



Lab scale experiments for permeable reactive barriers against contaminated groundwater with ammonium and heavy metals using clinoptilolite (01-29B)

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Abstract

Batch tests and column tests were performed to determine the design factors for permeable reactive barriers (PRBs) against the contaminated groundwater by ammonium and heavy metals. Clinoptilolite, one of the natural zeolites having excellent cation exchange capacity (CEC), was chosen as the reactive material. In the batch tests, the reactivity of clinoptilolite to ammonium, lead, and copper was examined by varying the concentration of cations and the particle size of clinoptilolite. One gram of clinoptilolite showed removal efficiencies of more than 80% against those contaminants in all cases except in very high initial concentrations of ammonium (80 ppm) and copper (40 ppm). The effect of particle size of clinoptilolite was not noticeable. In the column tests, permeability was examined using a flexible-wall permeameter by varying particle sizes of clinoptilolite. When the washed clinoptilolite having the diameter of 0.42–0.85 mm was mixed with Jumunjin sands in 20:80 ratio (w/w), the highest permeability of 2×10^{-3} to 7×10^{-4} cm/s was achieved. The reactivity and the strength property of the mixed material were investigated using a fixed-wall column, having eight sampling ports on the wall, and the direct shear test, respectively. Clinoptilolite was found to be a suitable material for PRBs against the contaminated groundwater with ammonium and/or heavy metals.

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Keywords: Permeable reactive barriers; Clinoptilolite; Ammonium; Heavy metal

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1. Introduction

In Korea it has been reported that leachate leaked from unsanitary landfills is contaminating the surrounding soils and groundwater, and the contamination by heavy metals is very serious in areas neighboring abandoned mines, especially in Kang-won province. Recent news in Korea reports that the ammonium concentration in the untreated leachate from the landfills is as high as 2000 ppm, and the heavy metal concentrations around abandoned mines exceed the limiting regulations by over 10 or 20 times. So an immediate solution is required for the attenuation of ammonium and heavy metals in groundwater in those areas.

One of the most promising alternative technologies to conventional remediation methods, such as pump-and-treat, is the passive in situ treatment of groundwater contaminants using the *permeable reactive barriers* (PRBs, Gillham and O'Hannesin, 1991). In PRBs, reactive material is placed in the subsurface in the path of a plume of contaminated groundwater. Typically, contamination is carried into the PRBs under natural gradient condition (creating a passive treatment system) and treated water comes out of the other side (Fig. 1) [1].

In theory, the field application of PRBs presents a series of advantages in relation to pump-and-treat, including low operation costs, low maintenance, and low on-going energy requirements. Although investigation efforts for removing chlorinated hydrocarbons with natural and modified irons have been closely studied in Korea, very little is known about designing of PRBs for remediating the contaminated groundwater with ammonium and heavy metals.

Zeolites from abundant natural deposits were investigated by many researchers for the purpose of cleaning up wastewaters. Heavy metals in the water were removed successfully by natural and modified zeolites [2–4]. The removal of ammonium from municipal and industrial wastewater was one of the most significant commercial applications [5,6]. Among the most frequently studied natural zeolites, clinoptilolite is shown to have high selectivity for certain cations such as NH_4^+ , Pb^{2+} , Cd^{2+} , Zn^{2+} , and Cu^{2+} [2,6]. Phillipsite shows 70%

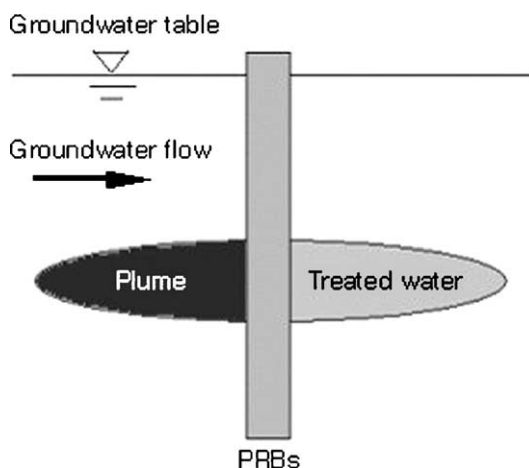


Fig. 1. Schematic diagram of PRBs.

higher ion exchange capacity than clinoptilolite, but it has shortcomings for general use, such as less physical strength and much higher cost than clinoptilolite [7]. In this study, clinoptilolite was chosen as a reactive material for the treatment of ammonium, lead, and copper.

