

## Stabilization Pb, Zn, and Cd-Contaminated Soil By Means of Natural Zeolite

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*This article aims to investigate the stabilization of Pb, Zn, and Cd contained in contaminated soil from a former mining site in Montevecchio, Sardinia, using clinoptilolite-rich tuff from Pentafalos, Evros. The study included (1) batch experiments and their environmental characterization and (2) column experiments. The first tests involved 1-month pot experiments with varying soil-zeolite mixtures, and their evaluation was carried out by standard USEPA leaching tests (TCLP, EPT test, SPLP). Moderate solubility reductions were recorded according to the TCLP (Pb: 38%, Zn: 33%, and Cd: 32%) due to the introduction of competing Na ions in the solution, while the EPT test showed more significant variations (Pb: 55%, Zn: 74%, and Cd: 46%). A major decrease is achieved in both cases by 10% w/w zeolite addition. The study was complemented by column experiments involving soil-zeolite mixtures eluted by CH<sub>3</sub>COOH solutions (0.003N and 0.05N). The solubility of Pb was reduced by 50 to 60% compared with the control column, thus indicating the considerable selectivity of clinoptilolite for Pb. In addition, Na and Ca measurements in the leachates confirmed that the immobilization of Pb was mainly attributed to ion exchange reactions.*

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## INTRODUCTION

**Z** eolites are hydrated aluminosilicate minerals, with porous structure, exhibiting valuable physicochemical properties such as cation exchange, molecular sieving, catalysis, and sorption. Among numerous zeolite species, clinoptilolite is considered as the most effective exchanger, especially for  $\text{NH}_4$ , Cs, and Sr ions, possessing increased cation exchange capacity and stability in acidic environments. A large European clinoptilolite deposit is located in Metaxades, Thrace, in Northern Greece, with estimated reserves of 15 million tons (Arvanitides, 1998).

The ion exchange of various metal ions such as Pb, Zn, Cd, Cu, Ni, etc., for Na and Ca in different natural zeolites such as mordenite, clinoptilolite, philipsite, and erionite (Barrer and Townsend, 1976; Loizidou and Townsend, 1987; Kesraoui-Ouki *et al.*, 1994) and synthetic zeolites like A, X, Y, and P (Sherry and Walton, 1967; Gal and Radovanov, 1974; Christidis *et al.*, 1996) has been investigated by many researchers since the 1960s. Most studies focused on the kinetic and thermodynamic properties of each system and the estimation of critical values (equilibrium constant, standard enthalpy, free energy, etc.) for the ion exchange reactions.

Current research on metals stabilization by natural or synthetic zeolites is focused mainly concentrated on the influence of the zeolite addition on the bioavailability of metals (Chlopecka and Adriano, 1996a; Lin *et al.*, 1998; Leppert, 1990). Edwards *et al.* (1999) evaluated the amendment of three contaminated soils using synthetic zeolites P, 4A, and Y and found that according to sequential extraction procedures the reduction in the metal content of the mobile fractions varied between 42 and 70%. Campbell and Davies (1997) studied the ability of clinoptilolite to immobilize radioactive caesium contained in sheep-grazing soils from Great Britain. Analyses of rye grass tissues revealed that 10% zeolite addition in peat and in loamy soil caused rapid immobilization of caesium. Shanableh and Kharabsheh (1996) examined the reactivity of a mixture containing faujasite and phillipsite used soil artificially contaminated with Pb, Cd, and Ni. As they report, leaching of metals was reduced by 40 to 97 % for Pb, 50% for Ni, and 60% for Cd. Haidouti (1997) used alfalfa and rye grass as indicator plants to assess the applicability of clinoptilolite from Metaxades, Greece, in soil contaminated by mercury. The presence of zeolite in application rates varying from 1 to 5% caused mercury solubility reduction up to 86% in shoots and 58.2% in roots of the plants. Applications of zeolites in contaminated soil remediation are still limited, but research on these materials is continuously progressing because they offer an attractive solution with minimal or insignificant impact on the environment.

Several *in situ* and *ex situ* soil remediation technologies have been developed over the last 10 to 15 years, depending on the nature, concentrations, and physical state of the pollutants present, the type of soil, and the specific aspects of the site. The removal of pollutants is based on one or more of the following mechanisms:

molecular separation, phase separation, chemical destruction, and biodegradation (Rulkens and Honders, 1998).

