

Stabilization of Cd, Ni and Pb in soil using natural zeolite

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Abstract

A natural zeolite additive was used to reduce the leaching of Pb^{2+} , Cd^{2+} and Ni^{2+} from a soil contaminated with mixtures of the three metals. The additive contained approximately 35% active zeolite ingredients: Faujasite and Phillipsite. The additive enhanced the sorption capacity of the soil and reduced leaching. Lead leaching was reduced by more than 97% using a minimum of 25% additive at the lowest contamination level, 500 mg/kg of each metal, to 40% additive at the highest contamination level, 5000 mg/kg of each metal. Using up to 50% additive, nickel leaching was reduced by a maximum of approximately 50%, and cadmium leaching was reduced by a maximum of 60%. Cadmium leaching reduction decreased from a maximum of approximately 60% at the lowest contamination level, to a maximum of 25% at the highest level. The leaching reduction results were normalized to exclude the effects of dilution resulting from the additive. The results from the repeated leaching column experiments confirmed the selectivity of the additive and the satisfactory leaching reduction results achieved for Pb.

Keywords: Natural zeolite; Lead; Cadmium; Nickel; Contaminated sandy soil; Stabilization; Leaching reduction

1. Introduction

Natural zeolites are widely available in a variety of geologic environments, and are available in Jordan. Zeolites gained popularity in the field of pollution abatement, including the control of hardness, heavy metals, ammonium nitrogen, air pollutants and radioactive contaminants. Zeolites may also be used to reduce the leaching of selected ions from contaminated soils [1]. In this study, a natural zeolite additive

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was used to reduce the leaching of mixtures of Cd, Ni and Pb from contaminated soil samples. In the leaching process, metal ions moved from the soil particles to the zeolite additive particles where their movement was terminated and were stabilized.

The properties of natural zeolites were reported by many investigators [1–4]. In general, Pb^{2+} is favourably removed compared with many divalent cations, including Ca^{2+} , Ni^{2+} and Cd^{2+} . For the usual cation exchangers, Helfferich [4] reported the following selectivity series: $\text{Pb}^{2+} > \text{Ca}^{2+} > \text{Ni}^{2+} > \text{Cd}^{2+} > \text{Mg}^{2+} > \text{Na}^{1+} > \text{H}^{1+}$. The presence of a variety of substances in the soil leachate matrix has major effects on the treatment results. Leachates from contaminated soils are likely to contain, in addition to the contaminants, a variety of ions and other substances. The various cations are likely to compete for the available sorption sites according to factors such as: the concentration of the cation and the selectivity of the additive. The combined effects of the various substances on each other's removal may be neutral, enhancing or inhibiting [5]. Nevertheless, small quantities of a successful additive should enhance the capacity of the soil/additive mixture to retain the pollutant and minimize leaching. Lime and pozzolanic binders are commonly used for stabilization/solidification of metallic waste streams [6–11]. Non-traditional binders [12] include: slags [13], humic, fluvic, and other organic acids [14], zeolites [1] and xanthate sludges [15].

Sandy soils are common in Jordan and many industrial and waste disposal sites are located on top of sandy soils. Many of the disposal sites are contaminated with heavy metals. A research effort [16–18] was undertaken at the University of Jordan to demonstrate the effectiveness of immobilization and soil washing techniques in minimizing the leaching of metals from contaminated soils. A variety of stabilization additives were used, including: lime, cement, pozzolanic additives, and natural zeolites. The results of Pb, Cd and Ni stabilization using a natural zeolite additive are discussed in this paper.

2. Materials and methods

A clean [18] construction sandy soil sample was collected from a site near the University of Jordan and was oven dried at 103 °C for 6 h and thoroughly mixed. The soil was characterized for selected parameters, Table 1, including: pH, size distribution and texture. The organic content of the soil was low as indicated by the low volatiles content, Method 2540E [19], and chemical oxygen demand (COD), Method 5220B [19]. Three soil samples were separately contaminated with mixtures of Cd^{2+} (cadmium nitrate), Ni^{2+} (nickel nitrate) and Pb^{2+} (lead nitrate) at three contamination levels, 500 mg/kg of each metal, 1000 mg/kg of each metal, and 5000 mg/kg of each metal. In preparing the contaminated soils, three-0.51 mixed metal solutions were prepared. The first solution contained a mixture of 1 g/l Cd, 1 g/l Ni and 1 g/l Pb. The second solution contained 2 g/l of each metal, and the third solution contained 10 g/l of each metal. Each solution was acidified using 5 ml concentrated nitric acid. Three, 1 kg dried soil samples were separately mixed with