This study presents an overview of the key design factors for the development of PRBs against groundwater contaminated with ammonium and heavy metals using clinoptilolite. The permeability of the material within the barrier under the stress imposed by overburden soil, and the strength of the barrier, composed of reactive material, need to be estimated for design purposes as well as removal efficiency of the barrier. Permeability of the material was estimated using flexible-wall permeameters. The flexible-wall method of confinement may model field conditions where existing lateral forces or excess overburden can possibly deform the soil with closing connected pores [8]. The strength property of the materials was estimated by a direct shear test in a shear box filled with water, simulating fully saturated aquifer.

2. Test materials and methods

2.1. Materials

Clinoptilolites (Silver & Baryte Ores Mining Co. S.A., Greece) having 0–0.15, 0.42–0.85 (prepared by sieving the 0–1 mm fraction), 1–2.5 mm particle sizes were used as reactive materials, whose size variation was determined on the basis of the sizes of commercial products. Table 1 shows the reported physico-chemical properties of the clinoptilolite (Silver & Baryte Ores Mining Co. S.A., Greece). Ammonium, lead, and copper solutions were prepared from their standard solutions; NH_4^+ (1002 mg/l, pH 4.5, Cica-reagent, Kanto Chemical Co. Inc., Japan), Pb^{2+} (1000 mg/l, pH 1.2, Cica-reagent, Kanto Chemical Co. Inc., Japan), and Cu^{2+} (1002 mg/l, pH 1.2, Cica-reagent, Kanto Chemical Co. Inc., Japan), respectively, with being made up in deionized water (18.2 M Ω , milli-Q water, milli-pore, USA). The diluted solutions had the pH range of 4.72–5.48 for ammonium and the pH range of 2.61–3.22 for heavy metals according to their initial concentrations. These pH ranges could prevent the cations from precipitating to container walls.

Table 1
Physico-chemical properties of clinoptilolite^a

Properties	Measurement
Color	Greenish-ivory
Hardness (Mohs)	3.5–4
Humidity (%)	8 (maximum)
Pore volume	0.34
Specific density (g/cm ³)	2.16
Apparent bulk density (g/cm ³)	0.85–1.1
Thermal stability (°C)	Up to 500
Alkaline stability (pH)	7–11
Acidic stability (pH)	2–7
Cation exchange capacity (meq./100 g)	150

^a Data for clinoptilolite from Silver & Baryte Ores Mining Co. S.A., Greece.

2.2. Batch experiments with ammonium, lead, and copper

Samples consisting of 100 ml of 20, 40, and 80 mg NH_4^+ /l aqueous solution and 1 g of dry clinoptilolite having different particle sizes were prepared in 250 ml flasks. The flasks were mixed vigorously on a shaker under ambient conditions. Periodically, 5 ml of the aqueous solution was withdrawn, and centrifuged to separate the solid phase. The concentrations of ammonium (NH_4^+) in solution were analyzed using ion chromatograph (IC, Waters, US). The heavy metal-removal experiments were carried out in the same manner as the ammonium-removal experiments except that the initial concentrations ranged from 10 to 40 mg heavy metals/l because of the heavy metals' ion valency (2+). Metals were analyzed using inductive coupled plasma (ICP, ICPS-1000IV, Shimadzu, Japan). Blank test was neglected because target contaminant ions are non-volatile and hardly biodegradable by using bacteria-eliminated water.

2.3. Permeability test using flexible-wall permeameter

A flexible-wall permeameter was used to estimate the permeability of soil specimens under the overburden soil pressure (Fig. 2). In the flexible-wall permeameter, the specimen was set up under a state of triaxial stress, which could be controlled to model the in situ state of stress. The specimens were made of clinoptilolite and Jumunjin sand (fixed ratio of 20:80 (w/w), respectively) with varying particle sizes of clinoptilolite. The soil property index and size distribution curve of the Jumunjin sand are presented in Table 2 and Fig. 3,

