

Changes in hydraulic conductivity of sand-bentonite mixtures accompanied by alkaline alteration[†]

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ABSTRACT: Highly alkaline environments induced by cementitious materials in radioactive waste repositories are likely to alter montmorillonite, the main constituent of bentonite buffer materials, and are likely to cause the physical and/or chemical properties of the buffer materials to deteriorate. The deterioration may cause variation in hydraulic conductivity of the buffer. However, empirical data on the variation of hydraulic conductivity are scarce, mainly because the alteration of compacted buffer materials, sand-bentonite mixtures, is extremely slow. In this study, laboratory experiments were performed to observe changes in hydraulic conductivity of sand-bentonite mixtures, accompanied by their alkaline alteration, using NaOH-based solutions at 80–90°C. Series-1 multi-step alteration/water conduction experiments resulted in an increase in the hydraulic conductivity by one order of magnitude over a 200 day period. Series-2 single step alteration/water conduction experiments revealed a decrease in the montmorillonite contents with time and a resulting increase in the hydraulic conductivity by 30 times over the 67 day period. Series-3 simultaneous alteration/water conduction experiment also demonstrated an increase in the hydraulic conductivity by 30 times over the 150 day period. The results proved that the alkaline alteration of the bentonite buffer can increase the hydraulic conductivity. The data obtained in this study are useful for verification of the code that will be used for assessing the alteration.

KEYWORDS: alteration, bentonite, radioactive waste disposal, hydraulic conductivity, simulation

Montmorillonite is the main constituent of bentonite clay buffer materials in radioactive waste repositories. Highly alkaline environments induced by cement-based materials are likely to alter montmorillonite, and then to deteriorate the physical and/or chemical properties of the buffer materials.

This deterioration may cause variation in hydraulic conductivity of the buffer and induce major uncertainties in the radionuclide migration analysis. Empirical data on the variation of hydraulic conductivity are, however, scarcely available mainly because the alteration of compacted buffer materials in a sand-bentonite mixture specimen is extremely slow (Yamaguchi *et al.*, 2007).

Ruhl & Daniel (1997) reported high hydraulic conductivity of clay liners when 0.1 mol l⁻¹ sodium hydroxide was permeated. Lee & Sinha (2001), on the other hand, measured hydraulic conductivity for clay liners of bentonite and kaolinite mixtures using

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distilled water and 0.1 mol l^{-1} sodium hydroxide as the permeant and reported almost the same hydraulic conductivity. The Radioactive Waste Management Funding and Research Center (2002) performed a permeability test for a 7/3 mixture of sand and montmorillonite with a $6 \times 10^{-3} \text{ mol l}^{-1}$ $\text{Ca}(\text{OH})_2$ solution at 80°C for 360 days. They reported changes in the concentration of elements in the eluted water with time and no changes in the hydraulic conductivity. Cuisinier *et al.* (2008) performed a series of alteration experiments for compacted Manois argillite and its mixtures by circulating portlandite-saturated water with a pH of 12.4 at 20°C and 60°C for 12 months. They reported changes in microstructure of the specimens given by mercury intrusion porosimetry. Although they concluded that alkaline solute would dramatically affect the hydraulic properties of the materials over a long period of time, they did not report changes in the hydraulic properties of the specimens during the fluid circulation. Yokoyama & Nakamura (2010) and Yokoyama *et al.* (2011) performed permeability tests using compacted bentonites and alkaline solutions, and observed changes in hydraulic conductivity accompanying bentonite alteration. The alteration would, however, be significantly limited in their experiments because the specimens were held by upper and lower plates with only small holes. The diffusive transport of alkaline components into the specimen during the immersion periods were significantly limited by the experimental setup with small holes (Yokoyama & Nakamura, 2010).

In this study, laboratory experiments were performed to observe changes in hydraulic conductivity of sand-bentonite mixtures accompanied with their alkaline alteration using NaOH-based solutions at $80\text{--}90^\circ\text{C}$.

