Effects of OH⁻ activity and temperature on the dissolution rate of compacted montmorillonite under highly alkaline conditions

TAKUMA SAWAGUCHI*, MANABU TSUKADA, TETSUJI YAMAGUCHI AND MASAYUKI MUKAI

Waste Safety Research Group, Nuclear Safety Research Center, Japan Atomic Energy Agency, Tokai, Ibaraki 319-1195, Japan

ABSTRACT: The highly alkaline environment induced by cementitious materials in a deep geological disposal system of high-level radioactive waste is likely to alter montmorillonite, the main constituent of bentonite buffer materials. Over long time periods, the alteration may cause the physical and/or chemical barrier functions of the buffer materials to deteriorate. In order to evaluate the long-term alteration behaviour, the dissolution rate, R_A (kg m^{-3} s^{-1}), of compacted pure montmorillonite (Kunipia-F) was investigated experimentally under conditions of hydroxide ion concentration of 0.10–1.0 mol dm^{-3} at temperatures of 50–90°C. The dissolution rate data, including those from a previous study at 130°C, were formulated as a function of the activity of hydroxide ions, a_{OH^-} (mol dm^{-3}), and temperature, T (K), and expressed as $R_A = 10^{4.5} \cdot (a_{OH^-})^{1.3} \cdot e^{-55000/RT}$ by multiple regression analysis, where R is the gas constant. The dissolution rate of montmorillonite was greater in the compacted montmorillonite than in the compacted sand-bentonite mixtures. The difference can be explained by considering the decrease in a_{OH^-} in the mixtures accompanied by dissolution of accessory minerals such as quartz and chalcedony. The dissolution rate model developed for pure montmorillonite is expected to be applied to bentonite mixtures if quantification of the decrease in a_{OH^-} is achieved somehow.

KEYWORDS: compacted montmorillonite, highly alkaline conditions, dissolution rate, activity of hydroxide ions, temperature, accessory minerals.

Highly alkaline environments induced by cementitious materials in a deep geological disposal system for high-level radioactive waste are likely to alter montmorillonite, the main constituent of bentonite buffer materials, affecting adversely the physical and/or chemical barrier functions of the buffer materials. In order to evaluate the long-term alteration behaviour, the dissolution rate of montmorillonite should be determined.

Various studies on the dissolution rates of clays in alkaline solutions used different pulverized smectites (Savage *et al.*, 1992; Bauer & Berger, 1998; Kubo *et al.*, 1998; Sato *et al.*, 2004; Rozalén *et al.*, 2008, 2009), and determined the rates under much lower solid/solution ratios than those of the disposal sites (Table 1). These data need some modification in order to evaluate the dissolution of buffer materials under the confined disposal conditions. Savage & Liu (2015) reported that the most relevant water/clay ratio ('porosity') should be used in modelling and experimental systems based on thermodynamic calculations illustrating that the water/clay ratio affected the magnitude and nature of

*E-mail: sawaguchi.takuma@jaea.go.jp

TABLE 1. Initial experimental conditions of previous studies on the dissolution rates of smectites.

Study	Experimental method	Solid	Solid form	Initial solid/solution ratio (g dm^{-3})	Initial pH	Temperature (°C)
Savage et al. (1992)[1]	Batch	Clays	Pulverized	0.25–1.0	12.5, 13.0	70
Bauer & Berger (1998)	Batch	Na-montmorillonite (Ceca smectite)	Pulverized	4.2, 6.3, 13	12.56–13.92 11.47–12.74	35 80
	Batch	Ca-smectite (Ibeco smectite)	Pulverized	4.2, 6.3, 13	12.56–13.92 11.47–12.74	35 80
Kubo et al. (1998)	Batch	Na-montmorillonite (Kunipia-F)	Pulverized	1.0	10.5, 11.5, 12.5, 13	50, 80, 100
Sato et al. (2004)	Flow	Na-montmorillonite (Kunipia-P)	Pulverized	1.0[2]	8–13	30, 50, 70
Rozalén et al. (2008)	Batch	K-montmorillonite	Pulverized	0.1, 2.0	1.0–13.5	25
Rozalén et al. (2009)	Flow	K-montmorillonite	Pulverized	0.026–0.14[2]	1.3–13.5	25
	Flow	K-montmorillonite	Pulverized	0.025–0.20[2]	1.19–13.32	50
	Flow	K-montmorillonite	Pulverized	0.031–0.15[2]	1.19–13.53	70
Nakayama et al. (2004)	Batch	Sand-bentonite (Kunigel V1) mixtures	Compacted	4000[3]	13, 13.5, 14	50, 90, 130, 170
Sawaguchi et al. (2013)	Batch	Na-montmorillonite (Kunipia-F)	Compacted	1800[3]	12.74, 13.13, 13.54	130

[1]The flow experiments were also performed in this study for which the solid/solution ratio was not identified.
[2]The value was calculated by dividing the initial amount of solid by the total volume of through-flowing fluid.
[3]The volume of solution is that of the pores in compacted specimens.

TABLE 2. Chemical composition of highly alkaline solutions for the alteration experiment.