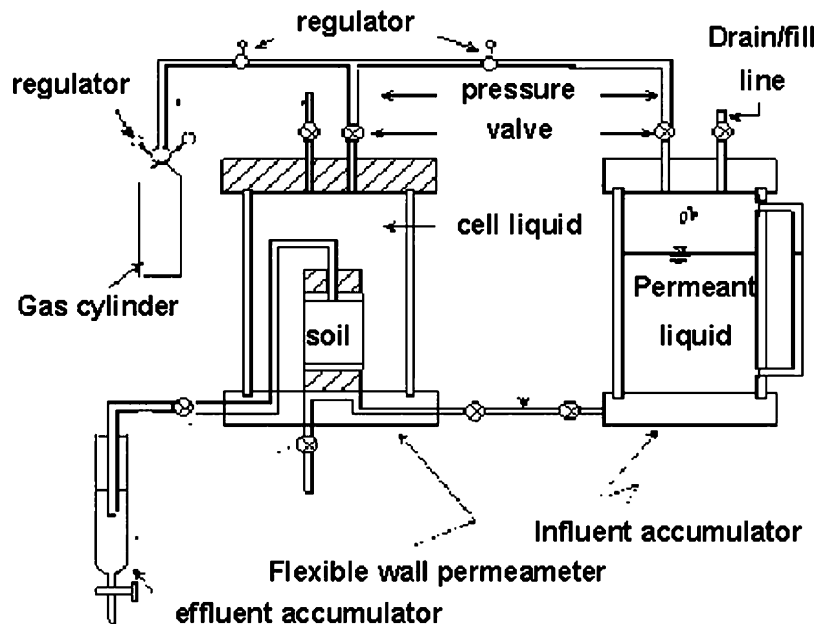


Fig. 2. Schematic diagram of flexible-wall permeameter.

Table 2
Soil property index for Jumunjin sands

Test	Index
Sieving test	Poorly graded sand ^a
Specific gravity test	2.64
Relative density test (t/m^3)	1.66 (maximum), 1.33 (minimum)

^a The united classification method.

respectively. The mould was prepared for making the specimens with mixed soils having 10% water contents. A membrane was fastened to the inside of the mould using a vacuum pump, and a bottom pedestal, porous plastic, and filter paper were subsequently emplaced in that order. While operating the pump, the mixed soils were poured into the mould, and compacted with a tamper 10 times in three discrete layers. The filter paper, porous plastic, and top pedestal were then emplaced in that order at the top of the specimen. Then, the vacuum pump was turned off so that the membrane could encapsulate the specimen with other materials. Fig. 4 shows the process of preparing the specimens. All the specimens tested were 3 cm in diameter and 7 cm in height. The cell was filled up with water for applying confining pressure. The confining pressure to the soil specimens in the cell was 10 psi, which corresponds, approximately to 4 m of overburden soil, and the head pressure applying to the influent solution in the reservoir was 5 psi, which corresponds, approximately to 50–60 (m/m, dimensionless) of hydraulic gradient. Hydraulic gradient was calculated by dividing the head pressure by column length and unit weight of water. The permeability, k (cm/s) of each specimen was calculated by measuring the volume of effluent solution and dividing the amount by the values of cross-sectional area of column, calculated hydraulic gradient, and elapsed time.

2.4. Removal experiment with landfill leachate using fixed-wall column

The fixed-wall column having eight sampling ports on the wall was used to estimate the removal capacity of washed 0.42–0.85 clinoptilolite mixed with Jumunjin sand by 20:80

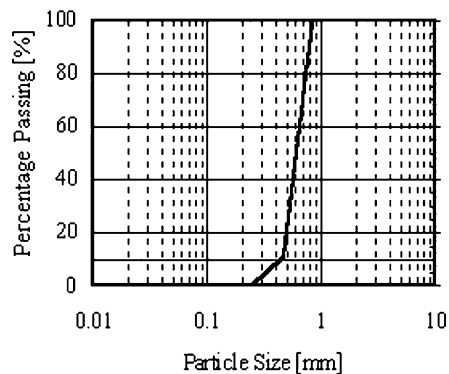


Fig. 3. Particle size distribution of Jumunjin sand.

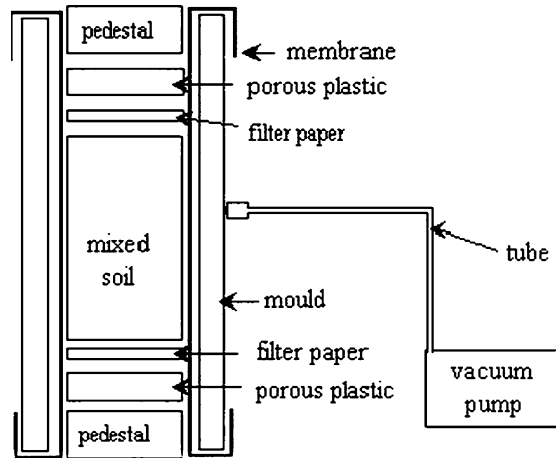


Fig. 4. Preparation of the specimen.