EXPERIMENTAL

The water conduction experimental apparatus is shown in Fig. 1. We performed a preliminary experiment to degrade a sand-bentonite mixture by sequentially permeating 1 mol l^{-1} NaOH solution at 90°C , 1 mol l^{-1} NaOH solution at 70°C and 1 mol l^{-1} NaCl solution at 70°C . However, the experiment was unsuccessful, in that the flow rate of the permeant water became unstable. This was interpreted as an artifact due to generation and stagnation of air in the mixture specimen. The water conduction experimental apparatus was modified by removing the membrane filter and leaving only a sintered stainless steel filter, and by equipping the pressurizing tank with a preheater. The sintered stainless steel filter (with a pore diameter of $10 \mu\text{m}$) was good enough to support the specimen and to prevent fine particles from washing down. Three types of experiments were then carried out using 50:50 mixtures of sand and bentonite in specimens with a diameter of 50 mm, thickness of 10 mm and a dry density of $1.6 \times 10^3 \text{ kg m}^{-3}$. A Na-type bentonite, Kunigel V1, and silica sands of two different grain sizes ($0.1\text{--}0.85 \text{ mm}$ and $0.85\text{--}2 \text{ mm}$) were used as shown in Yamaguchi *et al.* (2007).

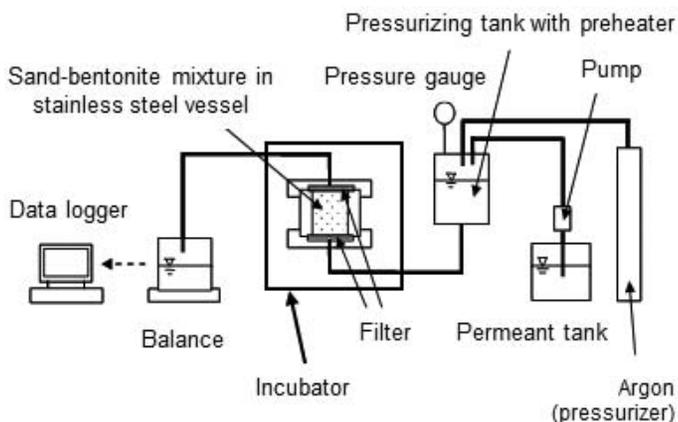


FIG. 1. Schematics of the water conduction experimental apparatus. The preheater that the pressurizing tank is equipped with was added after a preliminary experiment.

Series-1: Multi step alteration/water-conduction experiments

Two sand-bentonite mixture specimens were used in hydraulic conductivity measurements and alkaline alteration processes alternately. The hydraulic conductivity was determined by permeating the specimens with 1.0 mol l⁻¹ NaCl solution at 40°C over 0–14, 35–49, 70–84 and 108–300 day periods. Meanwhile the specimens were immersed in pH-adjusted, simulated alkaline groundwater at 90°C (Nakayama *et al.*, 2004) to allow alteration over 14–35, 49–70 and 84–108 day periods. The concentrations of Na, OH⁻, Si, Al and Ca in the simulated alkaline groundwater was 1.1, 1.0, 2.9 × 10⁻², 2.6 × 10⁻³ and 2.5 × 10⁻⁵ mol l⁻¹, respectively. In the final water-conduction step, the effect of the ionic strength on the hydraulic conductivity of the altered specimens was checked by permeating the specimens with 0.3 mol l⁻¹ NaCl solution for 45 days. The hydraulic pressure of 0.005–0.01 MPa was applied to obtain measurable effluence. The pH and the concentrations of Al, Ca, Na and Si in the permeate were analysed by combination-glass electrode, Inductively Coupled

Plasma-Atomic Emission Spectrometry (ICP-AES), and the molybdisilicate method.