The present study involves the assessment of a clinoptilolite-rich tuff from Pentalofos, Evros, as a stabilizing agent, for a contaminated soil sample that originates from the area along the river banks at the Levante dam, Montevecchio, Sardinia. This is a former lead-zinc pyrite mining district, where through the combined action of wind and surface waters, the contaminants have been dispersed in an area of 30 to 40 km<sup>2</sup> around the mine. The assessment of the magnitude and the extent of soil contamination has indicated extremely high metal concentrations Pb (120 to 11,350 ppm), Zn (140 to 11,400 ppm), and As (18 to 1180 ppm) and a volume on the order of 2 Mm<sup>3</sup> of more or less contaminated tailings composed of fines transported from the washing plant. The thickness of the tailings and soils ranges from 20 cm to 2 m, which over the years they have been variously reworked and transported also by farmers ploughing the land for agricultural use (Dessi, 1999). Nowadays, the area is deserted due to the harmful effects of the contamination, and potential rehabilitation methods are continuously evaluated. Stabilization of soil and oxidic tailings from Montevecchio by means of phosphate salts has been investigated by Xenidis *et al.* (1999) and proven successful for the immobilization of Pb.

## MATERIALS AND METHODS

### Sampling—Samples Preparation

A composite soil sample representing the soil horizons typical of the contaminated area on the banks of the river, flowing from Levante tailings of Montevecchio, was prepared. The stratigraphic sequence of the sample consists of: (1) brownish clayey soil with average thickness 0.3 to 0.5 m, corresponding to the topsoil horizon, which has been created probably by the action of farmers that mix the contaminated soil with soil from uphill, (2) tailing muds, which represent flotation muds that are disseminated outside the tailing dam of Levante along the entire length of the river, for a distance of 20 km. The tailing's average thickness is 0.3 to 1.2 m. The zeolitic tuff was provided by Silver and Baryte S.A. that mines the deposit of the village Pentalofos, Evros. The material was crushed and milled before its delivery.

### Characterization of the Samples

For the characterization of the samples, conventional analytical methods as well as regulatory and modified leaching tests were performed. The chemical analysis of the soil and the zeolite sample was carried out by acid digestion (HF and HNO<sub>3</sub>/

HCl) and subsequent determination of the elements in the solution using Atomic Absorption Spectrophotometry (AAS, Perkin Elmer 2100), except for the Si and Al that were measured by fusion at 1000°C. Loss on ignition was determined by heating at 1000°C for 1 h (Soil Science of America, 1982; Perkin Elmer, 1982).

The mineralogical analysis was conducted by combining X-ray diffraction (XRD, Siemens D5000) and Scanning Electron Microscopy with Energy Dispersive X-ray Spectroscopy (SEM/EDS). The particle size distribution of the soil sample was determined by wet sieving (>63 µm) followed by laser analysis using a Master Sizer/E, Malvern Instruments (1 to 63 µm). Paste pH determination was performed according to the US EPA method 9045C (1995), while cation exchange capacity (CEC) measurements of the soil and the zeolite samples were done by saturation with 1 M CH<sub>3</sub>COONH<sub>4</sub> at pH 7 for 24 h (US EPA method 9080, 1986). Metal speciation of the soil sample was carried out by the five-stage Sequential Extraction Procedure following Tessier *et al.* (1979). The five soil fractions correspond to the exchangeable, carbonate, reducible, oxidizing, and residual part of the soil.

Three different toxicity tests were used for the environmental characterization of the soil sample. The Toxicity Characteristic Leaching Procedure (TCLP) (US EPA method 1311, 1992), the Extraction Procedure toxicity test method and structural integrity test (EPT test) (US EPA method 1310A, 1992), and the Synthetic Preparation Leaching Procedure (SPLP) test (US EPA method 1312, 1994). The toxicity measurements were complemented by determination of the phytoavailable fraction by leaching with 0.02 M Na<sub>2</sub>-EDTA (ethylenediaminetetraacetic acid, C<sub>10</sub>H<sub>16</sub>N<sub>2</sub>O<sub>8</sub>) in 1N CH<sub>3</sub>COONH<sub>4</sub> at pH 7 and solid/liquid ratio 1:10 for 1 h.

### Stabilization Methodology

The effectiveness of the zeolite to stabilize the contaminated soil sample was evaluated by pot experiments. 600 g of contaminated soil with particle size <2 mm were mixed with the calculated dose of zeolite and placed in a 1-L pot. The proportions of zeolite added to the soil ranged from 0 to 25% (on a dry basis). The addition ratio of zeolite was specified based on the cation exchange capacity of the zeolite and the total metal content of the soil. The pots were carefully eluted with deionized water, and the drainage was recycled to the pot several times every day. The treatment lasted for 1 month.

### Evaluation of the Stabilization

The treated soil samples were subjected to environmental leaching tests in duplicate to evaluate the stabilizing capacity of the zeolite for the contaminated soil. The conducted tests were the US EPA Toxicity Characteristic Leaching Procedure

(TCLP), the US EPA Extraction Procedure toxicity test method and structural integrity test (EP test), and the US EPA Synthetic Preparation Leaching Procedure (SPLP).