(w/w), respectively (Fig. 5). The column was 3.5 cm in diameter, 80 cm in height, and made of Pyrex[®] glass. Column was compacted in the same manner as for the specimen of flexible-wall permeameter. The reservoir was filled up with filtered landfill leachate collected from the Kim-po municipal landfill operated since 1992. The landfill leachate was collected at the connecting point between a leachate carrying pipe and the leachate treatment system. Leachate having 2400 mg NH₄⁺/l was injected into the column using a peristaltic pump (Master Flex, Cole-parmer Co., USA) at a flow rate of 0.4 ml/min. Samples (200 μl) were collected from the eight sampling ports on the wall after 24, 47, 100 h. The sampling ports were located at the distance of 2, 8, 13, 18, 24, 32, 42, 56 cm from the inlet of column.

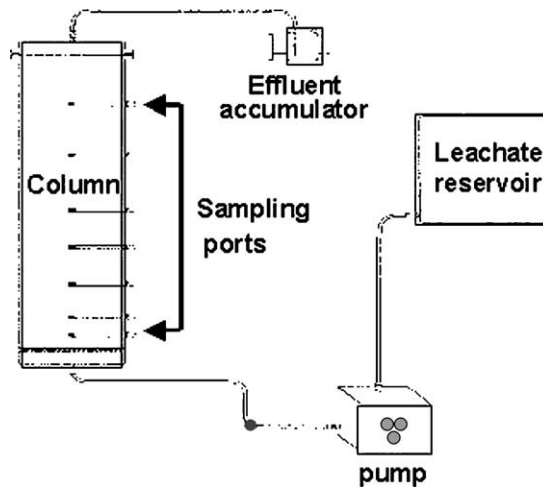


Fig. 5. Schematic diagram of fixed-wall column.

And then the concentrations of ammonium in the sample were analyzed with IC (Waters, USA), while the analysis on the heavy metals (Pb, Cu) was not performed because of their very low concentrations in the influent.

2.5. Direct shear test

Fractures and cracks caused by structural failures of the PRBs might form undesirable preferential flow paths through which contaminated groundwater pass without proper reactions with filling materials. This could void or decrease the appropriate functions of PRBs, and eventually lead to a failure to treat the contaminated groundwater. The strength properties of PRB materials need to be verified before a field application. To estimate the strength property of the clinoptilolite/sand specimen, direct shear test was performed. The shear box was filled with water to simulate the fully saturated aquifer, and confining pressure was varied over the range of 0.4–1.0 kg/cm², based on the flexible-wall permeameter pressure of 10 psi (about 0.7 kg/cm²). The test procedures were obtained from ASTM D3080.

3. Results and discussion

3.1. Batch experiments with ammonium, lead, and copper

Ammonium, lead, and copper uptakes by clinoptilolites are presented in Fig. 6. Most of the cations in the solutions, over 90% of their equilibrium concentration, were removed within 2 h (Fig. 6a–c). This is the favorable condition for reactive materials, making thickness of the barrier lessened. It was clear that, for all cations, as the initial concentration of the cations was increased, the removal capacity of unit clinoptilolite was decreased (from 86.3 to 66.3% in ammonium, from 99 to 98.7% in lead, and from 76.8 to 15.82% in copper). It is because one cation works as a competing ion to the other ion, and as the initial concentration increase the competing effect for the limited exchangeable sites is severe. So, the total amounts of clinoptilolite used in the barrier have to be decided upon the initial concentration of influents. Lead was more selectively removed than the other ions due to its relatively high selectivity (Fig. 6b). This result is consistent with the selectivity order suggested by other research such as $\text{Pb}^{2+} > \text{Cu}^{2+} > \text{NH}_4^+$ [6]. Although the copper ion has higher selectivity than ammonium, it was less removed than ammonium (Fig. 6c). It is thought to be for the unique selectivity of clinoptilolite used in this study, although the reason for this phenomenon is still unclear.

In general PRBs design, as the particle size of reactive material decrease, reactivity of the material increases although permeability through the material decreases. So, it is very important in designing PRBs to find out the optimum particle size of reactive material. Ammonium and lead uptakes by clinoptilolite having different particle sizes are presented in Fig. 7. With decreasing the particle size, the removal efficiency is slightly increased because the probability for clinoptilolite particles to contact with the contaminant ions is increased and the path length of the contaminant ions to the exchanging site is shortened. But the variation of the efficiency between samples is less than 8% (Fig. 8a and b), and it indicates that the difference of the specific surface area is not remarkable in three samples, probably because clinoptilolites are very porous materials. It is eventually dependent on

