



# Stabilization of cadmium contaminated soils using synthesized zeolite

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## Abstract

This research investigates the effect of synthesized zeolite on stabilizing Cd-contaminated soil, using 0.01 M CaCl<sub>2</sub> leaching solution in batch and column experiments. The zeolite was synthesized from fly ash obtained from a Coal-Fired Power Plant, by adding 2 N NaOH and subjecting to 90°C for 24 h. The experiment used two groups of soil samples: (1) addition of Cd to four series of background soils: Pinchen, Jente, Erlin and Chengchung; (2) actual contaminated soils from Chungsing and Tsasta sites. The result of the batch experiment indicates that the addition of zeolite reduces Cd leaching from all types of contaminated soils. The more zeolite added, the lower Cd concentrations were detected in the leaching solution. The stabilized Cd in soils in the presence of zeolite is also demonstrated in the column experiments; the leachate contains insignificant Cd, and Cd depth analysis of the soil columns shows little Cd migration. For example, for Pinchen and Jente soils, after 12 and 49 pore volumes of leaching solution, the remaining Cd levels in the soils were 12% and 35%, respectively, of the original Cd values with no zeolite added, as compared to 96% and 99% in the presence of 16% zeolite. The higher cation exchange capacity of the zeolite/soil mixtures and higher pH are responsible for stabilizing Cd in soils. The effect is most useful in application to the acidic sandy soils to prevent contaminated heavy metals from leaching. © 1998 Elsevier Science B.V. All rights reserved.

*Keywords:* Zeolite; Contaminated soil; Cadmium; Stabilization

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## 1. Introduction

Throughout its impressive era of economic expansion, Taiwan has not, however, paid enough attention to the treatment of industrial wastewater and industrial solid wastes.

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Today, there are many polluted sites in Taiwan with soils contaminated by heavy metals. Metals in soil are not biodegraded by natural process, and remain in the ecosystem. They would seep into groundwater or even channel into the food chain by crops planted on such soil. Heavy metals become extremely hazardous when they finally find their way into human or animal bodies.

There are three major reclamation technologies for metal-contaminated soils: biological, agricultural engineering, and physicochemical treatment. The bio-treatment method is through planting, harvesting and eventually removing non-edible crops in contaminated areas to remove metals from the soil [1]. The problem with this method is that it takes a long time to observe any effect; and it cannot prevent the pollution from expansion. The two agricultural methods of earth-swap and deep plowing also have risks. The earth-swap, although the most direct improvement method, is extremely costly; the deep plowing method, on the other hand, might disturb and further contaminate groundwater. The physicochemical methods include extraction, stabilization and solidification. Adding zeolite into the soil is one example of stabilization methods.

Zeolite consists of crystallized silicate with porous structure. The material has received great interest in a wide array of applications since the 1950s [2] because of its high specific surface area (several hundreds  $\text{m}^2/\text{g}$ ) and superior capability in adsorption, cation exchange and catalyzation [3].

This research is intended to capitalize on zeolite's superior cation exchange capacity (CEC) to reduce the transport of the heavy metal Cd in soils, and to stabilize and prevent Cd from being adsorbed by crops or migrating into groundwater. The research also explores the possibility to maximize waste material recycling by synthesizing zeolite from waste fly ash collected from a coal-fired power plant. The soil samples were taken from several different representative soil series in Taiwan with different pH values. Cd was added to representative soil samples to simulate contamination, and zeolite was subsequently added to study its effect on Cd stabilization. To obtain other important references in heavy metal stabilization in soils, the soil column leaching experiments were also conducted.

