

Influence of alkaline (pH 8.3–12.0) and saline solutions on chemical, mineralogical and physical properties of two different bentonites

T. HEIKOLA^{1,*}, S. KUMPULAINEN², U. VUORINEN¹, L. KIVIRANTA² AND P. KORKEAKOSKI³

¹ VTT Technical Research Centre of Finland, Otakaari 3K Espoo, 02044 VTT, Finland, ² B+Tech Oy, Laulukuja 4, 00420 Helsinki, Finland, and ³ Posiva Oy, Olkiluoto, 27160 Eurajoki, Finland

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ABSTRACT: The interaction of two different bulk bentonites (Na- and Ca-types) with three types of simulated cement waters (pH 9.7, 11.3 and 12.0) and one saline groundwater simulate (pH 8.3) as a reference, was studied in batch reactors at 25°C. The solution pH was monitored in order to keep the pH as steady as possible by replacing the leaching solution with fresh one when needed. After 554 days, one set of parallel samples was removed from the experiment in order to investigate the possible changes in the bentonite materials.

The buffering capacity of bentonite was clearly observed, especially at the beginning of the high-pH experiments, as the pH of the leaching solutions decreased quite dramatically due to interaction with bentonite. The solution chemistry results showed a decrease of Ca content in all leachate samples, but especially in pH 12.0 experiments. Small amounts of silica were released throughout the experiment. Both bentonites in pH 12.0 experiments also released detectable amounts of Al, while in the lower pH experiments the levels were below detection limit. These observations were also supported by chemical analyses of the bentonite materials. Only minor changes were detected in the mineralogy, and they were mainly concentrated on experiments at pH 11.3 and pH 12.0. The measured swelling pressure showed an increase in pH 12.0 experiments. The results obtained in this research may facilitate modelling of bentonite interaction with high-pH solutions.

KEYWORDS: bentonite buffer, alteration, batch, bentonite, alkaline, saline spent nuclear fuel, underground repository.

In Finland, disposal of spent nuclear fuel is planned in a deep bedrock repository based on a multi-barrier concept. Bentonites and smectite-rich clays, e.g. Friedland clay, are intended to be used as

buffer and backfill materials. Construction of the repository will also need various supporting cementitious structures. In saturated groundwater environments, degradation of cementitious materials produces chemically aggressive and highly alkaline solutions which may affect the established safety functions of the bentonite by inducing mineralogical and chemical changes over considerable periods of time.

* E-mail: tiina.heikola@vtt.fi

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In order to reduce the effects of a high-pH plume, investigations for development of low-pH cement formulations started in 2002, among others in a joint project between Posiva, SKB and NUMO (Bodén & Sievänen, 2005). The aim of the project was to achieve at least one well-quantified, tested and approved low-pH injection grout to be used in a repository. The target was to obtain material with a pore solution pH ≤ 11 . The pH of the pore solution depends on the phases that are present. In OPC (Ordinary Portland Cement) materials the pore solution pH stays high (>12.5) as long as alkali hydroxides and portlandite are present. The pH value of the pore solution starts to decrease when dissolution of C-S-H phases are involved. In the low-pH materials pozzolans such as silica fume, which is very reactive, are used to bind most of the portlandite to form C-S-H phases and thereby lower the pH of cement leachates that are less harmful to bentonite clay (Kronlöf, 2005).

Bentonites are predominantly composed of the clay mineral smectite which is the key mineral in respect to the set safety functions of bentonite, e.g. high expandability. It is known that the most important parameter affecting the dissolution of smectites is pH, and that smectite dissolution becomes significant at pH > 13 . On the other hand, Kaufhold & Dohrmann (2011) have shown that bentonites are surprisingly resistant against solutions at pH around 12 and up to 90°C. When considering long periods of time in the scale of a repository performance and the modelling needs of assessing the dissolution and precipitation processes in systems of bentonite and alkaline solutions, it is also important to know the processes even at pH < 12.5 . The interaction between bentonite clay and cement pore fluids is a complicated process and a number of uncertainties and limitations need to be considered. Savage & Benbow (2007) have provided a comprehensive review of the factors that contribute to the degradation of bentonite due to interaction with cement. According to them, there are a number of potential constraints, including mass balance, thermodynamics, mass transport and kinetics. Lack of knowledge of the type of secondary minerals formed complicates mass balance issues, as the minerals may consume or generate hydroxide ions. From the thermodynamic point of view the variation of silicon speciation and quartz solubility with pH significantly affects the hydrolysis reactions of montmorillonite and, thus its stability. In compacted,