Element	Concentration (mol dm^{-3})					
	Alteration temperature					
	50°C	70°C		90°C		
OH⁻	1.0	0.30	1.0	0.10	0.30	1.0
Na	1.1	1.1	1.1	1.1	1.1	1.1
Al	2.6×10^{-3}	1.1×10^{-3}	2.4×10^{-3}	1.3×10^{-3}	1.8×10^{-3}	2.6×10^{-3}
Ca	1.0×10^{-4}	1.3×10^{-4}	6.0×10^{-5}	1.0×10^{-4}	1.2×10^{-4}	1.7×10^{-5}
Si	2.7×10^{-2}	3.0×10^{-2}	3.1×10^{-2}	3.1×10^{-2}	2.6×10^{-2}	2.9×10^{-2}
pHe[1]	13.81	13.38	13.80	12.76	13.34	13.81

[1]The 'pHe' is a measured value of pH using a ROSS® combination-glass pH electrode at room temperature (~25°C).

alteration. The dissolution rates in compacted sand-bentonite mixtures were determined experimentally and formulated under hydroxide ion activities, a_{OH^-}, of 0.04–0.57 mol dm^{-3} and temperatures of 50–170°C (Nakayama *et al.*, 2004; Yamaguchi *et al.*, 2007). The dissolution rates in the mixtures, however, were smaller than that in pulverized montmorillonite and depended more heavily on a_{OH^-}. Yamaguchi *et al.* (2007) suggested that different a_{OH^-} in pore water from that in the external solution might be responsible for this dependence, although this was not verified. Sawaguchi *et al.* (2013) studied the dissolution rates of compacted pure montmorillonite at 130°C and showed greater dissolution rates than those in the mixtures. The explanation given for the difference was that the dissolution of montmorillonite in the mixtures was inhibited by decreasing the a_{OH^-} stemming from

the dissolution of accessory minerals such as SiO_2 polymorphs (quartz, chalcedony, *etc.*) in the mixtures.

In the present study, the dependence of the dissolution rate of compacted montmorillonite (Kunipia-F) on OH⁻ activity and temperature were investigated experimentally to clarify the effect of accessory minerals on the dissolution rate under compaction.

EXPERIMENTAL

The dissolution rate for montmorillonite under compaction was obtained through a time-dependent variation in the amount of remaining montmorillonite in the compacted montmorillonite altered by highly alkaline solution. The experimental method was the same as in previous studies (Nakayama *et al.*, 2004; Yamaguchi *et al.*, 2007; Sawaguchi *et al.*, 2013) and
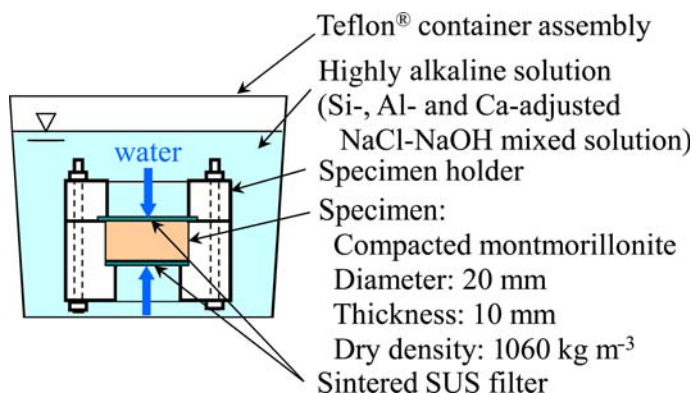

FIG. 1. Schematic drawing of the experimental configuration of the saturation process before the alteration of compacted montmorillonite.
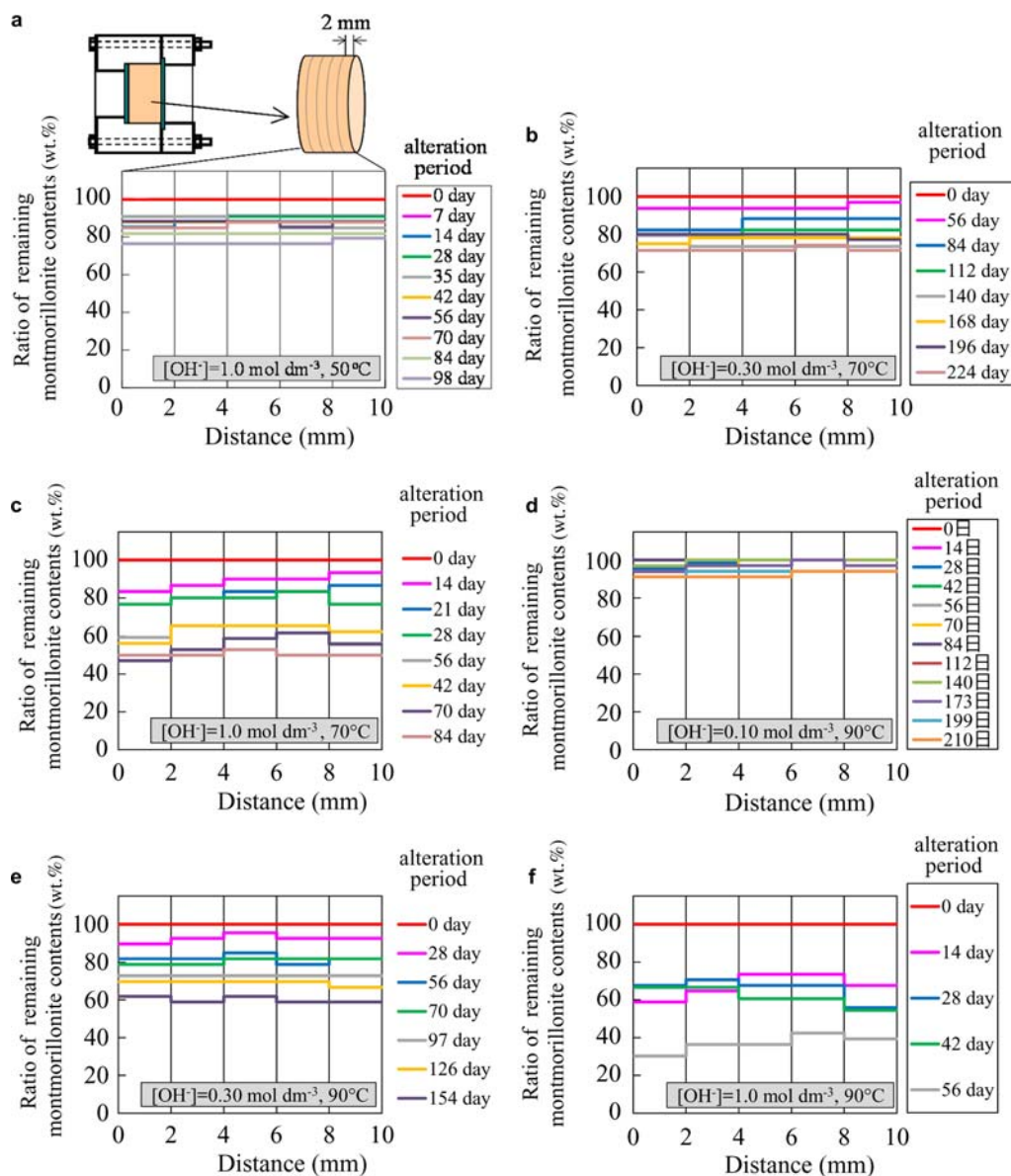
FIG. 2. Spatial distribution of weight ratio of remaining montmorillonite contents in the specimen altered by the alkaline solutions. (a) OH⁻ concentration of 1.0 mol dm⁻³ at 50°C, (b) 0.30 mol dm⁻³ at 70°C, (c) 1.0 mol dm⁻³ at 70°C, (d) 0.10 mol dm⁻³ at 90°C, (e) 0.30 mol dm⁻³ at 90°C, and (f) 1.0 mol dm⁻³ at 90°C.