Table 1
Selected characteristics of the tested raw soil

Soil parameter	Measurement value
Moisture content (%)	0.1
pH (1 weight water:1 weight soil) (S.U.)	8.4
Organic content as indicated by:	
(i) Volatile content @ 550 °C (%)	0.2
(ii) Chemical oxygen demand (mg/kg)	1600
Gravel content ^a (%)	1.8
Sand content ^a (%)	95.9
Silt and clay content ^a (%)	2.3

^a ASTM, American Society for Testing and Materials [22].

each of the three solutions in plastic containers. The three contaminated soil samples were thoroughly mixed and oven dried at 103 °C for 6 h. The dried, contaminated soil samples were mixed and stored in plastic bags. The initial contamination levels were measured using the Nitric Acid Digestion procedure, Method 302D [19, 20]. The digestion results were variable and the measured metals concentrations in the contaminated soils were in the range 86% to 117% of the intended nominal contamination levels of 500 mg/kg, 1000 mg/kg, and 5000 mg/kg.

The zeolite additive was obtained from the Ministry of Natural Resources of Jordan, in the form of 2–5 mm grains containing zeolite and soil. The samples were hammer crushed and wet sieved (sieve No. 200, 75 µm) until the apparent turbidity disappeared. The zeolite additive retained on the sieve was ground, using a ball mill, to a size passing sieve No. 200. The ground samples were repeatedly agitated for 24 h in flasks containing five volumes of 0.1 N HCl solution added to one volume zeolite. The HCl solution was used to dissolve the calcium carbonate formations coating the zeolite surfaces (confirmed by the bubbling of CO₂). The additive was then rinsed, dried, and batch regenerated using a 10% NaCl solution (10 volumes NaCl solution added to 1 volume zeolite additive). Samples of the prepared zeolite additive were tested in the Geology Department at the University of Jordan using an X-Ray Diffractometer and were found to contain two types of zeolites [3]: (1) Faujasite, and (2) Phillipsite. The estimated zeolite content of the tested samples was in the range 35–40% [3]. The sorption capacity of the additive was determined using solutions containing 25 mg/l of one of the three metals. In addition, the capacity of the additive was determined using a mixture containing 25 mg/l of each of the three metals. In determining the sorption capacity, increasing quantities of the additive were added to individual flasks containing 100 ml metal solutions. Each flask was shaken for 2 h using a wrist shaker. A portion of the supernatant was decanted and centrifuged at 4000 rpm for 15 min and the concentration of metals was measured in the supernatant. The solutions used in determining the capacity of the additive had a pH of approximately 5.5. A summary of the identified zeolite additive characteristics is presented in Table 2.

Table 2
Summary of identified zeolite additive characteristics

Parameter	Description/value
Identified zeolite ingredients	Faujasite and Phillipsite [3]
Percentage zeolites in additive	35–40% [3]
Additive particle size	Passing sieve No. 200 (75 μ m)
Single metal batch sorption capacity (25 mg/l single metal solution, Fig. 1)	73 mg/g for Pb, 16 mg/kg for Cd, and 6 mg/g for Ni
Mixed metals batch sorption capacity (25 mg/l of each metal solution, Fig. 1)	43 mg/g for Pb, 13 mg/kg for Cd, and 9 mg/g for Ni

Soil treatment was achieved by mixing the additive with the contaminated soil. The leaching of metals from the contaminated and treated soil samples was determined using a modified toxicity characteristic leaching procedure, TCLP [21]. In the modified TCLP test, the solids were added to individual bottles and extracted with a weight of extraction fluid equal to 20 times the weight of the solids. The TCLP extraction fluid suitable for the contaminated soil and contaminated soil plus zeolite samples was buffered at a pH of 4.93 ± 0.05 and consisted of 5.7 ml glacial acetic acid and 64.3 ml of 1.0 N NaOH diluted to 1 l. The tightly closed extraction bottles were rotated in a rotary extractor at 30 rpm for 18 h. After completion, the contents of the TCLP bottles were centrifuged for 15 min. The concentration of metals was measured using flame atomic absorption, FAA, spectroscopy.