bentonite, diffusion controls the mass transport and hence the amount of bentonite that can dissolve. Furthermore, possible mineral alteration that takes place may cause a change in the porosity and as a result change the hydraulic conductivity and thereby affect solute diffusivities. Mineral dissolution rates are known to increase with pH and/or temperature, but considerable uncertainties exist concerning the montmorillonite dissolution kinetics at a high pH range. The rate of dissolution may be inhibited by the dissolved Si or otherwise affected by the presence of the secondary minerals.

The objective of this study was to investigate the buffering capacity of bentonite against high-pH solutions and the possible alteration of bentonite in alkaline cement leachates. Batch experiments with two different bulk bentonites at 25°C were started in order to gain information on these questions. The pH values chosen bound the pH domain of interest when low-pH cementitious materials are considered.

METHODS

Solution pH-values were determined with a commercial glass electrode (ROSS® Sure-flow®) and standard calibration solutions (pH 7, 10 and 13). The solution chemistry was determined using inductively coupled plasma atomic emission spectroscopy (ICP-AES: Ca, Mg, Na, Si), flame atomic absorption spectroscopy (FAAS: K), ion chromatography (IC: SO₄, Br), titration (Cl) and high-resolution inductively coupled plasma mass spectrometry (HR-ICP-MS: Al, Fe). Mineralogical compositions of the bentonites were studied with Philips X'Pert MPD diffractometer (XRD), using Rietveld refinement, Fourier transform infrared spectroscopy (FTIR) and quantitative Greene-Kelly testing. Oriented XRD mounts were prepared from separated clay fractions ($<2 \mu\text{m}$) using filter-membrane peel-off technique. The mineralogical sample preparation and measurement methods are described in more detail in Kiviranta & Kumpulainen (2011). The chemical composition of the bentonites was determined by analysing LOI (loss on ignition), concentrations of elements using ICP-AES and carbon content with combustion (Leco). The cation exchange capacity of bentonite was measured spectroscopically at 620 nm from the supernatant after Cu(II)-triethylenetetramine absorption (Meier & Kahr, 1999; Ammann *et al.*, 2005). The amount of exchangeable cations was determined with ICP-AES and FAAS after NH₄Cl

extraction (Belyayeva, 1967; Jackson, 1975). The swelling pressure of bulk bentonite was measured by compacting air-dry material to a fixed-volume swelling pressure cell (24–25 mm in diameter) with a sample density of approximately 1.6 g/cm³. In order to compare clay materials of different densities the effective montmorillonite dry density (EMDD) was calculated after Dixon *et al.* (2002). The measurement method is described in detail in Kiviranta & Kumpulainen (2011).

MATERIALS

Bentonite

Two bentonites, Wyoming-type Na-bentonite and Ca-bentonite from Milos, Greece, being considered for use in the underground nuclear waste facility in Olkiluoto (Finland), were studied. Both materials were provided by Posiva Oy. The initial bentonite materials were characterized in Finland by B+Tech (Kiviranta & Kumpulainen, 2011) and are referred to later in the text as the initial materials/samples.

The mineralogical composition of the samples as well as the water ratios, cation exchange capacities and swelling indexes of the bulk materials are given in Table 1.