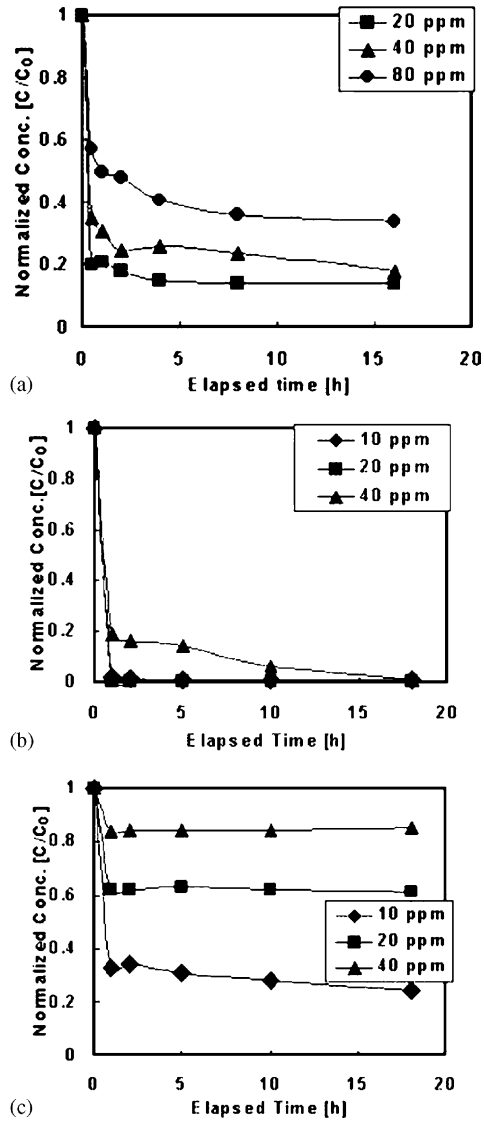


Fig. 6. (a) Ammonium; (b) lead; (c) copper removal with clinoptilolite varying initial concentration.

the permeability of clinoptilolite rather than reactivity to choose the proper particle size of clinoptilolite for PRBs.

3.2. Permeability test using flexible-wall permeameter

Throughout the preliminary tests, permeability of the specimen made of 100% clinoptilolite (0–1 mm particle size) was found to be too low around 1×10^{-6} cm/s. To control

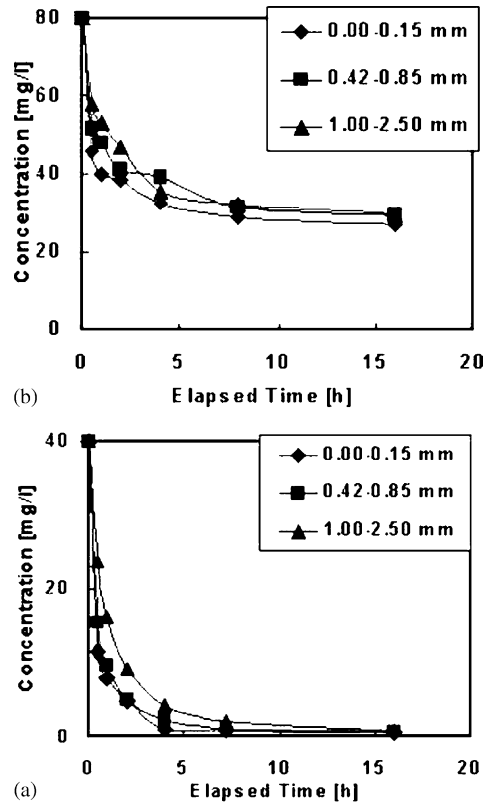
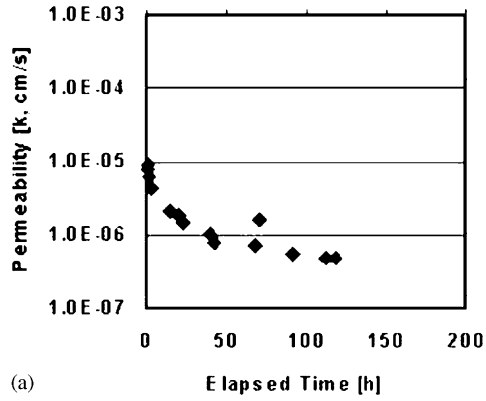


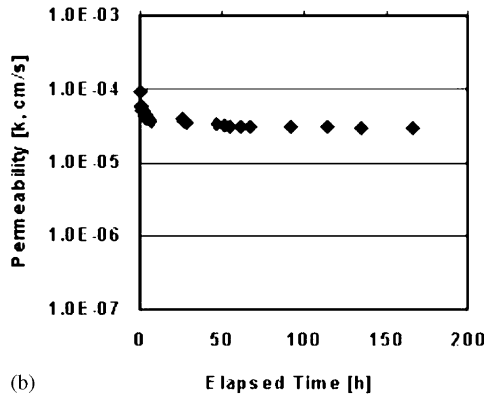
Fig. 7. (a) Ammonium; (b) lead removal varying the particle size of clinoptilolite.