## 2. Materials and methods

### 2.1. Synthesized zeolite

The fly ash used in this research was collected from the electrostatic collector in the Tai-power Dalin Coal-Fired Power Plant. The fly ash has a specific weight of  $2.43 \text{ g}/\text{dm}^3$  and pH value is approximately 11.4 (water-to-solid ratio = 10). Its CEC is approximately  $8.1 \text{ meq}/100 \text{ g}$  and specific surface area is  $3 \text{ m}^2/\text{g}$ . Zeolite was synthesized by mixing 300 g fly ash with 3000 ml of 2 N NaOH in a 5-l stainless steel reactor. The open system was then subject to temperature at  $90^\circ\text{C}$  and mixing at 250 rpm for 24 h [4]. After the reactor content cooled down to room temperature, the Whatman  $0.45 \mu\text{m}$  paper was used to separate solid and water. The solid residue was then rinsed with a large quantity of deionized water, dried for 1 day at  $105^\circ\text{C}$ . The final zeolite-like material was stored away for further experiments. For comparison, the CEC of the

synthesized zeolite is about 20 times more than that of fly ash, or 160 meq/100 g, with pH = 10.5 (water-to-solid ratio = 10).

## 2.2. Soil samples

The uncontaminated soil samples were obtained from Taiwan for four representative soil series: Pinchen, Jente, Erlin and Chengchung. The four soil series represent 73% of all agricultural soil in Taiwan [5]. Additionally, two contaminated soil samples from areas near the Gaoyin Chemical Plant in Datan Village, Taoyuan County, and Jili Chemical Plant in Chunglu Village, Luchu City, were used. The basic physical and chemical properties of the soil samples used in this research are illustrated in Table 1.

The simulated contaminated soil samples were prepared by adding 1000 mg/l CdCl<sub>2</sub> solution to obtain approximately Cd content of 70 mg/kg. The mixture was stirred up and placed at 25°C environment for air drying. The samples were ground, water was then added until the water content reached the field level. This wet/air-dry cyclic procedure was repeated five times to allow sufficient mixture of Cd and the soil samples to simulate actual field conditions.

## 2.3. Experiments

Several different portions of zeolite were added into the contaminated soil samples ranging from 0.5 to 16 g/100 g of soil. The mixtures were subject to the same air-dry/re-wet procedure three times to achieve equilibrium. In the batch extraction experiment, these mixture soil samples were placed in 125 ml flasks, adding 100 ml of 0.01 M CaCl<sub>2</sub> solution with a pH value of 6.3, shaken for 1 h under constant 25°C and 150 rpm conditions. The solution content was then filtered, and the filtrate was used for pH and Cd measurements.

The purpose of the column experiment was to simulate and study the Cd migration in the soil samples after zeolite was added. For simulated contaminated soil samples, 20 cm of clean soil was initially placed at the bottom of the 40-cm diameter column, with

Table 1  
Physical and chemical characteristics of soils used in the experiments

Soil series	Particle size fractions <sup>a</sup> (%)			pH <sup>d</sup>	CEC <sup>a</sup> (meq/100 g)	Organic Matter <sup>a</sup> (%)	Cd <sup>d</sup> (mg/kg)
	Sand	Silt	Clay				
Pinchen (Pc)	17	45	38	4.3	8.4	2.0	N.D. <sup>c</sup>
Jente (Je)	35	47	18	5.4	6.4	2.1	N.D.
Erlin (Eh)	16	39	45	7.1	9.1	2.6	N.D.
Chengchung (Cf)	49	14	37	7.8	10.7	1.5	N.D.
Chunghsing <sup>b</sup> (Ce)	22	45	33	5.1	8.8	1.4	6.9
Tsasta <sup>b</sup> (Ts)	84	7	9	5.4	4.2	1.0	9.5

<sup>a</sup>The soil properties were obtained from Lee and Zheng [6].

<sup>b</sup>Collected from actual Cd contaminated agricultural soil.

<sup>c</sup>N.D.: Less than detection limit.

<sup>d</sup>Experimental data.

additional 10 cm of Cd contaminated soil (with or without zeolite addition) on top [7,8] to demonstrate whether the Cd migration has reached the bottom layer. For actual contaminated soil samples, the entire 30 cm depth was filled with contaminated soil (with or without zeolite addition).