the experimental conditions were the same as in a previous study by the present authors (Sawaguchi *et al.*, 2013), except for the temperature conditions.

The montmorillonite (Kunipia-F, a commercial product of Kunimine Industries Co. Ltd., Japan) was compacted in specimen holders to obtain a dry density of 1060 kg m⁻³ or porosity of 0.6. The porosity of 0.6

was selected by considering porosity variations of 0.4–0.8 through the experiment for the mixtures (Nakayama *et al.*, 2004). The Si-, Al- and Ca-adjusted NaCl-NaOH mixed solutions used in the previous experiment (Nakayama *et al.*, 2004) were also used in the present study (Table 2). The alkaline solutions were prepared by adding NaCl, NaOH, sodium metasilicate
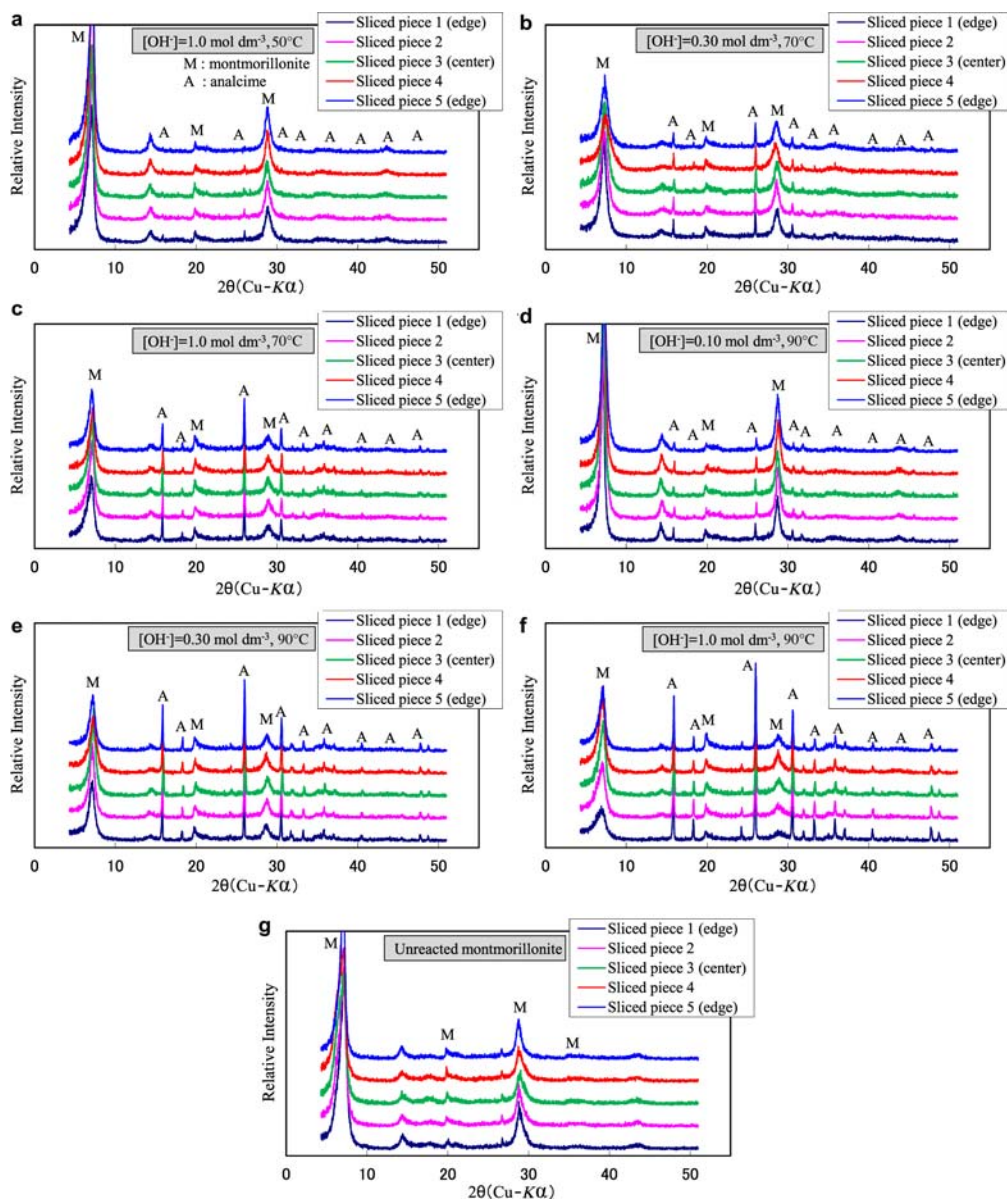
FIG. 3. Mineral compositions of the five slices analysed by XRD: (a) after 98 days, OH⁻ concentration of 1.0 mol dm^{-3} at 50°C; (b) after 224 days, 0.30 mol dm^{-3} at 70°C; (c) after 84 days, 1.0 mol dm^{-3} at 70°C, (d) after 210 days, 0.10 mol dm^{-3} at 90°C; (e) after 154 days, 0.30 mol dm^{-3} at 90°C; (f) after 56 days, 1.0 mol dm^{-3} at 90°C; and (g) unreacted montmorillonite. M: montmorillonite, A: analcime.