Series-2: Single step alteration/water-conduction experiments

The sand-bentonite mixture specimens were immersed in the simulated alkaline groundwater solution at 90°C for 14, 27, 51 and 67 day periods, respectively, for alteration. The hydraulic conductivity was determined for the altered specimens by permeating the specimen with 0.3 mol l⁻¹ NaCl solution at 40°C. Hydraulic pressures between 0.005 and 0.05 MPa were applied to obtain measurable effluents.

Series-3: Simultaneous alteration/water-conduction experiment

A sand-bentonite mixture specimen was permeated with 0.3 mol l⁻¹ NaOH solution at 80°C. The hydraulic pressure of 0.01–0.10 MPa was applied to obtain measurable effluents. The hydraulic pressure and the flow rate of NaOH solution yielded the hydraulic conductivity. The specimen was cut into three parts, flow inlet, middle and

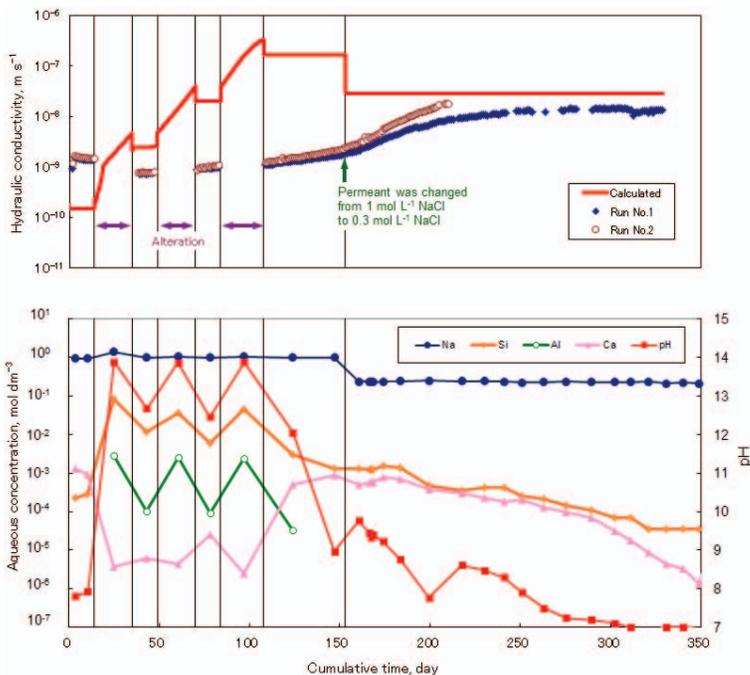


FIG. 2. The result of the multi-step alteration/water-conduction experiments (series-1).

outlet, and analysed for montmorillonite contents by the methylene-blue adsorption titration method (Nakayama *et al.*, 2004).

RESULTS AND DISCUSSION

The series-1 experiments gave an increase in the hydraulic conductivity with time as shown in Fig. 2. Although the final hydraulic conductivity, $(1.6 \pm 0.2) \times 10^{-8} \text{ m s}^{-1}$, was not very far from the predicted value by MC-BENT (Yamaguchi *et al.*, 2008), $2.9 \times 10^{-8} \text{ m s}^{-1}$, the course of the alteration was different from the prediction. The 14 day period of water-conduction was considered to be too short to observe accurate hydraulic conductivity of the altered specimen. The amount of montmorillonite in the specimen decreased by 6.36 g from initial amount of 7.85 g. The decrease is consistent with the amount of dissolved montmorillonite of 7.83 g predicted by the kinetic dissolution model for montmorillonite in the bentonite buffer material (Yamaguchi *et al.*, 2007):

$$R_A = 3.5 \times 10^3 (a_{\text{OH}^-})^{1.4} \exp(-51000/RT) \quad [\text{kg m}^{-3} \text{ s}^{-1}] \quad (1)$$

where R_A is the dissolution rate of montmorillonite ($\text{kg m}^{-3} \text{ s}^{-1}$), a_{OH^-} the activity of hydroxide ions (mol l^{-1}), R the gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), T the absolute temperature (K).