Two glass columns, 5 cm diameter by 60 cm height, were used in the repeated extraction experiments. One column was filled with 0.75 kg, 5000 mg/kg contaminated soil sample. The second column was filled with 0.75 kg soil mixture containing 20% zeolite additive. The metals were extracted using 0.1 N HCl solution. The extraction fluid was pumped up the column at a slow rate that ensured filling the voids within the soil particles. The fluid was maintained 5 cm above the soil sample and was drained after 24 h of contact. The extraction cycles were repeated eight times.

3. Results and discussion

The sorption capacity of the zeolite additive was affected by the competition among the metal ions in solution. When the solution contained only one metal, the sorption capacity (Fig. 1) reached 73 mg/g for Pb, 16 mg/g for Cd, and 6 mg/g for Ni. For the solution containing a mixture of the three metals, the sorption capacity (Fig. 1) reached 43 mg/g for Pb, 13 mg/g for Cd, and 9 mg/g for Ni. Clearly, the zeolite additive was selective in removing Pb from solution. When applied to treat the contaminated soil, the additive achieved satisfactory leaching reduction results for Pb and poor results for Ni and Cd. The minimum quantity of the additive required to reduce the leaching of Pb to below the TCLP limit of 5 mg/l (Table 3) was approximately 5% at the lower contamination level, 500 mg/kg of each metal, 13% at the

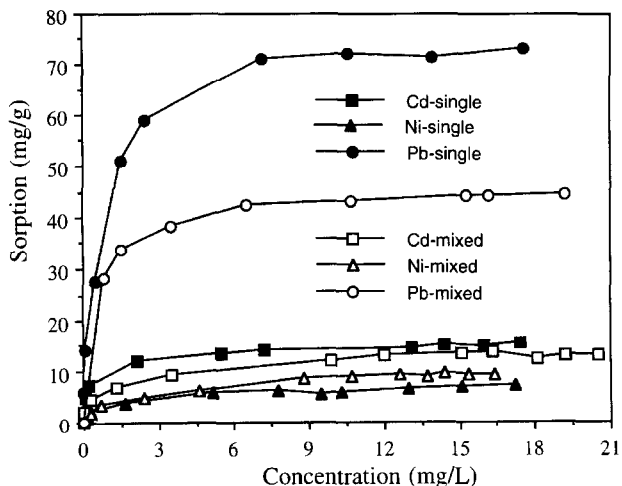


Fig. 1. Sorption capacity of the zeolite additive (single metal solution, mixed metals solution).

Table 3
Leaching results (mg/kg) before and after treatment

Zeolite ratio (%)	Contamination level (mg/kg)								
	500			1000			5000		
	Cd	Ni	Pb	Cd	Ni	Pb	Cd	Ni	Pb
0.0	20.3	12.3	18.5	40	27	34	221	156	159
0.2	17.8	12.2	18.4	—	—	—	—	—	—
0.5	17.1	11.5	15.5	39	26	33	—	—	—
1.0	15.4	10.4	12.0	37	24	27	220	137	150
2.0	14.5	9.3	6.4	—	—	—	—	—	—
2.5	—	—	—	36	22	23	215	127	125
4.0	13.5	9.1	5.5	—	—	—	—	—	—
5.0	12.5	8.3	2.5	35	20.0	17.0	209	116	95
9.0	10.6	7.8	1.9	33	19.0	6.5	205	114	74
13.0	8.9	7.0	1.5	29	17.0	3.3	—	—	—
17.0	8.5	6.7	1.3	27	15.3	2.1	162	90	28
20.0	7.9	6.5	<1.0	24	14.5	1.9	—	—	—
23.0	6.2	5.9	<1.0	20.0	12.1	<1.0	147	89	14.0
26.0	—	—	—	18.3	11.7	<1.0	—	—	—
29.0	5.7	5.7	<1.0	17.0	11.3	<1.0	134	70	9.5
33.0	5.5	4.5	<1.0	15.1	9.7	<1.0	114	62	5.8
38.0	5.4	3.9	<1.0	13.5	8.9	<1.0	102	56	3.3
41.0	5.2	3.7	<1.0	—	—	—	96	53	2.3
44.0	—	—	—	10.6	7.1	<1.0	—	—	—
46.0	—	—	—	—	—	—	86	51	2.0
50.0	—	—	—	—	—	—	82	47	1.7