nonahydrate (Na$_2$SiO$_3$·9H$_2$O) and small amounts of aluminium standard solution (Al concentration of 1000 mg dm^{-3} and HNO$_3$ of 0.2 mol dm^{-3}) and calcium standard solution (Ca concentration of 1000 mg dm^{-3} and HNO$_3$ of 0.1 mol dm^{-3}) to deionized water to obtain chemical compositions shown in

Table 2. Potassium, although usually present in cementitious water, was not added to the experimental solutions because the dissolution rate of montmorillonite in KOH-NaOH mixed solutions where K-feldspar was formed was identical to that in an NaOH solution (Yamaguchi *et al.*, 2007). The specimen holder
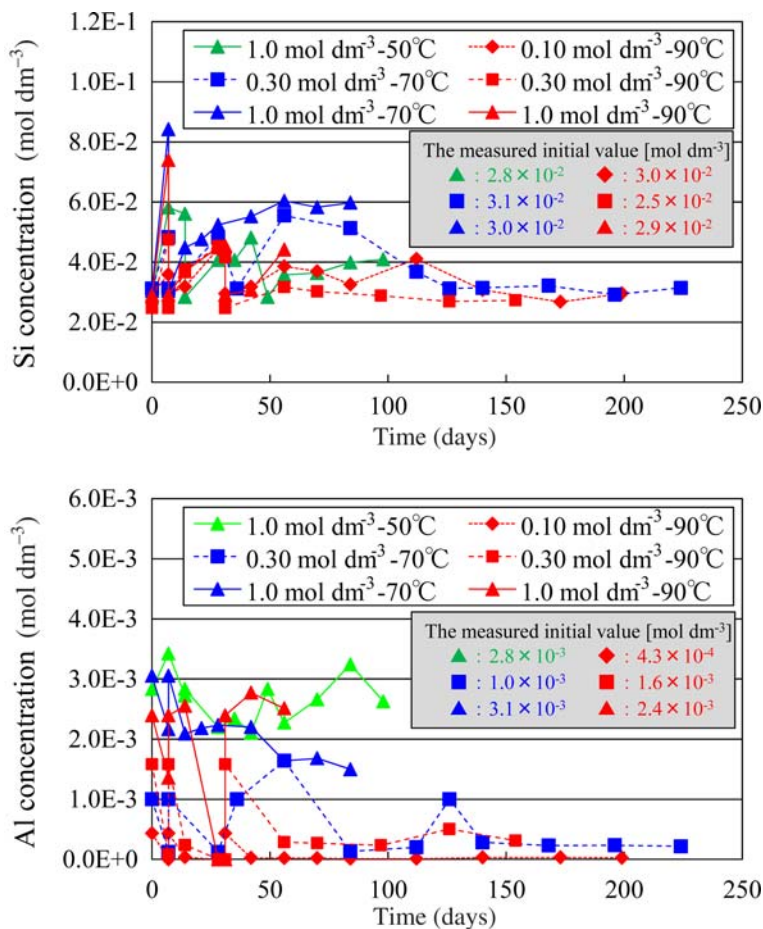
FIG. 4. Time courses of Si- and Al-concentrations in alkaline solutions used in the alteration experiment. The initial measured values of Si and Al concentrations are shown. In order to keep the variations of pH in the assemblies within ±0.2, the alkaline solutions were replaced by fresh solutions after 14- and 49-day periods at 50°C (OH$^-$ concentration of 1.0 mol dm^{-3}), 7-, 36- and 126-day periods at 70°C (0.30 mol dm^{-3}), 7-day period at 70°C (1.0 mol dm^{-3}), and 7- and 31-day periods at 90°C (0.10, 0.30 and 1.0 mol dm^{-3}).

was soaked in the alkaline solution in a Teflon® container assembly at room temperature under vacuum for 1 week to saturate the specimen (Fig. 1). Then, the assembly was contacted with 0.065 dm^3 of the alkaline solution in a sealed stainless steel container and kept at 50, 70 and 90°C in an oven to observe montmorillonite dissolution over a reasonable time period. The alkaline solution was replaced by fresh solution when necessary to minimize changes in the concentration of OH$^-$. The necessity was decided by monitoring the pH of mock-up assemblies each week. When the measured value of pH decreased by >0.1 pH units from the initial value, the alkaline solution in all assemblies of the same condition was exchanged for the initial solution.

Therefore the variations of pH in the assemblies were kept within ±0.2 pH units, during the alteration period. The pH was measured at ∼25°C using a ROSS® combination-glass pH electrode (Orion 8172BNWP, Thermo Scientific, Inc., USA) calibrated with 7.00 and 10.01 pH buffers and 1 mol dm^{-3} NaOH solutions. Each of the assemblies was taken from the oven at the fixed sampling time. The compacted montmorillonite specimen was pushed out from the holder by 2 mm at a time using a screw presser and was sliced with a steel blade. Each sliced piece was weighed, freeze-dried at −110°C, ground using a mortar and pestle, redried at 90°C and then analyzed for the amount of remaining montmorillonite by the conventional methylene-blue
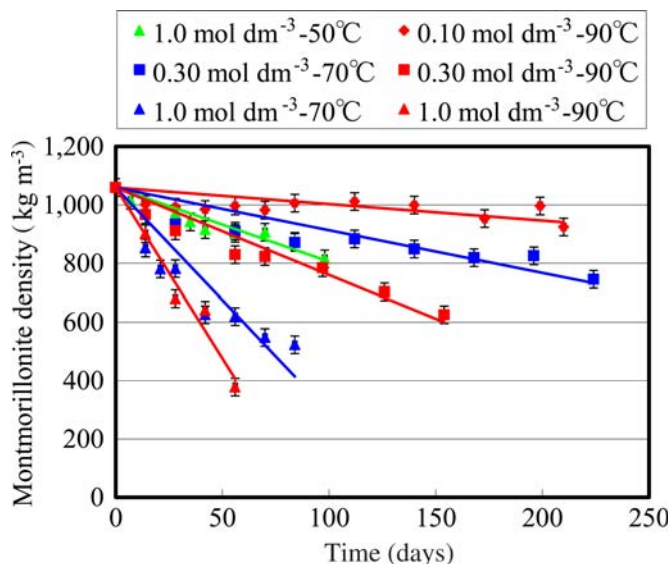
Fig. 5. Time courses of montmorillonite densities in compacted Kunipia-F under highly alkaline conditions. Bars represent the errors from the determination of the montmorillonite density by the methylene blue adsorption titration. The straight lines were obtained by the least-squares method.