Figure 2 also shows the pH and the concentration of major elements in the permeate. No effluent of montmorillonite gel was observed in the permeate. The pH of the permeate was around 12.8, far from the pH 8 of the NaCl solution after the first alteration period and also the second. The alkaline solution brought in during the alteration periods was incompletely replaced by the NaCl solution. The pH was 12, 30 days after the third alteration period; it took more than 46 days to be lowered below 10. When the permeant is changed, it takes many days for the porewater to be replaced. The concentration of Ca is low at alteration periods and at water conduction periods shortly after the alteration period when the pH is high and is as high as 10^{-4} – $10^{-3} \text{ mol l}^{-1}$ at pH 8–10. The concentration of Ca increases through cation exchange and decreased by the formation of $\text{Ca}(\text{OH})_2$ or Ca-rich CSH at higher pH. The concentration of Si shows similar trends with the pH. This is because silicon is more soluble in higher pH solutions through hydrolysis. The pH over the first alteration period is almost identical to

that of the second and the third; nevertheless, the concentration of Si is higher over the first alteration period than those of the second and the third. A portion of the quartz in the sand-bentonite mixture dissolves thermodynamically (Yamaguchi *et al.*, 2007); the high Si concentration over the first alteration period is probably due to the dissolution of the quartz. Because Al is released to the solution with dissolution of montmorillonite and is soluble in high alkaline solution as hydrolysed form, $\text{Al}(\text{OH})_4^-$, the concentration is correlated with the pH. When the pH is between 8 and 10, the concentration of Al is under the detection limit. The formation of analcime, $\text{NaAlSi}_2\text{O}_6$, is responsible for the low Al concentration in the NaOH-bentonite systems (Amaya *et al.*, 1999; Johnston & Miller, 1985). The concentration of Mg that is also released by montmorillonite dissolution is low. The low Mg concentration had been often presumed to be due to the formation of sepiolite (Yamaguchi *et al.*, 2008) with no convincing empirical proof.

In the series-2 experiments, a decrease of montmorillonite and increase in hydraulic conductivity were observed as shown in Fig. 3 and Table 1. Good agreement with the simulation by MC-BENT (Yamaguchi *et al.*, 2008) was observed when the effective montmorillonite dry density was high or in the range of 400–720 kg m^{-3} . In the effective montmorillonite dry density range lower than 200 kg m^{-3} , deviation was seen between the empirical and simulated hydraulic conductivities. The deviation could arise from the fact that our hydraulic conductivity model is based on the experiment where mixtures of bentonite and sand with specimen diameters of 0.1–2.0 mm, which is much coarser than those of secondary minerals formed during the alteration treatment.

The series-3 experiment gave an increase in the hydraulic conductivity with the progress of alteration as shown in Fig. 4. The amount of montmorillonite decreased to 5.7 g from the initial amount of 7.85 g. 27% of the montmorillonite dissolved in 150 days in the series-3 experiment, while 100% dissolved in 60 days in series-2. The dissolution rate is nine times as high in the series-2 experiment as that in the series-3, which is consistent with our dissolution model. The difference in a_{OH^-} , 1.0 mol l^{-1} in series-2 and 0.3 in series-3, brings a higher dissolution rate of 5.4 times to the series-2 deduced from the factor $a_{\text{OH}^-}^{1.4}$ in our model of the dissolution rate. The difference in the temperature, 363.15 K in series-2