The use of both the EP and TCLP tests is justified by the nature of the ion exchange process and the selectivity trends of the zeolite, as the first extraction fluid (acetate buffer) of the TCLP contains a considerable amount of competing Na ions. Therefore, the use of alternative leaching procedures (EP, SPLP) was considered for comparison purposes. It is well documented that the different leaching tests used for the assessment of pollutant's migration to contaminated soil many times produce variable results (Van der Sloot *et al.*, 1997). The difficulty in adopting a standard procedure is even greater when zeolites are involved due to the selectivity of the ion exchange process. Lin *et al.* (1998) use  $\text{CaCl}_2$  solutions for the assessment of Cd stabilization by zeolite in soil, while Shanableh *et al.* (1996) evaluate their results only with the TCLP test. In addition, cation exchange capacity measurements were carried out in each soil-zeolite mixture after the stabilization period, in order to evaluate the effect of the zeolite to the sorptive properties of the contaminated soil.

### Column Experiments

To assess the leachability of the main pollutant (Pb) under acidic conditions column experiments were performed. Five plexi-glass columns of 15 cm height and 10 cm diameter were filled with 500 g of dry soil-zeolite mixtures (5, 10, 15, and 20% w/w zeolite), while one of them contained no zeolite (control sample). All the samples were compacted with the addition of the optimum water quantity (8 to 12% w/w), before being extruded into the columns, in order to ensure slow saturation and to allow for the interactions to take place. The first extraction cycle involved 0.003 N  $\text{CH}_3\text{COOH}$  solutions of pH 5 and the second involved 0.05 N  $\text{CH}_3\text{COOH}$  solutions of pH 3. Each cycle was terminated when 12 bed volumes (1 BV = 425 ml) of solution percolated the columns at a feed rate of 1.2 L/d. The leachates were analyzed for Pb, Ca, Na, Mg, and K by AAS, while their pH and volume were also measured.

## RESULTS AND DISCUSSION

### Characterization of the Materials

#### *Soil Sample*

Based on the chemical analysis of the sample (Table 1), the major contaminants are Pb, Zn, Cd, and Ba because their concentration exceeds the Netherlands intervention values and both the Canadian and US EPA standards for agricultural soils

**TABLE 1**  
**Chemical Characteristics of the Soil and the Zeolite Samples**

Elements	Soil % w/w	Zeolite % w/w
Ca	0.58	2.56
Mn	0.12	—
Fe	4.80	0.86
K	0.92	1.33
Al	4.63	6.94
Na	0.15	0.74
Ti	0.45	0.19
Si		33.39
Mg	0.39	0.56
LOI	5.4	6.78
<i>mg/kg</i>		
Pb	8900	
Zn	7900	
Cd	50	
Cu	1600	
As	(<500)	
Ba	8600	
paste pH	6.5	7.8
CEC (meq/100g)	10	116

(Table 3). Analyses of the particular 6 particle size fractions (Table 2) proved that the metals are mainly concentrated (about 85% of Pb, 80% of Zn, and almost 80% of Cd) in the finer fraction of the soil (<63  $\mu\text{m}$ ). As a result, the availability of the pollutants to the environment via leaching mechanisms and wind erosion is increased and remediation of the soil is necessary.

The main mineralogical phases in the soil fractions that were revealed by the XRD analysis are quartz (most abundant), clay minerals (illite, kaolinite), mica (muscovite), and alkali feldspars (albite and microcline). Also, in the silt and clay fractions carbonate minerals such as calcite, siderite, and ankerite were identified, while small amounts of galena, cerrusite, and baryte were traced by the SEM/EDS analysis. The major contaminants (Pb and Zn) are mainly associated with carbonate minerals and with the Fe-Mn oxides and hydroxides.

Metals speciation in the soil sample as it was evaluated by the sequential extraction procedure confirmed the results of the mineralogical analysis. As seen in Table 4, 73% of total Pb and 71% of Zn were found in the carbonate (Ca-Fe-Mg carbonates) and the reducible (Fe-Mn oxides) fraction, while about 10% of each metal was highly available, being traced in the exchangeable fraction. Cd distribution, however, was different because 45% of the total quantity was found

**TABLE 2**  
**Distribution of Metals in the Different Particle Size Fractions of the Soil**

Particle size	Weight	Pb	Zn	Cd
mm	%	mg/kg (%)		
-2+1.18	1.6	2931 (0.5)	3408 (1.0)	43 (1.5)
-1.18+0.5	4.8	4571 (2.3)	5446 (3.0)	36 (3.5)
-0.5+0.32	4.3	4302 (2.0)	5956 (3.0)	43 (4.0)
-0.32+0.15	19.3	2850 (6.0)	3217 (8.0)	23 (9.0)
-0.15+0.063	13.1	2904 (4.5)	3058 (5.0)	16 (4.0)
-0.063	56.9	13389 (84.7)	11084 (80)	69 (78)

**TABLE 3**  
**Limit Values for Metal Concentrations in the Soil**

	Netherlands intervention values mg/L	Canadian Standards for agricultural soils mg/kg	USEPA Standards for agricultural soils mg/kg
Pb	530	375	20
Zn	720	600	1500
Cd	12	3	20
Cu	190	150	775
As	55	20	32
Cr	380	750	1540
Hg	10	0.8	9
Ni	210	150	230

