<1.0	87	<24	19.0	<1.0	447	<24
18	1.8	<1.0	44	<24	4.1	<1.0	100	<24	17.0	<1.0	414	<24

- (A) TCLP in mg/L after 7 days of curing.
- (B) TCLP in mg/L after 28 days of curing.
- (C) TCLP in mg/kg, corrected for dilution, after 7 days of curing.
- (D) TCLP in mg/kg, corrected for dilution, after 28 days of curing.

The results of Cd immobilization presented in Table 2 are reflective of the mechanisms involved in the process. Immobilization increased as the quantity of binder increased. However, the continued cement and contaminant interactions contributed the most to immobilization. Maintaining a high pH range, ensured by the addition of sufficient amounts of the binder, and producing a durable solidified product are essential to the success of the process.

The initial TCLP leaching results for untreated soil, at the three levels of Pb contamination, exceeded the USEPA TCLP limit. The TCLP limit for Pb in the TCLP extract is 5 mg/L. The initial TCLP results for Pb were as follows: 8.3 mg/L for the contamination level 535 mg/kg; 20.4 mg/L for the contamination level 960 mg/kg; and 30.5 for the contamination level 5,160 mg/kg. As presented in Table 3, Pb was effectively immobilized by cement in all treated soil samples. All treated samples achieved the TCLP limit. In addition, almost all of the measured Pb concentrations in the TCLP extract were below 1 mg/L. The measured reductions in Pb concentrations in the TCLP extract were in the range 76% to more than 96%.

The reaction of Pb with the silicates in the soil and cement results in retarding the cement setting reactions. An example showing the relative retardation of compressive strength is shown in Figure 1. The data in Figure 1 was normalized to indicate compressive strength as a percentage of the maximum value. The maximum measured compressive strength numerical value was 500 newtons/cm². The relative retardation of compressive strength was in the approximate range 10%

to 75%. The degree of retardation decreased as the cement ratio and curing time increased. A minimum 34.5 newtons/cm² (50 psi) compressive strength requirement⁽¹⁾ ensures that the stabilized/solidified product have appropriate strength to handle stress from overburden and moving equipment. The above requirement was achieved for all samples treated with cement ratios greater than 6%.

Table 3: Immobilization of Pb using cement.

Cem-ent Ratio (%)	Contamination Level = 535 mg/kg				Contamination Level = 960 mg/kg				Contamination level = 5,160 mg/kg			
	(A)	(B)	(C)	(D)	(A)	(B)	(C)	(D)	(A)	(B)	(C)	(D)
0	8.3	8.3	166	166	20.4	20.4	408	408	30.5	30.5	610	610
3	<1.0	<1.0	<21	<21	<1.0	<1.0	<21	<21	7.1	4.4	146	91
6	<1.0	<1.0	<21	<21	<1.0	<1.0	<21	<21	1.1	<1.0	23	<21
9	<1.0	<1.0	<22	<22	<1.0	<1.0	<22	<22	<1.0	<1.0	<22	<22
12	<1.0	<1.0	<23	<23	<1.0	<1.0	<23	<24	<1.0	<1.0	<23	<23
15	<1.0	<1.0	<24	<24	<1.0	<1.0	<24	<24	<1.0	<1.0	<24	<24
18	<1.0	<1.0	<24	<24	<1.0	<1.0	<24	<24	<1.0	<1.0	<24	<24

(A) TCLP in mg/L after 7 days of curing.

(B) TCLP in mg/L after 28 days of curing.

(C) TCLP in mg/kg, corrected for dilution, after 7 days of curing.

(D) TCLP in mg/kg, corrected for dilution, after 28 days of curing.

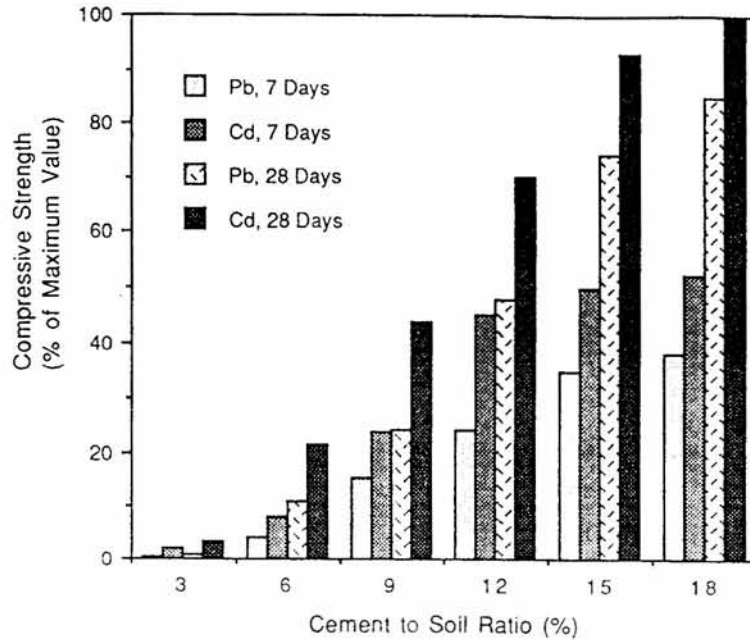


Figure 1. Compressive strength retardation due to Pb effects.

(Level of contamination=5,000 mg/kg)

Nickel was immobilized to a great extent by attachment to the soil particles. The initial TCLP results were generally low, below or at 5 mg/L and at all three levels of contamination. Nevertheless, stabilization/solidification, Table 4, resulted in significant further reductions in Ni leaching, exceeding 41% to more than 80%. In almost all treated samples, the concentrations of Ni in the TCLP extracts were below 1 mg/L. No TCLP limit for Ni-contaminated soils is available, however, a typical limit of 0.32 mg/L on the concentration of Ni in TCLP extracts of a variety of specific hazardous wastes is generally specified⁽¹⁾.

Table 4: Immobilization of Ni using cement.

Cem-ent Ratio (%)	Contamination Level = 420 mg/kg				Contamination Level = 880 mg/kg				Contamination level = 5,260 mg/kg			
	(A)	(B)	(C)	(D)	(A)	(B)	(C)	(D)	(A)	(B)	(C)	(D)
0	1.7	1.7	34	34	2.5	2.5	50	50	5.0	5.0	100	100
3	<1.0	<1.0	<21	<21	<1.0	<1.0	<21	<21	1.6	1.5	34	31
6	<1.0	<1.0	<22	<22	<1.0	<1.0	<22	<22	<1.0	<1.0	<22	<22
9	<1.0	<1.0	<23	<23	<1.0	<1.0	<23	<23	<1.0	<1.0	<23	<23
12	<1.0	<1.0	<24	<24	<1.0	<1.0	<24	<24	<1.0	<1.0	<24	<24
15	<1.0	<1.0	<26	<26	<1.0	<1.0	<26	<26	<1.0	<1.0	<26	<26
18	<1.0	<1.0	<27	<27	<1.0	<1.0	<27	<27	<1.0	<1.0	<27	<27

(A) TCLP in mg/L after 7 days of curing.

(B) TCLP in mg/L after 28 days of curing.

(C) TCLP in mg/kg, corrected for dilution, after 7 days of curing.

(D) TCLP in mg/kg, corrected for dilution, after 28 days of curing.

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