The columns were saturated with counter flow, drained several times in order to release air bubbles in the columns. The soil columns were then submerged with water for a week to achieve saturation. During experiment the columns were leaching with 0.01 M  $\text{CaCl}_2$  at a constant 10 cm water head. The leachate was collected and analyzed for Cd concentrations and pH values. At the end of experiment, the columns were allowed to drain naturally to determine the water content and soil sample height, in order to calculate the overall density and pore volume of the columns. After draining, the soil in the columns was collected, and separated by 2-cm interval and left for air-drying under room temperature. Cd contents in each of these soil samples were determined by the digestion method with aqua regia [9].

#### 2.4. Analytical methods

The zeolite size distribution was measured by CILAS Granulometer, Model 175. CEC value was determined by the indirect ammonium acetate method. Cd concentration was determined by Perkin-Elmer Atomic Absorption Spectrophotometer Model 5000. Soil sample pH values were determined with the water-to-soil ratios of 10, using a Metrohm 654 pH meter. The hydraulic conductivity was determined in soil columns at a constant head by monitoring leaching rate with time.

### 3. Results and discussion

In the experiment, different portions of zeolite were mixed with four Cd contaminated soil samples; the mixtures were subjected to several rounds of wet/air-dry cycles, then leached with 0.01 M  $\text{CaCl}_2$  solution. Fig. 1 illustrates the change in Cd concentration in the leachate. Without zeolite addition, the leachate Cd concentration was approximately 3.9 mg/l for Pinchen soil and 2.3 mg/l for Jente soil; yet only 0.25 and 0.1 mg/l for Erlin and Chengchung soil samples, respectively. The Cd leachability is due to the differences in the initial pH values present in these soil samples having similar CEC values (Table 1). The Cd partitioning between solid and liquid phase is affected by soil pH, complexation stability, organic functional group, solution ionic strength, and presence of other cations [10]. As pH of soil samples is lower as in the case of Pinchen and Jente soil, the Cd concentration in leachate should be higher [11]. Further, for these soil samples, it has been reported that the Cd exchangeable and adsorptive capabilities increase with decreasing pH in the soil samples [12]. Consequently, it is concluded that pH value in soil samples is one of the primary factors affecting Cd leachability.

The results in Fig. 1 also indicate that the addition of synthesized zeolite strongly inhibits the leaching of Cd in all soil samples. With the addition of 16 g zeolite/100 g soil, leachate Cd concentrations of all four samples were below 0.05 mg/l. In addition