**TABLE 4**  
**Concentration (Percentage) of the Major Polluting Metals in the Fractions**  
**of the Soil**

Fractions	mg/kg (%)		
	Pb	Zn	Cd
Exchangeable	929 (10.4)	584 (7.4)	22 (44.5)
Carbonate	3436 (38.6)	2648 (33.5)	13 (26.6)
Reducible	3111 (34.9)	2966 (37.5)	10 (20.0)
Oxidizing	557 (6.3)	220 (6.3)	0 (0.0)
Residual	868 (9.8)	1483 (18.8)	4 (8.9)
Total	8900	7900	49

in exchangeable form, and 47% in both carbonate and reducible form. Thus, Cd, which is considered as one of the most toxic heavy metals, was found very mobile, posing a great environmental threat. Similar observations regarding the speciation of metals were reported for contaminated soils from different origin (Chlopecka *et al.*, 1996a; Chlopecka *et al.*, 1996b).

According to the particle size analysis 44% of the sample consists of sand (0.02 to 2 mm), 26% of silt (0.002 to 0.02 mm) and 30% of clay. Thus, the soil may be characterized as sandy-clayey silt. In addition, the physical characteristics measurements proved that it is a neutral soil (pH = 6.5) with medium cation exchange capacity (10 meq/100g).

Table 5 summarizes the results of the toxicity and the bioavailability determinations. US EPA TCLP proved that the material is highly toxic for Pb because its solubility (57.3 mg/L) exceeded by far the regulatory limit (5 mg/L), while Cd solubility (1.1 mg/L) only marginally reached the respective regulatory limit (1 mg/L). Furthermore, increased solubility was recorded for Zn, accounting for 83.1 mg/L. The EP test resulted in increased Zn solubility value (83.1 mg/L) and relatively lower solubility value for Pb (5.5 mg/L) but still higher than the respective regulatory limit (5 mg/L), whereas only limited leaching of Zn was produced by the SPLP test. The discrepancies observed in the toxicity measurements are due to the different metal-binding capacity of the leaching reagents used in each test (CH<sub>3</sub>COOH + NaOH, CH<sub>3</sub>COOH, and HNO<sub>3</sub> + H<sub>2</sub>SO<sub>4</sub>) and the different amount of anions introduced by the leaching solution. Bioavailability determination by EDTA leaching resulted in increased levels of Pb (6320 mg/kg), Zn (2740 mg/kg), and Cd (25 mg/kg). These values exceed the permissible levels determined by both the Canadian and the US EPA standards for agricultural soils (Table 3).

#### *Zeolite*

According to the chemical assay of Table 1, the natural zeolite sample contains primarily Ca as exchangeable cation and small quantities of Na, K, and Mg. Its



**TABLE 5**  
**Toxicity Evaluation Results for the Soil Sample According to TCLP, EPT**  
**Test, SPLP, and Bioavailability Results According to EDTA Leaching**

	TCLP mg/L	US EPA limit mg/L	EP mg/L	SPLP mg/L	EDTA leaching mg/kg
Pb	57.3	5.0	5.55	<0.4	6320
As	<1.25	5.0	<1.25	<1.25	<1.25
Zn	83.1	—	132.75	0.62	2740
Cd	1.1	1.0	0.66	<0.04	25

theoretical CEC value, calculated by the chemical analysis, is 285 meq/100g. This value by far exceeds its effective CEC value measured by saturation with  $\text{CH}_3\text{COONH}_4$  (116 meq/100 g), suggesting that almost 50% of exchangeable sites are “active” (accessible to  $\text{NH}_4$ ).

Mineralogical analysis of the tuff revealed the existence of two zeolite species, namely, clinoptilolite  $\text{Na}_6[\text{Al}_6\text{Si}_{30}\text{O}_{72}]\cdot 24\text{H}_2\text{O}$  and heulandite  $\text{Ca}_4[\text{Al}_8\text{Si}_{28}\text{O}_{72}]\cdot 24\text{H}_2\text{O}$  (85%), 2 feldspar species, probably oligoclase and plagioclase (6%), smectite (4%), low temperature quartz (3%), and traces of mica, probably muscovite (2%). According to the particle size determination, the soil sample is very fine because 90% w/w is smaller than 123  $\mu\text{m}$ . Also, its specific area determined by absorption of He-N was found 15.6  $\text{m}^2/\text{g}$ .

### Pot Experiments

The extent of metals immobilization, according to the results of the applied leaching methods, is presented in Figures 1, 2, and 3. The TCLP leachability of Pb was reduced by 38%, whereas EPT results indicated a more abrupt decrease, which accounted for 55%. Evidently, the zeolite was selective in removing Pb from the solution, although it failed to decrease Pb solubility below the permissible level (5 mg/L) even by 25% addition. This fact is attributed to the presence of competing Na ions originating from the TCLP leaching solution. Application of the EPT resulted in low Pb solubilization for the control samples, which is owed to the pH value of the leaching solution ( $\text{CH}_3\text{COOH}$ , pH = 5). The zeolite addition caused significant reduction of Pb solubility. It is also noted that major decrease is achieved when the zeolite content increases up to 10%, while higher doses do not seem to alter considerably the results. The application of the SPLP test did not produce any measurable values for Pb, probably because of both the use of inorganic acids and the test pH value of 5.