the permeability, two different methods could be tried; varying the mixing ratio between clinoptilolite and sands, which is generally used as filter, under the fixed particle size of clinoptilolite, or varying the particle sizes of clinoptilolite under the fixed mixing ratio. In this study, permeability of the specimen was observed under the fixed mixing ratio (20:80 (w/w), clinoptilolite/sand) varying the particle size of clinoptilolites. Fig. 8 shows the change of permeability of the specimens containing clinoptilolite of 0–0.15, 0.42–0.85, and 1–2.5 mm particle sizes over 8 days. All specimens were made of clinoptilolite and Jumunjin sand (J-sand) in 20:80 ratio (w/w). The specimen containing 0.42–0.85 mm clinoptilolite shows the highest permeability ($k = 1 \times 10^{-4}$ to 4×10^{-5} cm/s) of the three specimens (Fig. 8b). This is due to the fact that 0.42–0.85 mm clinoptilolite has most similar particle size distribution curve with Jumunjin sands, and the mixed soil of clinoptilolite/J-sand is well sorted (or poorly graded) to achieve the highest void ratio (Fig. 9), and the highest permeability. Initial decreasing of the permeability might be caused by saturation of the specimen and by dust erosion of clinoptilolite clogging the existing flow paths.

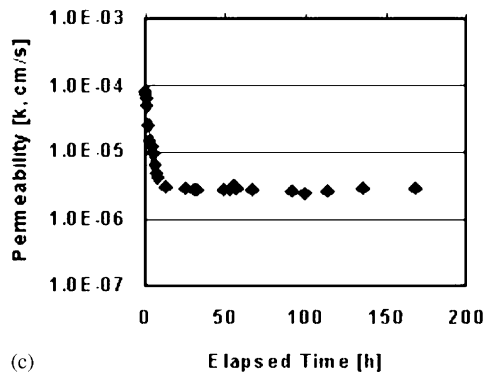
To estimate the effects of dust erosion on the permeability, 0.42–0.85 mm clinoptilolite was washed several times with deionized water (18.2 M Ω , milli-Q water, milli-pore, USA)



(a)



(b)



(c)

Fig. 8. Permeability in the specimen made of: (a) 0–0.15 m; (b) 0.42–0.85 mm; (c) 1–2.5 mm clinoptilolite and sand.

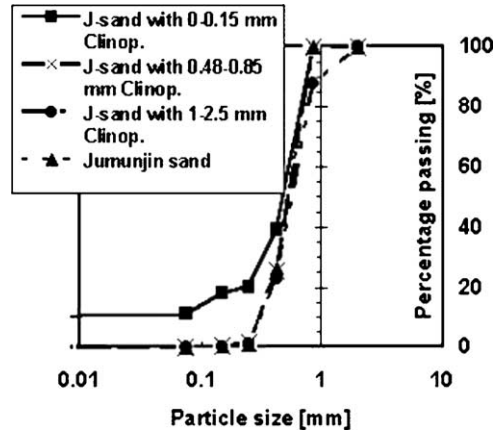


Fig. 9. Particle size distribution of mixed soils and Jumunjin sand.

before being mixed with Jumunjin sands, and another permeability experiment was carried out. To estimate the loss of exchangeable ions in clinoptilolite during washing, the wastewater after washing was collected, and exchangeable ions in clinoptilolite such as Na, Ca, K, Mg were analyzed with ICP (ICPS-1000IV, Shimadzu, Japan). The amounts found were less than 5 ppm, and it indicates that the loss of exchangeable ions during washing is negligible considering the cation exchange capacity (CEC) value of clinoptilolite used in this study (150 meq./100 g). Fig. 10 presents the permeability of the specimen containing 0.42–0.85 mm washed clinoptilolite. In Fig. 10, permeability of the specimen containing washed clinoptilolite ($k = 2 \times 10^{-3}$ to 7×10^{-4} cm/s) is about 10 times greater than that of containing non-washed clinoptilolite (Fig. 8b). This is due to the removed dusts or very small particles by washing which decreases the permeability of specimen in early period of experiment. Although they brought no comments on permeability changes in other

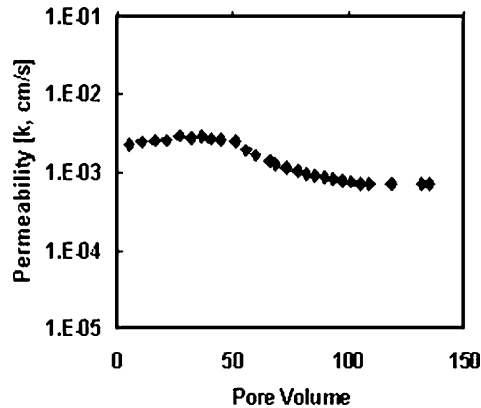


Fig. 10. Permeability in the specimen made of washed 0.42–0.85 mm clinoptilolite and sand.