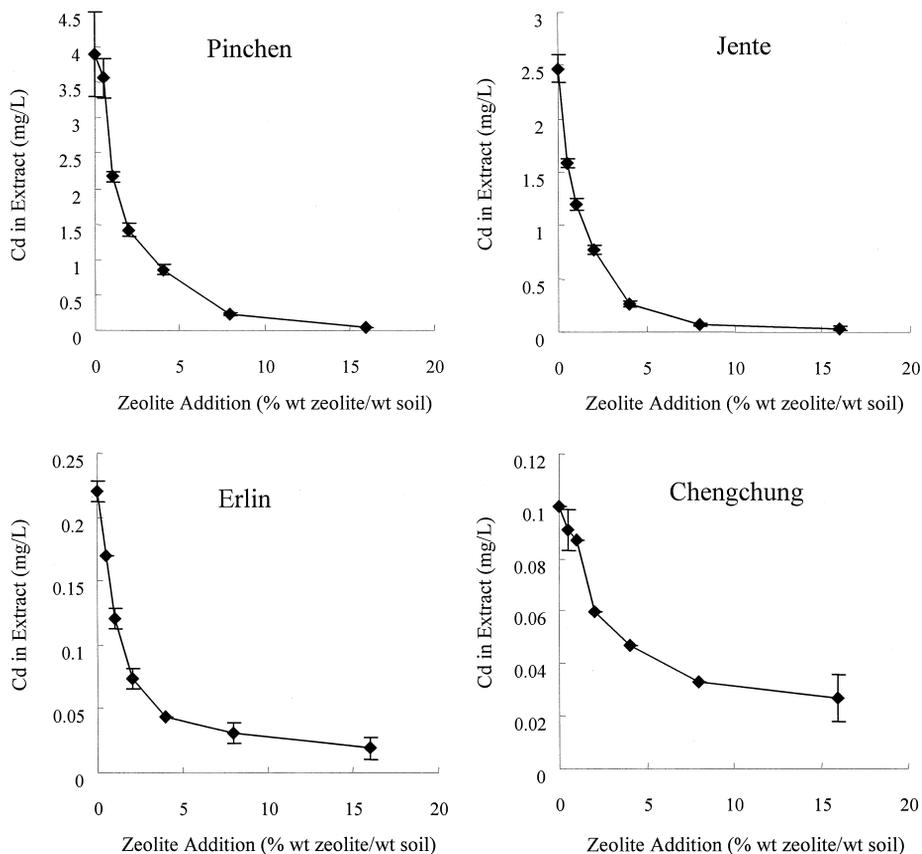


Fig. 1. Leachate Cd concentrations from simulated contaminated soils as a function of the zeolite dosages.

of the increased CEC of the soil mixture, the increased pH in the presence of zeolite (Table 2) is also responsible for the observed lower Cd migration. For example, pH of the Pinchen sample increased from 4.3 to 6.8 with the addition of 16% zeolite. For

Table 2  
Effect of different zeolite dosage on soil pH

Zeolite dosage (g/100 g soil)	Soil series					
	Pc <sup>a</sup>	Je	Eh	Cf	Ce	Ts
0	4.3	5.4	7.1	7.8	5.1	5.4
0.5	4.8	5.9	7.3	7.9	5.8	5.9
1	5.2	6.2	7.6	7.9	6.2	6.2
2	5.5	6.7	7.8	8.0	6.5	6.5
4	5.8	7.3	8.0	8.1	7.0	6.8
8	6.2	7.5	8.4	8.2	7.6	7.3
16	6.8	8.0	8.8	8.4	8.1	7.6

<sup>a</sup>Pc: Pinchen, Je: Jente, Eh: Erlin, Cf: Chengchung, Ce: Chungsing, and Ts: Tsasta.

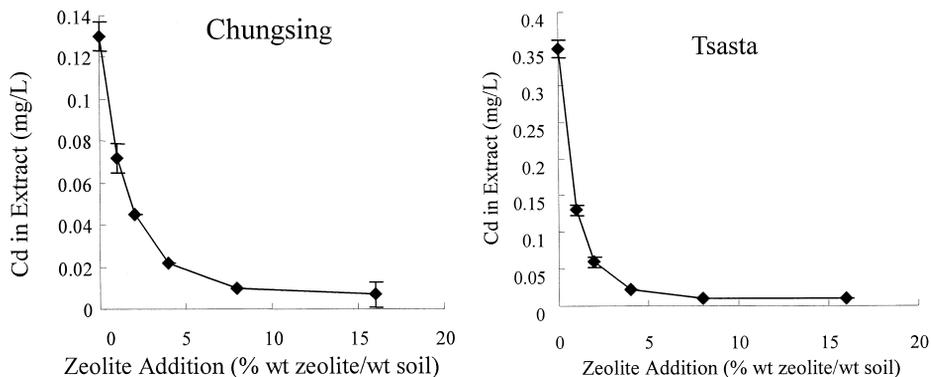


Fig. 2. Leachate Cd concentrations from actual contaminated soils as a function of the zeolite dosages.

sandy and loamy soil samples with pH between 4 and 7.7, the increase of one unit pH value will increase soil Cd holding capacity by 3 times [13]. Further, Cd uptake capacity of crops such as rice and wheat decreases as soil pH increases from 5.5 to 7.7 [14]. Therefore, the level of soil pH directly impacts the Cd holding capacity in soil and crops. Since adding zeolite raises soil pH, it will effectively inhibit the leaching of Cd from soil and uptake of Cd in crops.