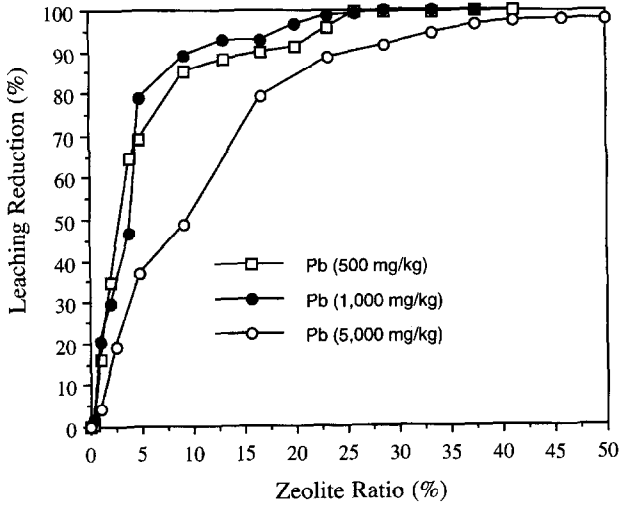


Fig. 2. Lead leaching reduction.

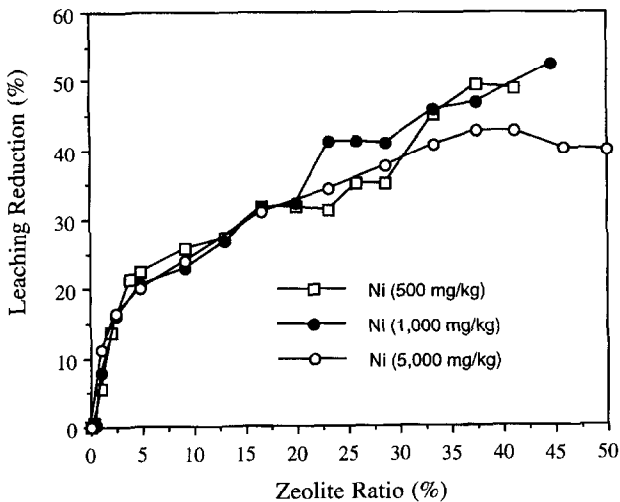


Fig. 3. Nickel leaching reduction.

intermediate contamination level, 1000 mg/kg of each metal, and 35% at the highest contamination level, 5000 mg/kg of each metal. For Ni and Cd, the concentrations in the TCLP extract remained in the range 3.7–47 mg/l for Ni, and 5.2–82 mg/l for Cd.

Soil treatment was achieved by mixing the zeolite additive with the soil samples. The addition of zeolite to soil diluted the contaminants and contributed to the observed leaching reduction results presented in Table 3. Accordingly, the leaching results in Figs. 2–4 were normalized to exclude the effects of dilution (i.e., for a

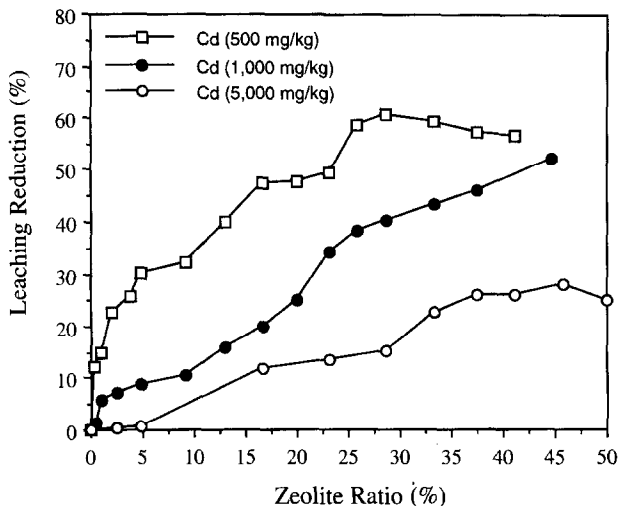


Fig. 4. Cadmium leaching reduction.