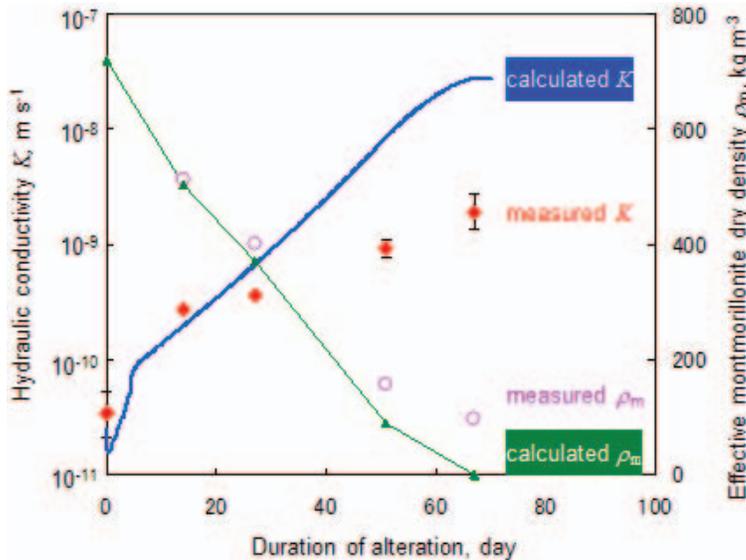


Fig. 3. The result of the single-step alteration/water-conduction experiments (series-2).

and 353.15 K in series-3, leads to a higher dissolution rate by 1.6 times to the series-2 deduced by the factor $\exp(-51000RT)$ in our model of the dissolution rate. Our dissolution model gives a higher dissolution rate to the series-2 than that of the series-3 by 8.6 times altogether.

Figure 4 also shows the aqueous concentration with time. The pH of the permeate became equal to the 0.3 mol l⁻¹ NaOH solution by the 120th day. By that time, the pH of the permeate was suppressed by chemical reactions with the minerals. The concentration of Si increased during the first 60 days and then levelled off. The dissolution of

silica can be a chemical reaction that suppressed the pH of the permeate. The concentration of Al increased with time, which suggested that the dissolution of montmorillonite continued throughout the experiment. The concentration of Ca decreased with time, which is consistent with the pH increase.

Although the final hydraulic conductivity showed good agreement with the simulation by MC-BENT (Yamaguchi *et al.*, 2008), the course of the increase, again, differed from the simulation. The pH of the permeate was lower than that of the 0.3 mol l⁻¹ NaOH solution until the 90th day, suggesting spatially inhomogeneous alteration of the specimen. The effective montmorillonite dry

TABLE 1. Results of the solid phase analysis after the hydraulic conductivity measurements in the series-2 experiments.

Alteration period (days)	Dry density (kg m ⁻³)	Remaining montmorillonite (kg)	Porosity (%)	Effective montmorillonite dry density (kg m ⁻³)
0	1600	7.85×10^{-3}	40.7	720
14	1270	6.28×10^{-3}	50.4	514
27	1230	4.96×10^{-3}	53.7	401
51	1140	1.84×10^{-3}	56.1	157
67	1070	1.13×10^{-3}	56.6	98