adsorption titration method (Hang & Brindley, 1970; Brindley & Thompson, 1970; Japan Bentonite Manufacturers' Association, 1991). In the present study, 2.5×10^{-4} kg of crushed sample and of pure montmorillonite (Kunipia-F) for calibration were used. Furthermore, the remaining reacted solid was analyzed by powder X-ray diffraction (XRD, Geigerflex, Rigaku Corp., Japan). The concentrations of Al and Ca in the contacted aqueous solutions were determined by inductively-coupled plasma atomic emission spectroscopy (ICP-AES, SII SPS 7800, SII Nanotechnology Inc., Japan) after filtering the solutions through a 0.45 μm PTFE (polytetrafluoroethylene) filter and acidifying into 0.5 N HNO₃. The concentration of Si was determined as SiO_2 by means of the molybdosilicate method (Rand *et al.*, 1976; Japanese Standard

TABLE 3. Dissolution rates of compacted montmorillonite under hydroxide ion concentrations of 0.10–1.0 mol dm^{-3} and temperatures of 50 to 130°C. The errors indicate a confidence limit of 68% (1σ).

Temperature	OH⁻ concentration (mol dm^{-3})	Activity of OH⁻ (mol dm^{-3})	Dissolution rate, R_A (kg m^{-3} s^{-1})	Alteration period (day)	Porosity variations[1]
50°C (323.15 K)	1.0	0.62	$(2.9 \pm 0.6) \times 10^{-5}$	98	0.54–0.60
70°C (343.15 K)	0.30	0.22	$(1.7 \pm 0.4) \times 10^{-5}$	224	0.52–0.60
	1.0	0.58	$(8.9 \pm 2.1) \times 10^{-5}$	84	0.57–0.65
90°C (363.15 K)	0.10	0.056	$(6.6 \pm 3.5) \times 10^{-6}$	210	0.56–0.62
	0.30	0.20	$(3.5 \pm 0.6) \times 10^{-5}$	154	0.56–0.61
	1.0	0.56	$(1.4 \pm 0.2) \times 10^{-4}$	56	0.55–0.60
130°C[2] (403.15 K)	0.10	0.057	$(6.9 \pm 1.1) \times 10^{-5}$	162	0.45–0.60
	0.30	0.17	$(3.8 \pm 0.5) \times 10^{-4}$	28	0.48–0.60
	1.0	0.58	$(8.8 \pm 1.4) \times 10^{-4}$	14	0.48–0.60

[1]Initial porosity was 0.60.
[2]Previous dissolution rate data at 130°C (Sawaguchi *et al.*, 2013).

Association, 2004; The Japan Society for Analytical Chemistry Hokkaido, 1994) and by UV spectrometry (U-3210, HITACHI, Ltd., Japan) after the filtration.

RESULTS AND DISCUSSION

The weight of montmorillonite in each sliced piece (W_{mont}, kg) was determined using equation 1:

$$W_{mont} = W_{dry} \cdot V_{titrb}(\text{alter})/V_{titrb}(\text{pure}) \quad (1)$$

where W_{dry} is the dry weight of each slice (kg), $V_{titrb}(\text{alter})$ is the total volume of methylene-blue solution added to titrate the altered sample (dm³), $V_{titrb}(\text{pure})$ is the total volume of methylene-blue solution added to titrate the pure montmorillonite (dm³). It is known empirically that slight differences in experimental procedure have a large influence on a result in the methylene-blue adsorption titration method (Miyoshi *et al.*, 2015). In the present study, efforts were made to minimize errors: (1) by having a single analyst perform a series of experiments; (2) by following a standard testing method; and (3) by using a micropipette to drop the fixed amount of suspension on the filter paper. The error in the results of the titration was estimated to be $\pm 7.4 \times 10^{-6}$ kg at 1σ, which brings an error of $\pm 9.9 \times 10^{-5}$ kg at 1σ into W_{mont}.

The montmorillonite content of each of the slices decreased with alteration time (Fig. 2). The XRD patterns of each slice also showed that the decrease in montmorillonite and the formation of secondary analcime ($NaAlSi_2O_6$), proceeded over time (Fig. 3). The alteration of primary minerals proceeded both at the centre and the edges of the specimens facing the alkaline solution so that uniform dissolution of montmorillonite in the compacted specimens was considered hereafter. The diffusive mass transfer of OH^- would be much greater than the rate of consumption in the compacted montmorillonite. The above-mentioned dissolution and formation of minerals is qualitatively consistent with the concentrations of Si and Al in the contacting solutions (Fig. 4). The concentrations of Si tend to be much greater than the initial values in all alkaline solutions, due to the dissolution of montmorillonite. The formation of analcime in the solutions rich in Si and Na concentrations probably consumed Al, which decreased the Al concentration. Although determination of the concentration of Ca was difficult due to interference with the high-concentration of Na, an increase in the concentrations of Ca was observed, probably due to

the dissolution of montmorillonite, which contains ~0.36 wt.% of exchangeable Ca (Ito *et al.*, 1993).