sample containing 20% additive with a measured TCLP leaching of 20 mg/l, the normalized leaching was calculated to be 25 mg/l). The normalized leaching reduction was based on the difference between leaching from the contaminated soil and the normalized leaching from the treated soil. The measured leaching results, in mg/l, are presented in Table 3. At the lowest contamination level, 500 mg/kg of each metal, the initial leaching reached 20.3 mg/l for Cd, 18.5 mg/l for Pb and 12.3 mg/l for Ni. After treatment, the leaching of Cd remained above 5 mg/l and the leaching of Ni and Pb decreased to below 5 mg/l. At the higher contamination level, 1000 mg/kg, the contaminated soil leaching results nearly doubled reaching 40 mg/l for Cd, 34 mg/l for Pb, and 27 mg/l for Ni. After treatment, the leaching remained above 10.6 mg/l for Cd and 7.1 mg/l for Ni. Lead leaching was reduced to below 5 mg/l. At the highest contamination level, 5000 mg/kg, the initial leaching significantly increased reaching 221 mg/l for Cd, 159 mg/l for Pb, and 156 mg/l for Ni. The leaching results remained above 82 mg/l for Cd, 47 mg/l for Ni and decreased to below 5 mg/l for Pb.

The normalized leaching reduction results are presented in Figs. 2–4. For Pb (Fig. 2), the leaching reduction exceeded approximately 97% at the three

Table 4
Normalized total quantity of repeatedly extracted metals

Metal in mixture	Without additive (mg/kg)	With 20% additive (mg/kg)	Reduction (%)
Cd	2010	2000	<1
Ni	2070	1760	15
Pb	2300	300	87

contamination levels. The leaching reduction results were approximately identical at the lower two contamination levels, 500 mg/kg and 1000 mg/kg, and decreased at the highest contamination level. Between 80% and 95% Pb leaching reduction was achieved using less than 20% of the additive. For Ni (Fig. 3), the leaching reduction results were approximately identical at the three contamination levels. Nickel stabilization increased, as the quantity of the additive increased, and reached approximately 40–50% at the three contamination levels. For Cd (Fig. 4), and unlike the results observed for Pb and Ni, the leaching reduction results decreased from approximately 60% at the lowest contamination level to 25% at the highest contamination level. The removal of Cd from the leachate was significantly affected by the competition among the various ions in solution at the three contamination levels. For Ni and Pb, the performance of the additive was consistent at the three contamination levels. The stabilization results presented in Figs. 2–4 agreed with the measured sorption capacity (Fig. 1) in that the additive achieved satisfactory Pb leaching reduction and poor results for Ni and Cd.

The effectiveness of stabilization was also tested using repeated leaching column experiments using 0.1 *N* HCl solution. The results are presented in Table 4. After eight extraction cycles, the quantity of metals leached from the contaminated soil (5000 mg/kg of each metal) reached approximately 46% for Pb and 40% for Ni and Cd. For the sample containing 20% zeolite additive, the extracted quantity was approximately 6% for Pb, 35% for Ni and 40% for Cd. The results from the repeated extraction experiments confirmed the observed satisfactory leaching reduction results for Pb and the poor results for Ni and Cd.

The main action of an effective sorption additive is to enhance the capacity of the soil/additive mixture to retain the contaminant and minimize leaching. Any clean additive, including clean soil, can reduce the TCLP leaching by dilution and active sorption. Generally, additives with sorption capacities greater than that of the clean soil enhance the overall sorption capacity of the soil/additive mixture. Nevertheless, the performance of different additives must be determined experimentally to account for the interferences and environmental factors. In the reported experiments, the sorption capacity of the soil/additive mixture continued to increase as the quantity of the additive in the mixture was increased. The increasing quantities of the additive resulted in a continuous decline in the concentration of metals in the TCLP extract. Using the data in Table 3, the relationship between the quantity of Pb retained by the soil/additive mixture after leaching and the additive ratio in the mixture was determined as presented in Fig. 5. The data indicated that while Pb leaching continued to decrease, the quantity of Pb retained by the soil/additive mixture increased to a maximum value then decreased as the quantity of the additive increased. The curves in Fig. 5 can be divided into two zones: in the first zone, even though the addition of zeolite reduced the quantity of Pb available for sorption due to dilution, the quantity of Pb retained by the soil/additive mixture increased. In the second zone, the quantity of Pb available for sorption decreased to the point where Pb sorption decreased. The threshold zeolite ratio dividing the two zones (Fig. 5) was approximately 6% at the lowest contamination level, 13% at the intermediate level, and 20% at the highest level. An effective additive should achieve the required