Solutions

Three types of simulated cement waters of different pH values (9.7, 11.3 and 12.0) and one saline groundwater simulate (pH 8.3) were used as leaching solutions as a reference. The pH values were chosen to demarcate the pH values of designed low-pH grout pore solution values, both at earlier and later stage in the course of cement degradation. The compositions were based on earlier cement leaching tests by Vuorinen *et al.* (2005) and Heikola (2009). The EQ3 code for aqueous geochemistry (Wolery, 1983) was used to calculate the equilibrium composition of the solutions in the absence of CO₂. In order to avoid CO₂ interference in the experiments with high-pH solutions the experiments were conducted inside an anaerobic glove-box (O₂ <1 ppm and low CO₂). The composition of the leaching solutions and each pH are given in Table 2. In order to simplify modelling of cement-bentonite interaction, some of the minor components were omitted from the leaching solution recipes, as well as components which could indicate dissolution of bentonite (Al, Mg). Nevertheless, silicon was included in the recipes even if it is expected to indicate dissolution of bentonite, because pore-water leached from low-

TABLE 1. Mineralogical composition (in wt.%), water ratios, CEC and swelling indexes of bulk materials (Kiviranta & Kumpulainen, 2011).

	Wyoming bentonite	Milos bentonite
Smectite	88.2	79.4
Quartz	3.5	1.0
Illite	0.1	3.2
Cristobalite	0.1	
Plagioclase	2.9	1.8
Calcite	0.2	4.3
Dolomite		5.7
K-feldspar	2.4	0.6
Biotite	0.3	tr
Chlorite	0.4	0.9
Hematite	0.1	0.7
Pyrite	0.8	1.5
Opal-A	0.3	0.4
Rutile	0.5	0.4
Gypsum	0.4	
Water ratio (%)	12.3	17.0
CEC (eq/kg)	0.863	0.909
Swelling index (ml/2 g)	22.0	10.9

tr = present as traces

TABLE 2. Composition of the solutions (meq/l).

Experiment =>	ol-gw8.3	cem9.7	cem11.0	cem12.0
pH	8.3	9.7	11.3	12.0
Na ⁺	208	205	210	235
K ⁺ L	0.6	0.8	0.9	0.9
Ca ²⁺	200	200	206	218
SiO ₂ (aq) (mmol/L)	–	0.04	0.02	0.004
Cl ⁻	408	408	421	432
Br ⁻	1.2	1.2	1.2	1.2
Ionic strength	0.50	0.50	0.52	0.53

pH cement materials contains silicon (Heikola, 2009).

All leaching solutions were prepared by first adding the main chemicals NaCl and CaCl₂ to MilliQ water (water purified with Millipore Milli-Q lab water system, ISO 3696) and flushed with N₂ or Ar (grade 6.0) in a vessel fitted with two quick-couplings allowing flushing with gas. (Note: there was a change of the inert gas used, from N₂ to Ar). Thereafter the solutions were brought into the glove-box and the other minor components were added to the solutions from stock solutions prepared and kept in the glove-box. Also the stock solutions had been flushed with Ar or N₂ prior to placing them in the glove-box.

EXPERIMENTAL SET-UP

Preparation of the bentonites for the experiments began by drying batches of each bulk material in a temperature cabinet at 105°C overnight. After that the bentonites were allowed to cool in a desiccator and then each sample was transferred into a glass bottle and closed with a cap fitted with quick couplings to enable flushing with nitrogen gas (grade N₂ 6.0). Both bentonites were flushed for two days in order to remove oxygen and carbon dioxide, and then transferred into the glove-box. In order to remove any moisture and remaining oxygen each bottle was emptied over a wide metal vessel and heated overnight on a hot plate. The oxygen release was monitored with an oxygen probe (Orbisphere) to ensure that no more oxygen was released.

In each experiment the solid to solution ratio used was 1/10. The individual samples were prepared by weighing 20 g of dried bentonite into a centrifuge bottle and adding 200 g of the

appropriate solution. The samples were placed on a platform shaker in order to maintain good contact of bentonite materials with the solutions. The evolution of pH in the samples was followed by measuring the pH value in the solution phase approximately twice a week. The leaching solutions were renewed once a month. For each renewal, centrifugation was used to separate the phases, then the solution was withdrawn and its chemical composition analysed. All the solutions were ultra-filtered (Macrosep[®] Advance Centrifugal Devices, 10K) before analysis in order to remove possible colloids. The amount of solutions exchanged in the experiments was approximately 145 ml/g of bentonite at the end of the experiment. This is much more than expected in repository conditions; e.g. Suzuki *et al.* (2008) have estimated that the L/S in real repository environment is 0.2 ml/ g. However, the target of our experiments was not to simulate actual repository conditions, but to gain knowledge of bentonite alteration and buffering capacity in alkaline conditions.