Fig. 1 further illustrates that the Cd concentration reaches a plateau after the addition of critical zeolite mass. Therefore, it is suggested that, due to economic concerns, the optimum level of zeolite addition in Pinchen and Chengchung soils is approximately 8 g/100 g soil; whereas for Jente and Erlin soils, approximately 4–8 g/100 g soil.

As for the actual contaminated soils, leaching experiments conducted revealed similar results (Fig. 2). Prior to adding zeolite, Cd concentrations in leachate were 0.12 mg/l and 0.35 mg/l for Chungsing and Tsasta soil, respectively. After the addition of 16

Table 3  
Properties of soil columns used for leaching experiments

	Soil column									
	A	B	C	D	E	F	G	H	I	J
	Soil series			Soil series			Soil series			
	Pc <sup>a</sup>	Pc	Je	Je	Ce	Ce	Ce	Ts	Ts	Ts
Dosage of zeolite (% wt./wt.)	None	8/100	None	8/100	None	4/100	8/100	None	4/100	8/100
Bulk density (g/cm <sup>3</sup> )	1.5	1.5	1.4	1.4	1.3	1.3	1.2	1.4	1.4	1.4
Pore volume (cm <sup>3</sup> )	143	135	134	134	163	161	167	148	140	152
Conc. of Cd in soil (mg/kg)	70	64.8	70	64.8	6.9	6.6	6.3	9.5	9.4	9.0
Weight of soil column (g)	550	560	540	540	495	480	467	510	543	530
Average velocity (mm/h)	1.1	1.1	5.9	4.5	20.3	1.3	1.1	257	35	32.9
Total volume of influent (l)	1.6	1.7	6.5	6.6	11.1	2.3	2.3	17.1	15.1	16.8

<sup>a</sup>Pc: Pinchen, Je: Jente, Ce: Chungsing, Ts: Tsasta.

g/100 g soil of zeolite, Cd concentrations in leachate decreased to below 0.005 mg/l. The optimum level of zeolite addition for these soils is about 4–8 g/100 g soil.

Table 3 shows the basic properties of soil columns used in this study under different conditions. The results of experimenting with two Pinchen soil columns demonstrated that column A, without adding zeolite, began to leach Cd after 2.2 pore volumes of  $\text{CaCl}_2$  solution (Fig. 3a). After passing 3.4 pore volumes of leaching solution, the Cd concentration in leachate reached the peak of 77 mg/l. Thereafter, the Cd concentration