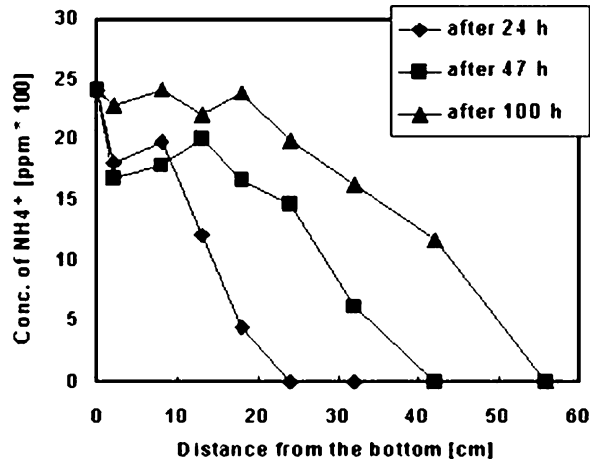


Fig. 11. Distribution of ammonium concentration along column length after 24, 47, 100 h.

researches [4,9], the gradual decrease in permeability of clinoptilolite was observed in this study. It could be explained that gradual decrease of permeability in the material was caused by hydration of clinoptilolite, and the effective porosity was reduced on the hydration. Hydration of clinoptilolite could be confirmed from the increased pH value from 6.8 in influent water to 7.9 in effluent water.

Hence, permeability can be controlled by using washed clinoptilolite because washing does not affect the removal efficiency of the material for removing contaminants in groundwater. But careful attention has to be paid to the permeability changes in the barrier for the hydration of clinoptilolite.

3.3. Removal experiment with landfill leachate using fixed-wall column

Fig. 11 shows the variations of the ammonium concentration along the column length from the bottom after 24, 47, 100 h. Ammonium concentration in the leachate was decreased along the column length as ammonium was exchanged with the exchangeable ions in clinoptilolite. As time passed, the removal efficiency of clinoptilolite near the inlet part of the column was decreased, and this condition continued to develop deeper into the column over time. In Fig. 11, the 0 value of ammonium concentration in y-axis does not indicate the full removal of ammonium in the leachate, rather the concentrations below the detection range of IC. More precise analysis is needed to determine the ammonium concentrations after treatment meeting the regulation (0.5 mg/l) on the contaminants concentration in effluent leachate. However, nearly 21 of leachate having 2400 mg NH₄⁺/l was treated with 300 g of clinoptilolite in the column, and supposing the residual concentration in the effluent of 100 mg NH₄⁺/l, the detection limit (1 mg NH₄⁺/l) when diluted with the factor of 100, the total amount of ammonium removed can be, approximately calculated to be 4600 mg (=21 × (2400–100) mg NH₄⁺/l). For reliable expectation on the longevity of PRBs, column test has to be performed for longer periods of time and the changes in material reactivity

have to be carefully observed. But neglecting the variables in barriers such as pH, reactivity of material, and permeability changes due to material hydration, particle precipitation, and pore clogging, the longevity of barrier could be ideally estimated with experimental results mentioned earlier. Supposing the dimension of barriers as 10 m long, 5 m deep, and 1 m wide, the amount of clinoptilolite filled in barrier would be calculated as 19.5 t (barrier volume/column volume \times 300 g). And the treatable amount of ammonium with barrier could be calculated as 3×10^8 mg ($= (4600 \text{ mg}/300 \text{ g}) \times 19.5 \text{ t}$). And supposing the ammonium concentration in contaminated groundwater of 10 mg/l and the groundwater velocity of 0.005 m/h, the treatable amount of groundwater is calculated as 3×10^7 l ($3 \times 10^4 \text{ m}^3$), and the longevity of PRBs of clinoptilolite mixtures as 1.2×10^5 h (almost 13 years $= (\text{treatable amount of groundwater}/\text{cross-sectional area of barrier})/\text{groundwater velocity}$).