The amount of montmorillonite in the compacted montmorillonite decreased linearly with time over several months under the conditions of OH^- concentration and temperature used (Fig. 5). The greater concentration of OH^- in the external solution and/or temperature resulted in the faster, linear decrease in montmorillonite content in accordance with previous studies (Nakayama *et al.*, 2004; Yamaguchi *et al.*, 2007; Sawaguchi *et al.*, 2013). The montmorillonite density can be expressed as:

$$\rho(t) = \rho(0) - R_A t \quad (2)$$

where $\rho(t)$ is the amount of montmorillonite in the altered compacted specimen (kg m⁻³), $\rho(0)$ is the initial density (kg m⁻³), R_A is the dissolution rate of compacted montmorillonite (kg m⁻³ s⁻¹) and t is the time after the contact with the alkaline solution (s). The calculated dissolution rates by equation 2 are listed in Table 3 together with previous R_A data at 130°C (Sawaguchi *et al.*, 2013).

The concentrations of OH^- ($[OH^-]$, (mol dm⁻³)) in alkaline solutions were kept within ±0.2 logarithmic units by changing the water with the new one during the reaction. The measured values of pH, pHe, through experimental time were averaged and converted into
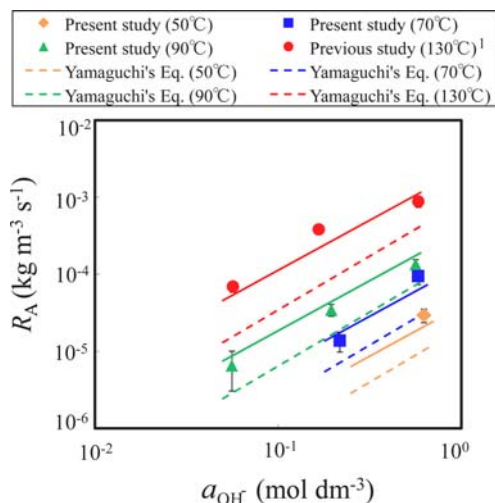

FIG. 6. Dependence of the dissolution rate of compacted montmorillonite, R_A (kg m⁻³ s⁻¹), on the activity of hydroxide ions, a_{OH^-} (mol dm⁻³), and on temperature, T (K). The solid curves are the calculated values using equation 3. [1]Dissolution rate in compacted montmorillionite at 130°C (Sawaguchi *et al.*, 2013).
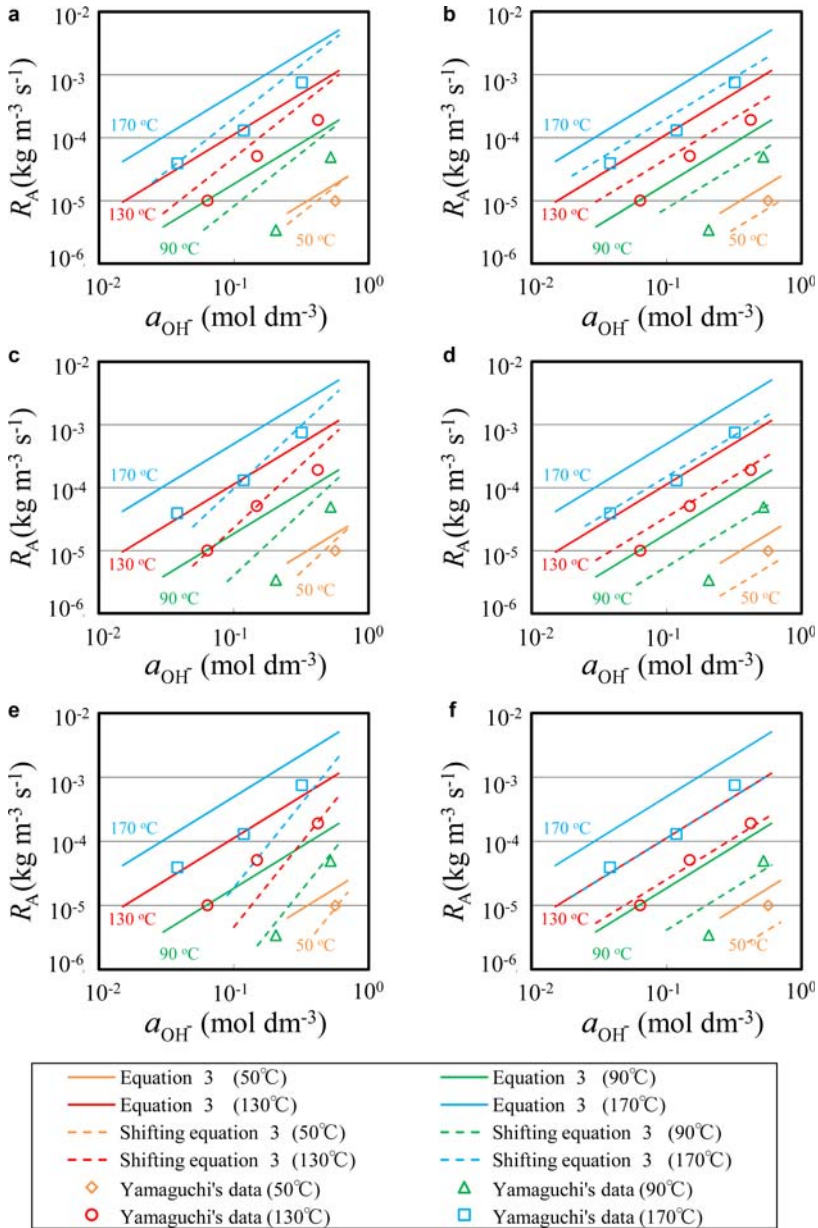
FIG. 7. Comparison between the dissolution rate of montmorillonite in the mixtures and the curves given by shifting equation 3: (a) by 0.05 mol dm⁻³; (b) by 0.1 mol dm⁻³; (c) by 0.2 mol dm⁻³; (d) by shifting by 0.3 logarithmic units; (e) by 0.4 logarithmic units; and (f) by 0.5 logarithmic units.