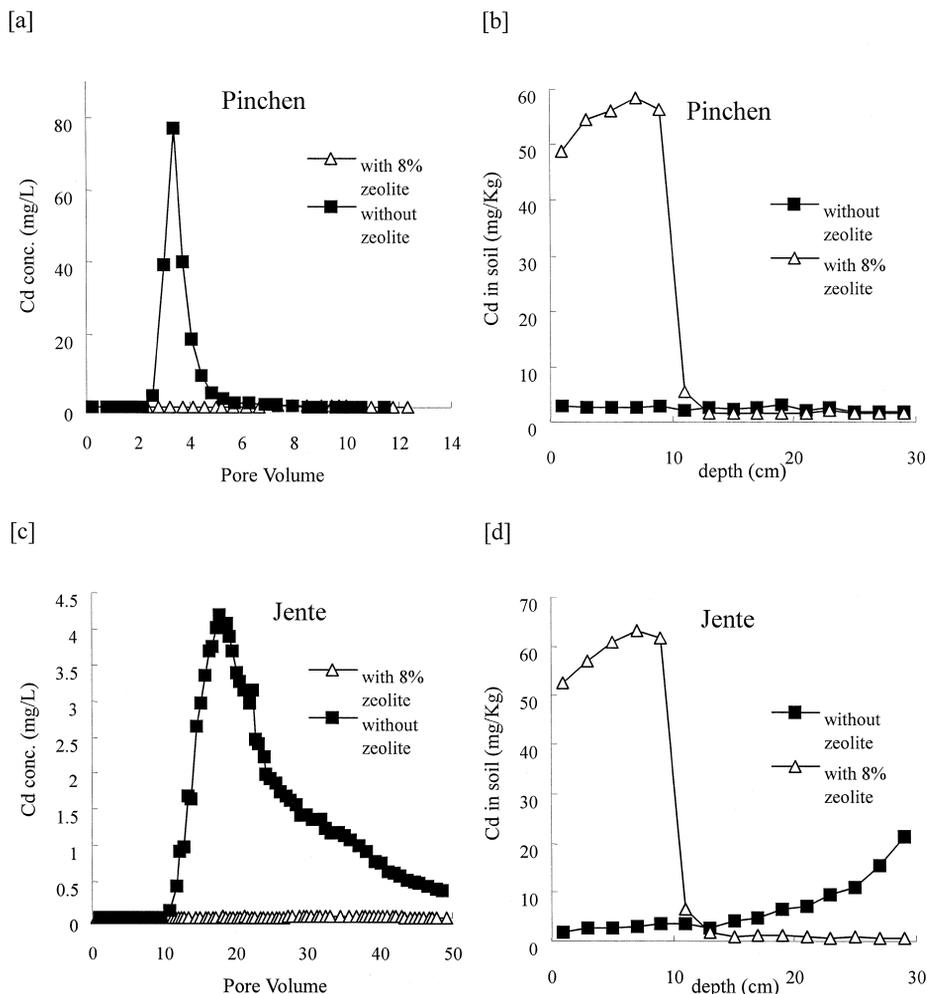


Fig. 3. Results of simulated contaminated soil column leaching experiment [(a) and (c):Cd concentration in effluent as a function of leachate pore volume, (b) and (d):Cd content variation as a function of soil column depth. Initial total Cd in soil samples: Pichen without zeolite, 39 mg; Pichen with zeolite, 36 mg; Jente without zeolite, 38 mg; Jente with zeolite, 35 mg. Cumulative leached Cd: Pichen without zeolite, 11 mg; Pichen with zeolite, 0.17 mg; Jente without zeolite, 8 mg; Jente with zeolite, 0.05 mg).

began a steep drop as the leaching volume increased until it reached a plateau. Cd was not detected in the leachate of Column B with the addition of 8 g/100 g soil of zeolite until 5.6 pore volumes; and the concentrations were never beyond 0.33 mg/l. A similar pattern is also observed for Jente samples, but with much slower Cd migration (Fig. 3c). It took more than 10 pore volumes of the leaching solution for Cd to be detected in the column effluent. Further analysis of the soil in different depths within the soil columns in the presence of zeolite also confirmed the fact that contaminated soils were stabilized in the upper layer (top 10 cm), resulting in negligible Cd migration (Fig. 3b,d); a phenomenon also observed in the leachate with almost undetected Cd concentration even after 40–50 pore volumes (Fig. 3c). The data in Fig. 3 reveal that the sum of the Cd mass observed in the leachate and that remained in the soil correlated well with that initially present in the contaminated soil layer.

Columns E–G (Chungsing soil) and H–J (Tsasta soil) contained actually contaminated soil samples. The results of the leaching experiment indicate that, for Chungsing soil, the migration of Cd is extremely slow even without zeolite addition. After 14 pore volumes of the leaching solution, Cd was not detected in the effluent (not shown), and Cd only moved from the top 10 cm to the mid-level (Fig. 4a). For column F with the 4% zeolite addition, Cd only slightly migrated from the top 3 cm to the next 3–5 cm level with the insignificant Cd levels in the effluent; the Cd level at 8% zeolite dosage (Column G) essentially remained the same. The result obtained for Tsasta soil is similar to that obtained for Pinchen soil in terms of almost no Cd detection in the leachate in the presence of zeolite. The Cd depth profiles (after 110 pore volumes) shown in Fig. 4b clearly indicate a stable Cd residual in soil; Cd stabilization increases as the quantity of added zeolite increases.