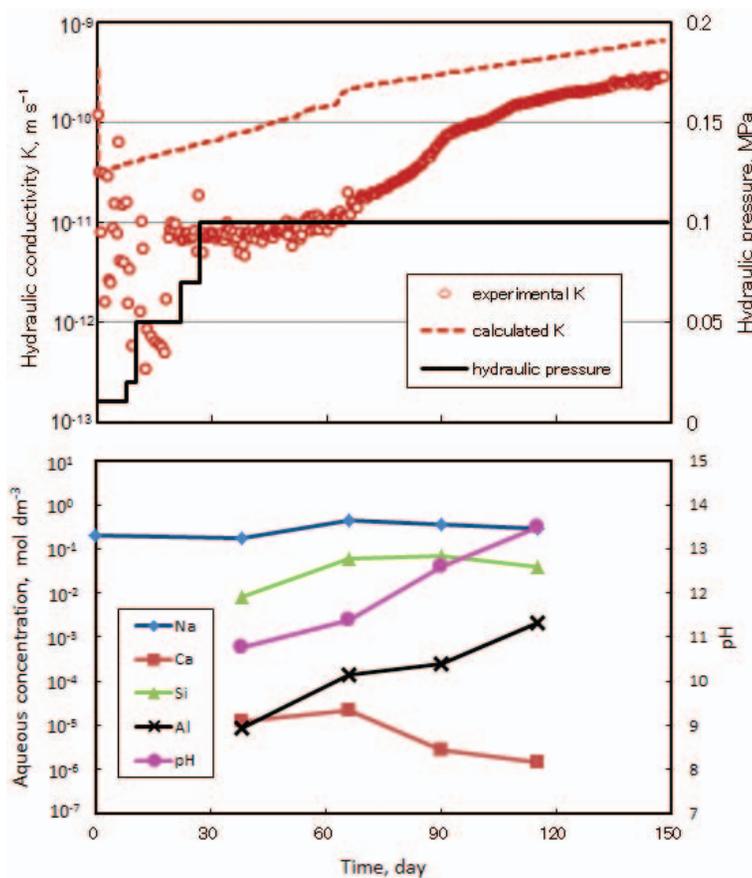


Fig. 4. The result of the simultaneous alteration/water-conduction experiment (series-3).

density was 0.40, 0.45 and 0.47 Mg m^{-3} for the fluid inlet, centre and outlet, respectively, which also showed the inhomogeneous alteration as shown in Table 2. Our dissolution model gives a linear correlation between montmorillonite content and

time and in our hydraulic conductivity model the logarithmic hydraulic conductivity correlates with the montmorillonite content. Consequently, our model correlates logarithmic hydraulic conductivity linearly with time as shown in Fig. 4. The results of

TABLE 2. Results of the solid phase analysis after the hydraulic conductivity measurements in the series-3 experiment.

Alteration period (days)	Position	Dry density (kg m^{-3})	Porosity (%)	Effective montmorillonite dry density (kg m^{-3})
0	Whole	1600	40.7	720
150	Inlet	1140	58.3	395
150	Middle	1280	53.2	451
150	Outlet	1250	54.2	467

the series-3 experiments shows different trends. The logarithmic hydraulic conductivity began increasing 60 days after the start of the experiment. Our model does not have high precision for the assessment of the hydraulic conductivity of non-homogeneously altered bentonite.

For the purpose of demonstrating the change in hydraulic conductivity of compacted bentonite accompanied by alkaline dissolution of minerals, the series-2 method, single step alteration/water-conduction experiments, in which the hydraulic conductivity determination is separated from the alteration process and is done only once per specimen, provides the most convincing results. The series-1 and the series-3 methods, being suitable for observing the change in the hydraulic conductivity with time, are not better than the series-2 method because the amount of montmorillonite can be determined only at the start and at the end of the experiment. Another problem in the series-1 experiment is that the changes in the properties of the permeant and of the specimen are not reflected in the change in hydraulic conductivity promptly.

CONCLUSION

In this study, three types of laboratory experiments proved that the alkaline alteration of bentonite buffer can increase the hydraulic conductivity. The data obtained in this study are useful for verification of the code that will be used for assessing the alteration. For the purpose of demonstrating the change in hydraulic conductivity of compacted bentonite accompanied by alkaline alteration, the series-2 method, in which the hydraulic conductivity determination is separated from the alteration process and is done only once per a specimen, provides the most convincing results. In the series-1 method, where the specimens were subject to hydraulic conductivity measurement and alkaline alteration alternately, the amount of montmorillonite can be determined only at the start and at the end of the experiment, and changes of the permeant are not promptly reflected in the hydraulic conductivity. The series-3 method, where the alteration and the hydraulic conductivity measurements proceeded simultaneously by permeation of NaOH solution through the specimens, demonstrates the change in the hydraulic conductivity accompanied by inhomogeneous alteration.

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