RESULTS

pH evolution

The results of the pH measurements are depicted in Fig. 1. In the Olkiluoto groundwater type solution (pH 8.3 experiment) the pH-values showed rather constant values around the initial value. In the pH 9.7 experiment the pH drop from the initial solution value was distinct, about one pH unit and remained rather constant throughout the experiment. A rather distinct wave-like pattern was detected in the higher pH experiments (pH 11.3 and pH 12.0), as a quick drop of pH values followed by gradual levelling off was observed after each

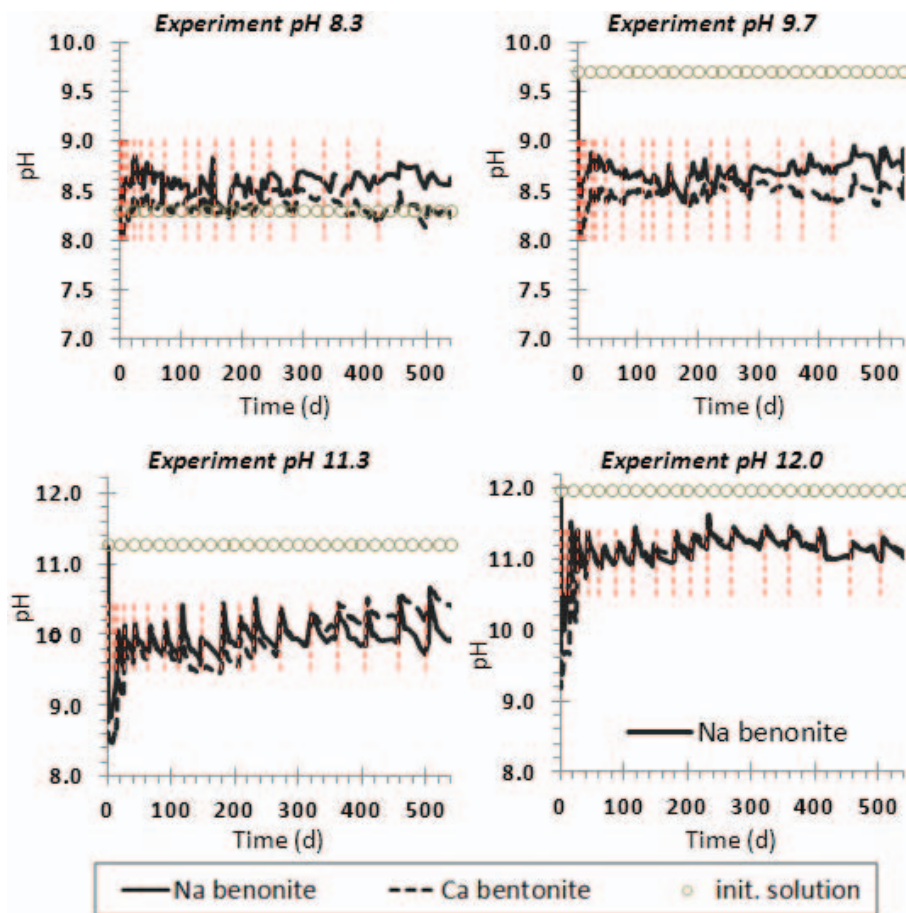


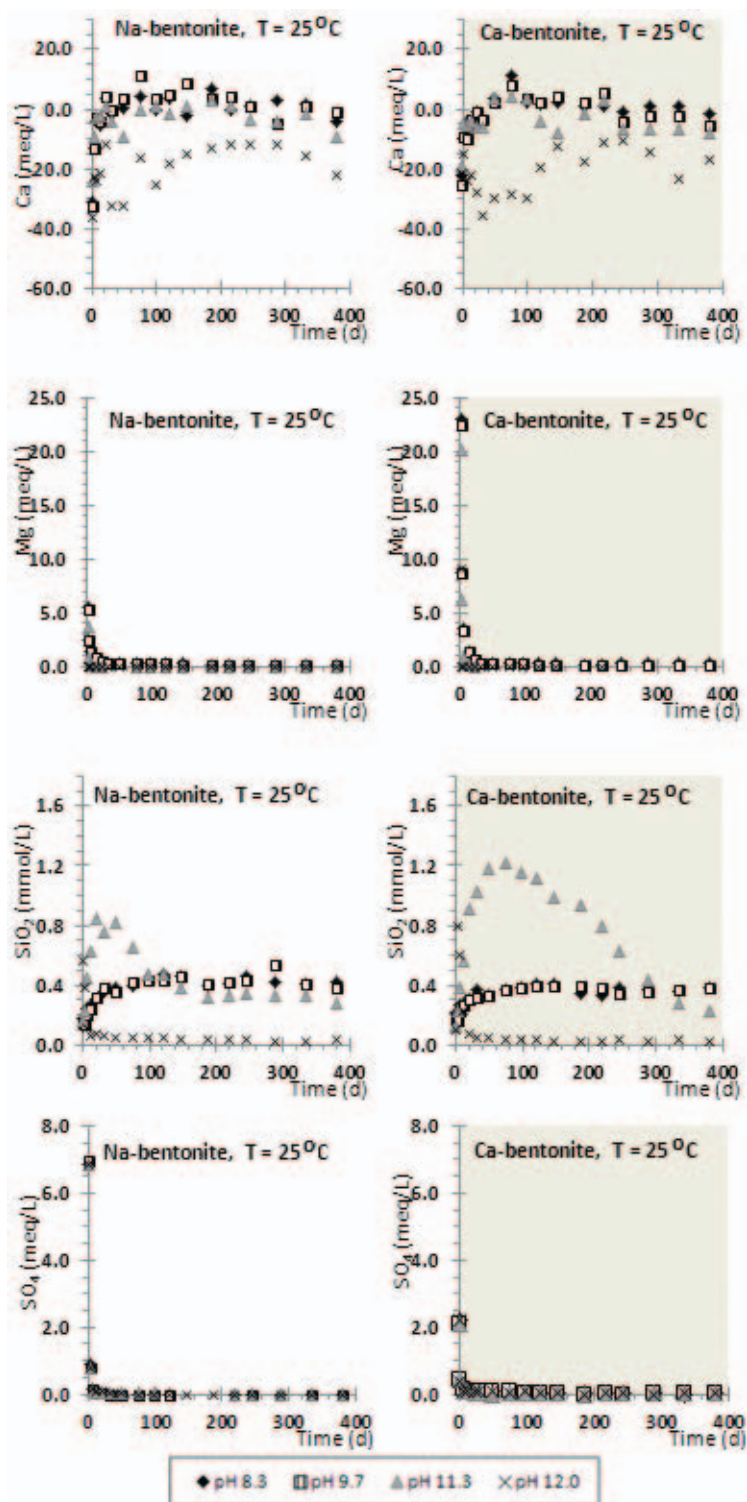
FIG. 1. Measured pH values in the leaching solutions (vertical dashed lines indicate the time of the solution exchange).

renewal of the leachates, especially at the beginning of the experiments. This decrease in the pH values diminished gradually during the experiment but a slight overall increase in the pH values was observed in the pH 11.3 experiments, whereas towards the end of the pH 12.0 experiment the pH values showed an overall levelling off.

As a general comment, of all the pH values measured it can be stated that pH values in the Ca-bentonite experiments were somewhat lower compared to those of Na-bentonite, although the difference decreased with time (especially in experiment at pH 12.0). This behaviour may be due to the higher carbonate mineral content of Ca-bentonite, which plays a major role in the pH buffering capacity of bentonite.