The decreased hydraulic conductivity with the addition of zeolite (Table 4) is responsible for slow Cd migration. Cd moves easily downward in soil with high

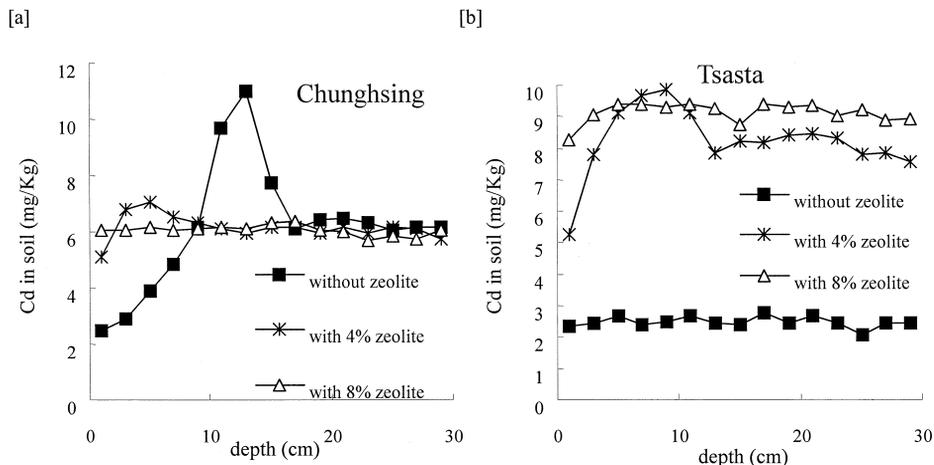


Fig. 4. Results of actual contaminated soil column leaching experiment (Cd content variation as a function of soil column depth).

Table 4  
Effect of zeolite dosage on the hydraulic conductivity of soil series

Dosage of zeolite (g/100 g soil)	Soil series <sup>a</sup>			
	Pc	Je	Ce	Ts
0	0.12	0.27	1.52	19.70
1	0.15	0.20	0.78	8.71
4	0.19	0.13	0.10	4.66
8	0.20	0.11	0.08	2.46

<sup>a</sup>Pc: Pinchen, Je: Jente, Ce: Chungsing, Ts: Tsasta.

hydraulic conductivity. Furthermore, the particle size of zeolite ( $D_{50} = 18 \mu\text{m}$ ) has its effect as well. For sandy and loamy soils, the addition of zeolite effectively reduces the average particle size, resulting in lower hydraulic conductivity in Chungsing and Tsasta soils. On the contrary for clayey soil, the addition of zeolite would slightly increase hydraulic conductivity as in the case of Pinchen soil. Therefore, the texture of the soil needs to be taken into consideration when adding zeolite for soil reclamation practices.

#### 4. Conclusion

The results of this research have demonstrated the capability of adding zeolite into soil to stabilize Cd content. There are major factors other than CEC that would affect zeolite capability in stabilizing Cd in soil: soil dilution, raising pH in soil, and altering hydraulic conductivity in soil. Adding zeolite is similar to adding extra volume of fresh soil, thus achieving soil dilution. Since zeolite pH is 10.5, adding zeolite into soil will increase mixture pH. The hydraulic conductivity of soil is also affected by the addition of zeolite; hence, influencing Cd migration. However, the hydraulic conductivity effect is highly correlated with physical and chemical properties of soil. It is most evident in acidic loamy soil, where the addition of zeolite would reduce heavy metal concentration in the leachate, as well as inhibit heavy metal migration in soil. For contaminated soils simulated in this study, the suggested zeolite dosage is approximately 0.1–0.2 g/mg Cd/100 g soil.

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