The results produced by the various leaching tests regarding Zn show significant decrease in its solubility, accounting for 74, 81, and 33% in the EPT, SPLP, and TCLP tests, respectively (Figure 2). In all cases, the major decrease takes place between 0 and 10% zeolite addition, suggesting that the variation of the zeolite content does not greatly affect Zn immobilization. The discrepancies produced by the leaching tests originate from the nature of the different solutions and especially from the existence of competing Na ions, as already mentioned above. Finally, Cd solubility in the soil, according to the TCLP, only marginally exceeds the regulatory limit (1 mg/L). Zeolite addition improves the soil by immobilizing 32% and 46% of the leachable Cd according to the TCLP and the EPT.

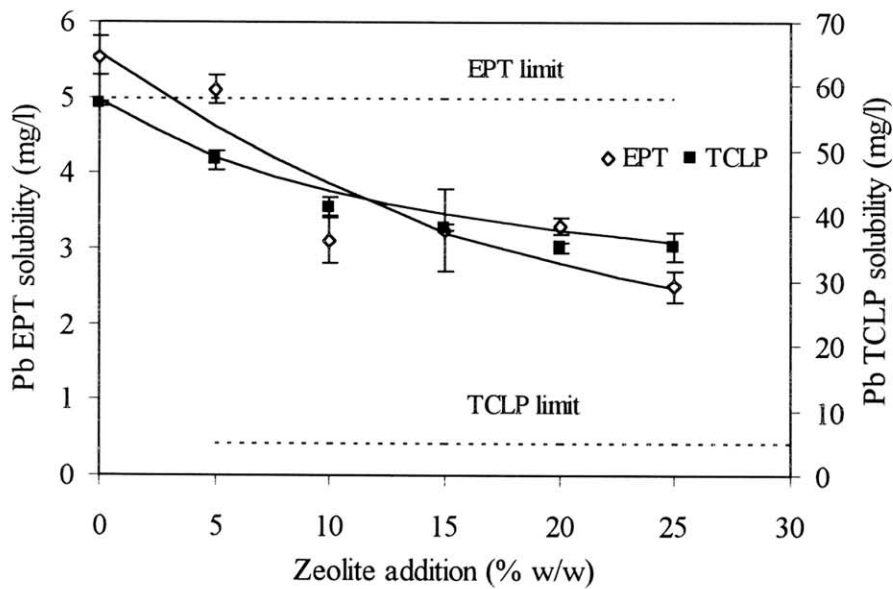
Shanableh *et al.* (1996) report the use of the TCLP test for evaluating the stabilization of Pb, Cd and Ni by faujasite and phillipsite in an artificially contaminated sample. According to the authors, the sorption capacity of the zeolites (especially for Pb) was affected by the competition among the metals in the solution, while 5 to 35% w/w of zeolite was needed (depending on the contamination level), to reduce Pb leachability below the TCLP limit. The effect of the existence of Na ions in the solution was not taken into account. Lin *et al.* (1998) also investigated the stabilization of Cd in artificially contaminated soil using synthetic zeolite from fly ash. Leaching was conducted with  $\text{CaCl}_2$  solutions aiming at extracting Cd contained in the exchangeable soil fraction. Up to now only limited references concerning zeolite assessments for soil remediation by leaching tests are available for comparison.

The cation exchange capacity of the soil increases by 2 to 3.4 times when zeolite addition varies between 5 and 25% w/w (Figure 7), suggesting that the presence of the zeolite render the soil a moderate cation exchanger.