[OH⁻] by the correlation equation between pHe and theoretically evaluated [OH⁻] of the initial solutions shown in Table 2: $[OH^-] = 10^{0.982 \times pHe - 13.6}$. Furthermore, representative values of activities of hydroxide ion, a_{OH^-}, for each experimental condition

were determined by multiplying [OH⁻] by the activity coefficients evaluated using the SIT (specific ion interaction) model (Lemire *et al.*, 2001).

The dissolution rates of compacted montmorillonite, including previously obtained data at 130°C, were

formulated as a function of a_{OH^-} (mol dm^{-3}) and temperature, T (K), by multiple regression analysis:

$$R_A = 10^{(4.5 \pm 2.5)} \cdot (a_{OH^-})^{1.3 \pm 0.4} \cdot e^{(-55000 \pm 16000)/RT}$$

(3)

where R is the gas constant (8.314 J mol^{-1} K^{-1}). The errors indicate the confidence limit of 68% (1σ). Equation 3 was compared with the formula of the dissolution rate of montmorillonite in the mixtures (Yamaguchi *et al.*, 2007): $R_A = 3500 \cdot (a_{OH^-})^{1.4} \cdot e^{-51000/RT}$ (Fig. 6). The dissolution rate is greater in the compacted montmorillonite than in the mixtures. In a previous study performed at 130°C (Sawaguchi *et al.*, 2013), the possibility that the dissolution of montmorillonite in the mixtures was inhibited by the increase of Si concentration in pore water and/or by the effect of the difference between bentonite specimens used in each experiment was ruled out. Therefore the difference in dissolution rates would be caused by the negative shift of, or decrease in, a_{OH^-} in the mixtures accompanied by dissolution of accessory minerals such as SiO$_2$ polymorphs.

Assuming that the shift would be linear by 0.05, 0.1 or 0.2 mol dm^{-3} or logarithmic by 0.3, 0.4 or 0.5 units, the dissolution rates of montmorillonite in the mixtures were estimated (Fig. 7). The curves given by shifting equation 3 by 0.05 mol dm^{-3} and by 0.4 logarithmic units reproduce the dissolution rate data in the mixtures well. Furthermore, trial calculations by considering the shift of a_{OH^-} were performed to reproduce the montmorillonite dissolution experiment of Yamaguchi *et al.* (2013), who compacted sand-bentonite mixture specimens immersed in 1 mol dm^{-3} NaOH solution at 90°C for 14, 27, 51 and 67 days. Figure 8 shows the montmorillonite densities after each alteration period and the calculated values obtained using the dissolution rates from equation 3 and those after shifting. The calculated values obtained by shifting equation 3 by 0.3 logarithmic units reproduced the experimental data better than by 0.05 mol dm^{-3}. These results indicate that the dissolution rate in the mixtures can be explained by equation 3 considering a shift of the a_{OH^-} in the mixtures, and that the shift may be logarithmic. The shift in logarithmic scale is more consistent than the shift in linear scale with the dependence on compacted montmorillonite, 1.3 ± 0.4, being closer to that for the mixtures, 1.4 ± 0.3. The shift in linear scale is not favoured because it gives an extremely low dissolution rate when applied to lower pH ranges.

The activation energy obtained (55 ± 16 kJ/mol) is consistent with that reported for the mixtures (51 kJ/mol, Yamaguchi *et al.*, 2007) and with that

determined for smectite dissolution in KOH solution (52 ± 4 kJ/mol, Bauer & Berger, 1998).

Yamaguchi *et al.* (2007) compared the formula of dissolution rate of montmorillonite in the mixtures with that of pure pulverized montmorillonite determined by flow-through experiments (Sato *et al.*, 2004) and pointed out that the difference in the dependence on a_{OH^-} made a large difference in the dissolution rate when the dependence was extrapolated to repository conditions. The formula obtained in the present study also gives a much lower dissolution rate than Sato *et al.* (2004) for a_{OH^-}, < 0.01 mol dm^{-3}. However it gives greater dissolution rate than Yamaguchi *et al.* (2007) by ~0.3 orders of magnitude.

In the present study, the dissolution rate of montmorillonite free of accessory minerals, under compacted conditions was formulated. In order to
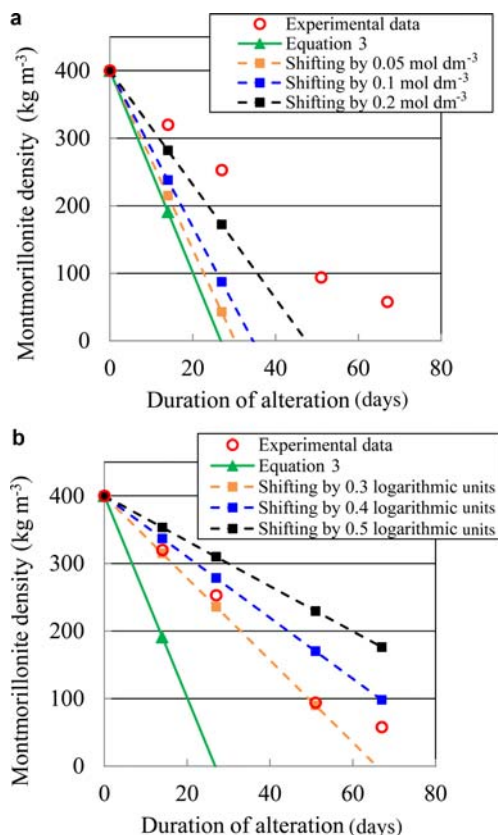
FIG. 8. The results of dissolution experiments for the compacted sand-bentonite mixtures (Yamaguchi *et al.*, 2013) and the calculation values evaluated using equation 3 taking into account shifting of a_{OH^-}: (a) 0.05, 0.1 or 0.2 mol dm^{-3}; and (b) 0.3, 0.4 or 0.5 logarithmic units.

provide reliable values for the long-term prediction of bentonite buffer performance under disposal conditions by using the dissolution rate equation, further study is necessary to quantify the decrease in a_{OH^-} accompanied by dissolution of accessory minerals such as SiO_2 polymorphs.