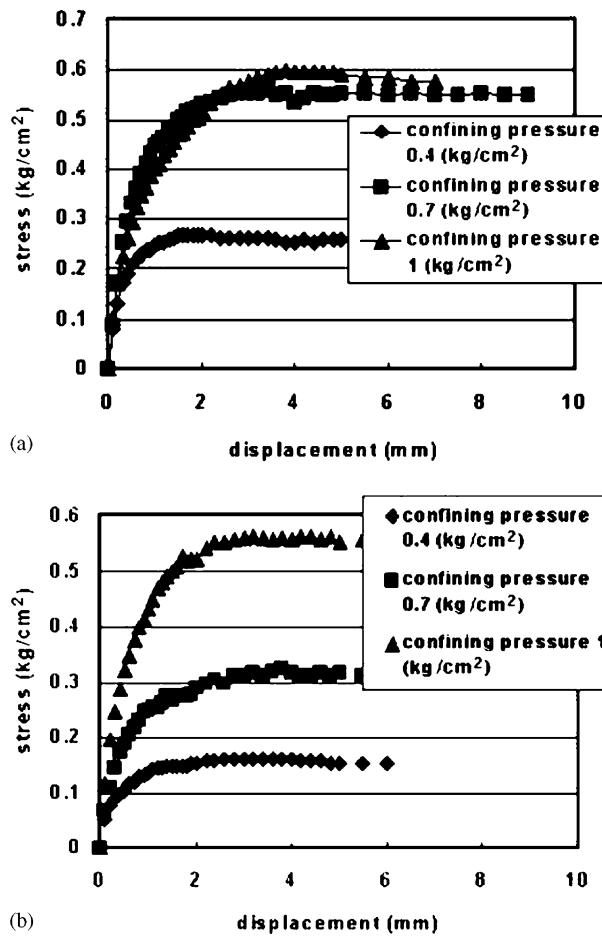


Fig. 12. Direct shear test results of: (a) mixed soil (0.42–0.85 mm clinoptilolite/sand, 20/80 weight fraction); (b) Jumunjin sand.

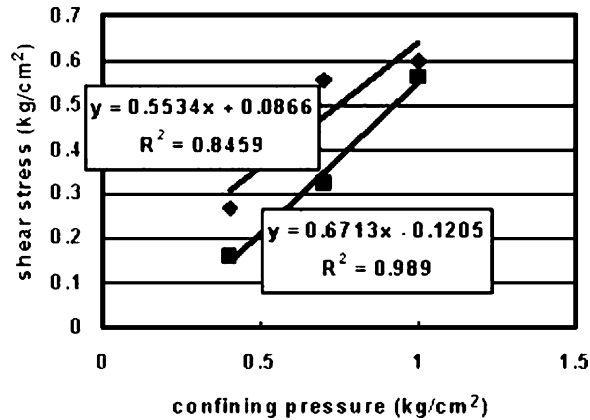


Fig. 13. Failure envelopes of mixed soil and Jumunjin sand.

But this calculation might overestimate the longevity of barrier, because it neglects the decrease of reactivity in clinoptilolite occurring as clinoptilolites encounter the contaminated groundwater coming into the barrier with its initial concentration over the time.

3.4. Direct shear test

Fig. 12a and b show the direct shear test results of the mixed soil (clinoptilolite/Jumunjin sands, unit weight of 2.51 g/cm^3) and Jumunjin sands (unit weight of 2.64 g/cm^3), respectively. In Fig. 13, strength of the mixed soil is slightly increased due to the cohesion of clinoptilolite while the friction angles remain similar as 27.3° and 28.9° . In other words, when the soil in the aquifer, which can be represented by Jumunjin sand, is replaced by reactive material (clinoptilolite/Jumunjin sands) the physical stability in the aquifer is not harmfully affected.

4. Conclusion

Clinoptilolite has the high removal efficiency (above 82% except copper ion), low cost, proper permeability ($k = 2 \times 10^{-3}$ to $7 \times 10^{-4} \text{ cm/s}$) when sieved to adequate size (0.42–0.85 mm) and mixed with sands, and the similar strength property ($\varphi = 28.9^\circ$) to soils in the aquifer ($\varphi = 27.3^\circ$). It is a promising reactive material which can be filled in the PRBs against contaminated groundwater with ammonium and heavy metals. For the field application, however, further research has to be performed on the problems such as high concentration occurring of exchanged ion like sodium in the effluent side of PRBs and gradual decreasing permeability of the PRBs due to hydration of clinoptilolite. And the field column experiments have to be performed in the concerning field conditions for the sufficient time period to predict the changes in the barriers during operation, and to confirm the longevity of barriers.

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