### Column Experiments

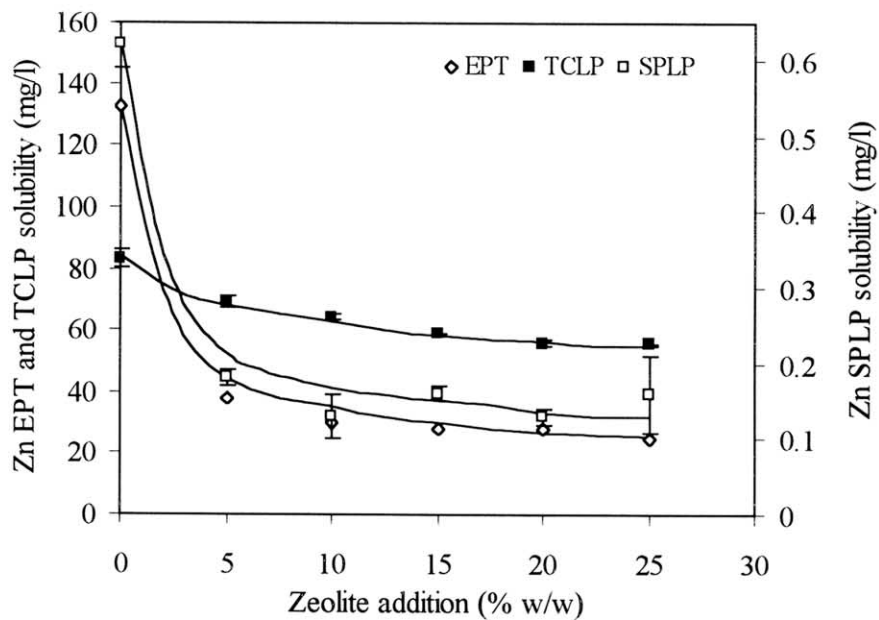
Figure 5 presents the influence of zeolite addition on soil's pH with respect to the volume of leaching solution. It is evident that 5% w/w addition only marginally increased pH values when elution was carried out by the concentrated solution (0.05N). However, 20% w/w zeolite addition was sufficient to increase pH values up to 9% corresponding to a pH value of 8.56 when the dilute  $\text{CH}_3\text{COOH}$  solution (0.003 N) was used and up to 7.3% with  $\text{CH}_3\text{COOH}$  0.05 N, respectively. The alkalizing efficiency of zeolites is due to the exchange of Na ions from the zeolite with H ions from the soil.

The leachability of Pb in the various columns is presented in Figure 5. After saturation of the samples with approximately 5 L of 0.003 N  $\text{CH}_3\text{COOH}$  solution, Pb was found immobile both in the control sample and in the mixtures. This is possibly due to the pH values observed during this stage, which vary between 6.5 and 7.8 and are considerably greater than the solubility pH value of  $\text{Pb}(\text{OH})_2$ . Measurable quantities of Pb were first traced when 490 ml of 0.05 N  $\text{CH}_3\text{COOH}$



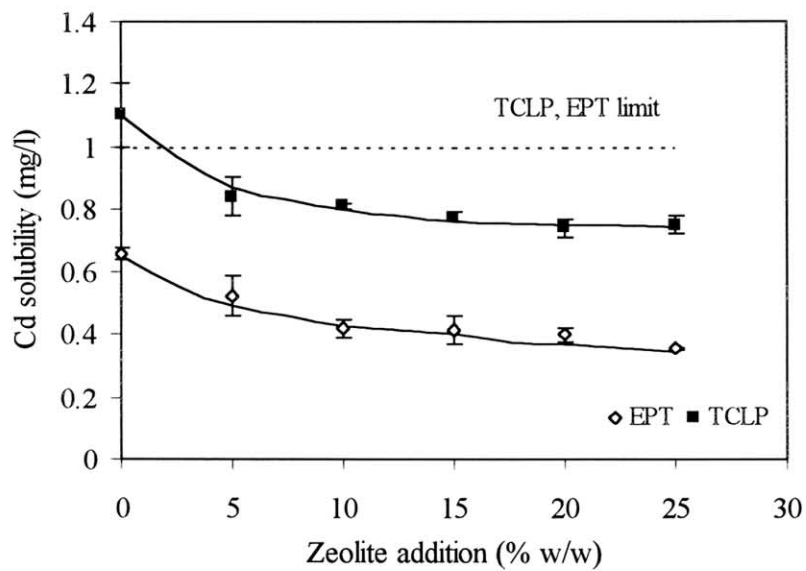
**FIGURE 1**

Results of Pb leaching by the EPT test and TCLP toxicity tests in the soil-zeolite mixtures.



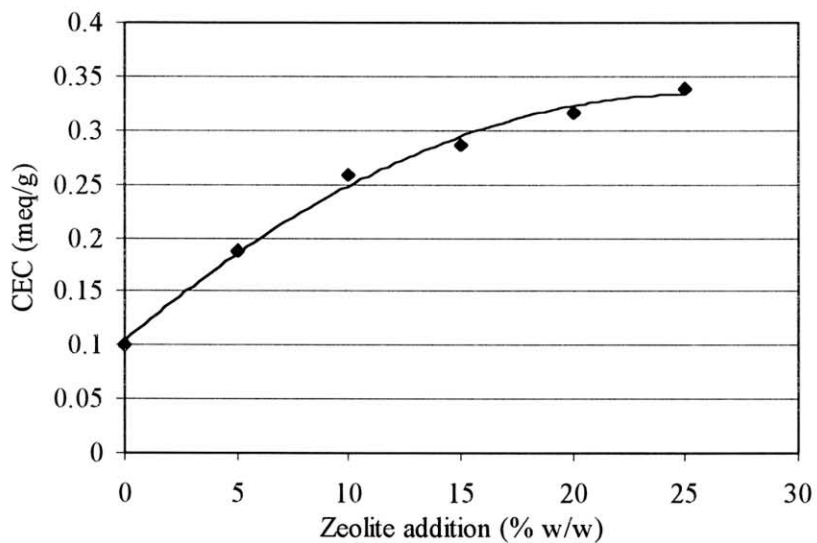
**FIGURE 2**

Results of Zn leaching by the EPT test, SPLP, and TCLP toxicity tests in the soil-zeolite mixtures.