CONCLUSIONS

The dissolution rate of the compacted montmorillonite (Kunipia-F) was formulated as a function of a_{OH^-} and temperature. The existence of accessory minerals decreased the dissolution rate of montmorillonite. The dissolution rate model developed can be used not only for pure montmorillonite but also for bentonite mixtures by taking into account the negative shift of a_{OH^-} in the mixtures accompanied by dissolution of accessory SiO_2 polymorphs.

REFERENCES

Bauer A. & Berger G. (1998) Kaolinite and smectite dissolution in high molar KOH solutions at 35°C and 80°C. *Applied Geochemistry*, **13**, 905–916.

Brindley G.W. & Thompson T.D. (1970) Methylene blue absorption by montmorillonites. Determinations of surface areas and exchange capacities with different initial cation saturations (clay–organic studies XIX). *Israel Journal of Chemistry*, **8**, 409–415.

Hang P.T. & Brindley G.W. (1970) Methylene blue absorption by clay minerals. Determination of surface areas and cation exchange capacities (clay–organic studies XVIII). *Clays and Clay Minerals*, **18**, 203–212.

Ito M., Okamoto M., Shibata M., Sasaki Y., Danhara T., Suzuki K. & Watanabe, T. (1993) Mineral Composition Analysis of Bentonite. PNC TN 8430 93–003, Power Reactor and Nuclear Fuel Development, Corporation, Tokyo (in Japanese).

Japan Bentonite Manufacturers Association (1991) JBAS-107-91 Measuring Method of Methylene Blue Adsorption Value of Bentonite. pp. 1–5 (in Japanese).

Japanese Standard Association (2004) 44 Silica (SiO_2), JIS K 0101 Testing method for industrial water. pp. 468–473 in: *JIS Handbook 53, Environmental Technology II (Water Contamination), 2004*, Japanese Standard Association, Tokyo (in Japanese).

Kubo H., Kuroki Y. & Mihara M. (1998) Experimental investigation on alteration of bentonite by concrete pore fluids. *Tsuchi-to-Kiso, The Japanese Geotechnical Society*, **46**, 31–34 (in Japanese).

Lemire R.J., Fuger J., Nitsche H., Potter P., Rand M.H., Rydberg J., Spahiu K., Sullivan J.C., Ullman W., Vitorge P. & Wanner, H. (2001) *Chemical Thermodynamics of Neptunium and Plutonium*, pp. 800–810, Elsevier, Amsterdam.

Miyoshi Y., Horiuchi Y. & Takagi T. (2015) Present state of methylene-blue adsorption-test for bentonite in Japan. *Journal of the Clay Science Society of Japan*, **53**, 26–36 (in Japanese).

Nakayama S., Sakamoto Y., Yamaguchi T., Akai M., Tanaka T., Sato T. & Iida Y. (2004) Dissolution of montmorillonite in compacted bentonite by highly alkaline aqueous solutions and diffusivity of hydroxide ions. *Applied Clay Science*, **27**, 53–65.

Rand M.C., Greenberg A.E., Taras M.J. & Franson M.A. (1976) *Standard Methods for the Examination of Water and Wastewater*. American Public Health Association, Washington, DC, pp. 484–492.

Rozalén M.L., Huertas F.J., Brady P.V., Cama J., Garcia-Palma S. & Linares J. (2008) Experimental study of the effect of pH on the kinetics of montmorillonite dissolution at 25°C. *Geochimica et Cosmochimica Acta*, **72**, 4224–4253.

Rozalén M., Huertas F.J. & Brady P.V. (2009) Experimental study of the effect of pH and temperature on the kinetics of montmorillonite dissolution. *Geochimica et Cosmochimica Acta*, **73**, 3752–3766.

Sato T., Kuroda M., Yokoyama S., Tsutsui M., Fukushi K., Tanaka T. & Nakayama S. (2004) Dissolution mechanism and kinetics of smectite under alkaline conditions. In: *Proceedings of the International Workshop on Bentonite-Cement Interaction in Repository Environment*, 14–16 April 2004, Tokyo, NUMO-TR-04-05, pp. A3-38–A3-41.

Savage D. & Liu J. (2015) Water/clay ratio, clay porosity models and impacts upon clay transformations. *Applied Clay Science*, **116–117**, 16–22.

Savage D., Bateman K., Hill P., Hughes C., Milodowski A., Pearce J., Rae E. & Rochelle C. (1992) Rate and mechanism of the reaction of silicates with cement pore fluids. *Applied Clay Science*, **7**, 33–45.

Sawaguchi T., Kadowaki M., Yamaguchi T., Mukai M. & Tanaka T. (2013) Alkaline dissolution behaviour of montmorillonite under compacted conditions. *Journal*

of Nuclear Fuel Cycle and Environment, **20**, 71–78 (in Japanese).

The Japan Society for Analytical Chemistry Hokkaido (1994) *Analysis of Water*, 4th edition. Kagaku-Dojin Publishing Company, Inc., Kyoto, Japan, pp. 181–184 (in Japanese).

Yamaguchi T., Sakamoto Y., Akai M., Takazawa M., Iida Y., Tanaka T. & Nakayama S. (2007) Experimental and modeling study on long-term alteration of compacted bentonite with alkaline groundwater. *Physics and Chemistry of the Earth*, **32**, 298–310.

Yamaguchi T., Sawaguchi T., Tsukada M., Kadowaki M. & Tanaka T. (2013) Changes in hydraulic conductivity of sand-bentonite mixtures accompanied by alkaline alteration. *Clay Minerals*, **48**, 403–410.