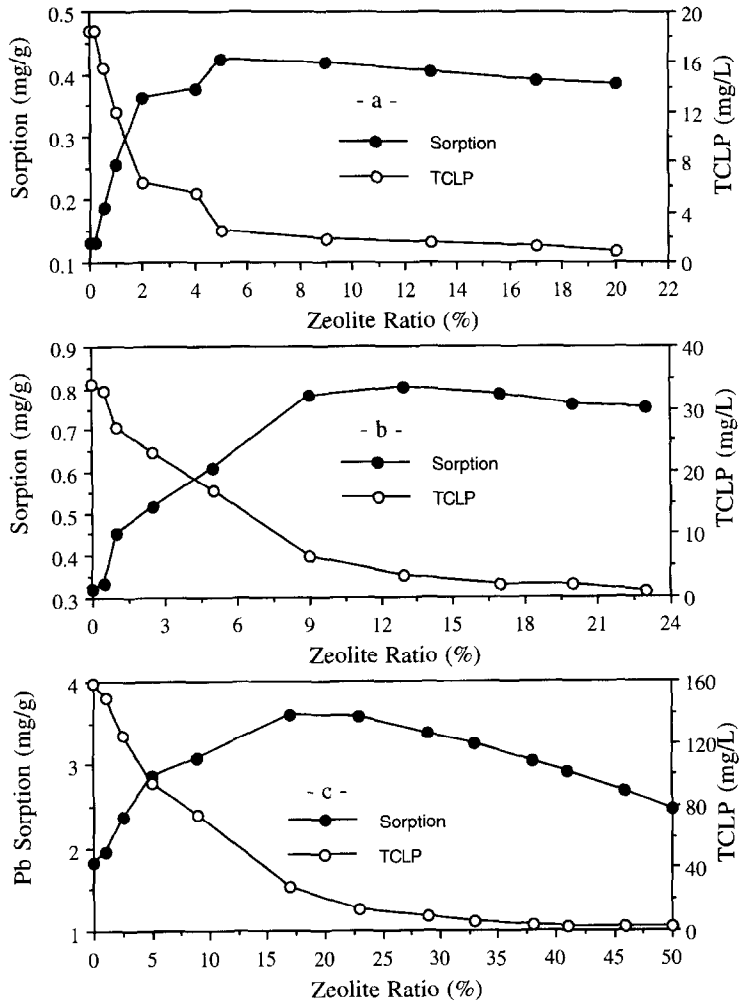


Fig. 5. Lead sorption and leaching reduction: (a) 500 mg/kg; (b) 1000 mg/kg; (c) 5000 mg/kg.

leaching reduction and maximize the sorption of the contaminant using additive quantities at or below the threshold value. The described condition was achieved at the lower contamination levels for Pb, where leaching was reduced to below the TCLP limit of 5 mg/l using an additive dose of approximately 5% at the lowest contamination level, and 13% at the intermediate level. At the highest contamination level, the additive dose required to reduce Pb leaching to below 5 mg/l exceeded the threshold value of 20% (Table 3).

4. Conclusions

The zeolite additive enhanced the sorption capacity of the soil and achieved satisfactory leaching reduction results for Pb and poor results for Cd and Ni. Lead leaching was reduced by more than 97% using a minimum of approximately 25% additive. The minimum quantity of zeolite required to reduce Pb leaching below 5 mg/l was 5% at the lowest contamination level, 500 mg/kg, 13% at 1000 mg/kg, and 35% at 5000 mg/kg. Nickel leaching was reduced by a maximum of approximately 50% and the maximum leaching reduction results for Cd decreased from approximately 60% at the lowest contamination level to approximately 25% at the highest level. The results indicated the potential of using zeolites for reducing metals leaching from contaminated soils. The selective sorption properties of the additive can be used to retain selected ions in the soil.

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