**FIGURE 3**

Results of Cd leaching by the EPT test and TCLP toxicity tests in the soil-zeolite mixtures.



**FIGURE 4**

Determination of the cation exchange capacity of the different soil-zeolite mixtures.

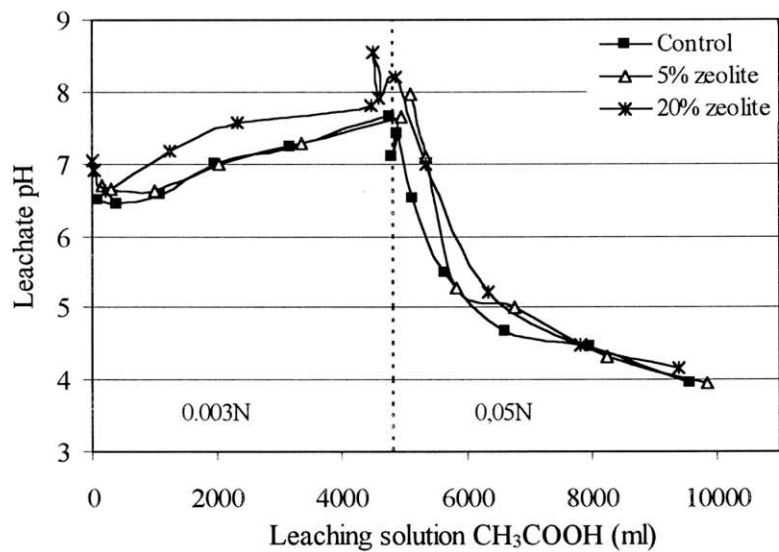


FIGURE 5

Leachate pH variation in respect with the leachant volume.

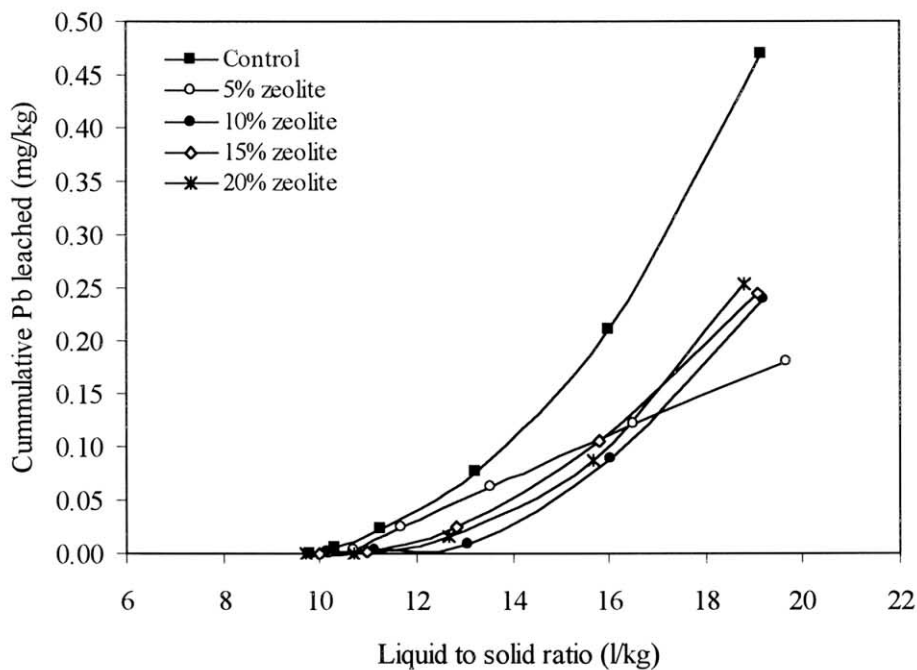
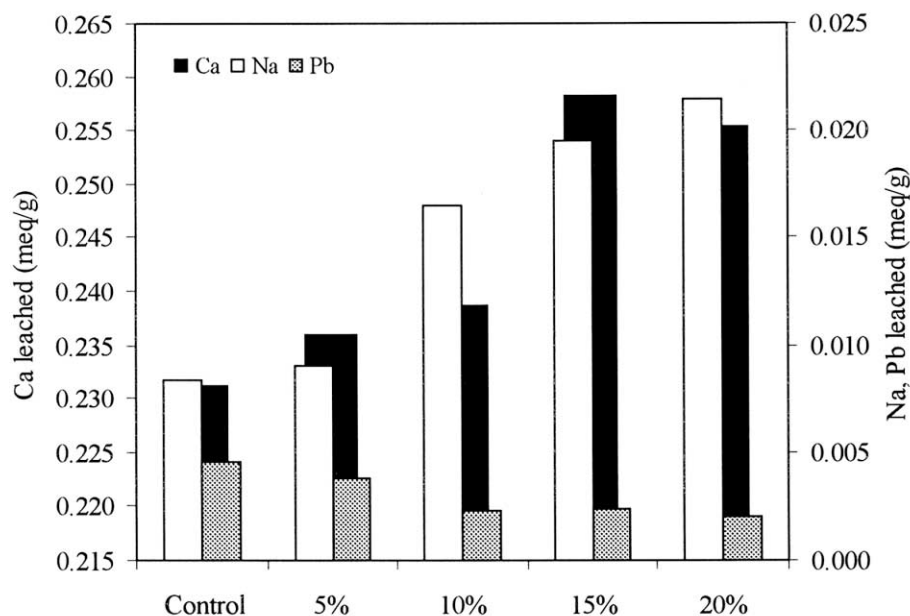


FIGURE 6

Breakthrough curve of Pb.



**FIGURE 7**

*Comparative presentation of Pb, Ca, and Na solubilities in meq/g for the various soil-zeolite columns.*

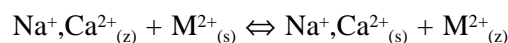
passed through the control column and the pH reached 5.5. Accordingly, the breakthrough points for the soil-zeolite mixtures correspond to increased leachate volumes (5%: 496 ml, 10%: 970 ml, 15%: 930 ml, 20%: 995 ml) and similar pH values (5.2 to 5.9).

The solubility of Pb drops due to the zeolite treatment as shown in the breakthrough curves of Figure 6. The final Pb concentration reductions after elution with 10 l of  $\text{CH}_3\text{COOH}$  solution were 61%, 49%, 48%, and 46% for each treatment, respectively, indicating that best results are obtained with 5% zeolite addition, while 10 to 20% additions provide results with insignificant variation. This unexpected sequence is justified considering the flow rates of the columns that vary significantly due to the hydration of the zeolite (control: 5 ml/min, 5% addition: 2.6 ml/min, 10% addition: 1.1 ml/min, 15% addition: 0.47 ml/min, 20% addition: 0.23 ml/min). It is suggested that as the percolation rates decrease,  $\text{CH}_3\text{COOH}$  accesses lead minerals easier, causing increasing dissolution of lead in the solution phase. Thus, even though the contact time between the solubilized Pb and the zeolite increases, the amount of Pb ions increases as well and their retention becomes difficult.

The reduction of Pb mobility is partially due to the buffering capacity of zeolites, which causes both the precipitation of metals in the form of hydroxides and their adsorption onto iron oxide surfaces. However, it is suggested

that the exchange reactions between Pb and Ca, Na ions accommodated within the zeolite channels represent the main retention mechanism. The correlation of the three competing ions is shown in Figure 7, where the decreasing trend of Pb concentration is presented against the reverse trend of Na and Ca total concentrations expressed in meq/g. The concentration values of Na and especially Ca are far from being stoichiometric to Pb concentration values, probably due to the dissolution of carbonate minerals occurring in low pH.

The increasing dissolution of Ca and Na in the soil solution, due to the reduction of pH, renders the study of the ion exchange reactions very difficult. The release of these cations, which are also present as exchangeable ions within the zeolite channels, influences the equilibrium between the zeolite phase and the solution phase:



where M: metal ions ( $\text{Pb}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ )

As a result, the above reaction may proceed to the left when excess of  $\text{Na}^+, \text{Ca}^{2+}$  is present in the solution, inducing the mobilization of previously retained metal ions. An additional consideration that renders the identification of the retained species even more difficult is the increased tendency of Pb and Zn to form organometallic complexes with  $\text{CH}_3\text{COO}^-$  under favorable conditions.

## CONCLUSIONS

The assessment of a natural zeolite-rich tuff from Evros, Greece, as a stabilizing agent for soil contaminated mainly with Pb and with Zn and Cd, indicated that the material generally works effectively. According to the results produced by environmental leaching tests (US EPA TCLP, EPT and SPLP), the addition of zeolite reduces considerably the solubility of Pb, Zn, and Cd in the soil. However, the solubility of Pb did not reach the TCLP regulatory limit, probably due to the interference of Na in the ion exchange process. Column leaching tests with  $\text{CH}_3\text{COOH}$  proved that Pb is immobilized by 50 to 60% due to the zeolite treatment, without recording any major discrepancies when the zeolite content was increased. Also, Zn and Cd leachabilities were considerably reduced when the columns were percolated by dilute solution of  $\text{CH}_3\text{COOH}$ .

The processes may be further assessed by speciation analyses in the spent soil-zeolite columns that would give information on the distribution of metals in the soil fractions. Also, the use of other leaching solutions (dilute acids, simulated acid rain,  $\text{MgCl}_2$ , and others) would provide an overall view of the zeolites capacity under variable conditions.

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