Leachate chemistry

Some results of the chemical analyses of the leaching solutions are presented in Fig. 2. As expected, ion-exchange processes in bentonites caused depletion of Ca and increase of Na at the beginning of the test in all the experiments, but more distinctly in Na-bentonite experiments. In general, depletion of Ca in the leachates diminished quite quickly except in the pH 12.0 experiments which showed slight continuous Ca depletion. In addition to Na release, K and Mg were also quickly released in the first couple of days in all experiments; one exception was the pH 12.0 experiment of Ca-bentonite, which showed constant release of small amounts of K throughout the experiment. In the case of Mg, approximately four



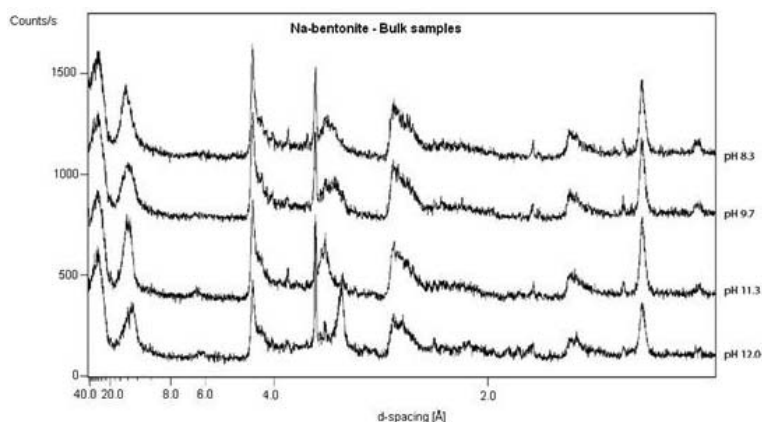


FIG. 3. XRD patterns of bulk Na-bentonite samples.

times more was present in the leachates of Ca-bentonite experiments compared to those of Na-bentonite, which can be explained by the higher initial content of Mg in Ca-bentonite. Another observation of the Mg contents was that more was present in the leachates of the pH 8.3 and 9.7 experiments compared to those of the higher pH experiments. In the pH 8.3 and pH 9.7 experiments, small amounts of Si were released relatively steadily from both bentonites, whereas in the pH 12.0 experiments an abrupt release occurred only in the first couple of days, while the pH 11.3 experiments showed a different pattern, an increase of Si content to a maximum around 40–50 days from the start was observed and thereafter a continuous decrease up to 150 and 380 days (Na- and Ca-bentonite, respectively) until levelling off to a rather steady release towards the end. This trend was more notable in Ca-bentonite as more Si was released. An increase in SO_4 concentration in the leachates was observed only within the first couple of days and almost three times more SO_4 was released in Na-bentonite experiments compared to those of the Ca-bentonite experiments. Both initial bentonites contained only small amounts of soluble sulfate according to Kiviranta & Kumpulainen (2011), but the gypsum content of Na-bentonite was higher even if small. Detectable amounts of Al were released from both bentonites in the pH 12.0

experiment, while in the other experiments the levels were below detection limit.

Bentonite samples

So far only one set of three sets of parallel samples in the experiment was analysed after 554 days from starting the experiments. The results of the analyses are given here.

XRD: Bulk samples. Randomly oriented XRD patterns of bulk materials are presented in Figs 3 and 4. The Na-bentonite samples showed a small decrease in the position of the smectite d_{101} line along the pH series. The most noticeable change was observed in the pH 12.0 experiment in which the intensity of calcite (CaCO_3) lines increased as well as the appearance of vaterite (CaCO_3) lines in both the pH 11.3 and 12.0 experiments. An increase in intensity of the calcite line and a decrease in intensity of the smectite lines were also observed in the Ca-bentonite samples in the pH 12.0 experiment. In the pH 9.7 and 12.0 experiments, there were small additional lines that could be assigned to laumontite ($\text{CaAl}_2\text{Si}_4\text{O}_{12} \cdot 4\text{H}_2\text{O}$), a member of the zeolite group.

The XRD patterns of samples in the d_{060} region are presented in Fig. 5. The position of the d_{060} lines decreased slightly in Na-bentonite in the pH 11.3 and pH 12.0 experiments, and in

FIG. 2 (facing page). Chemical composition (Ca, Mg, SiO_2 , SO_4^{2-}) of the leaching solutions of both bentonites (Na-bentonite on the left hand side, Ca-bentonite on the right hand side).

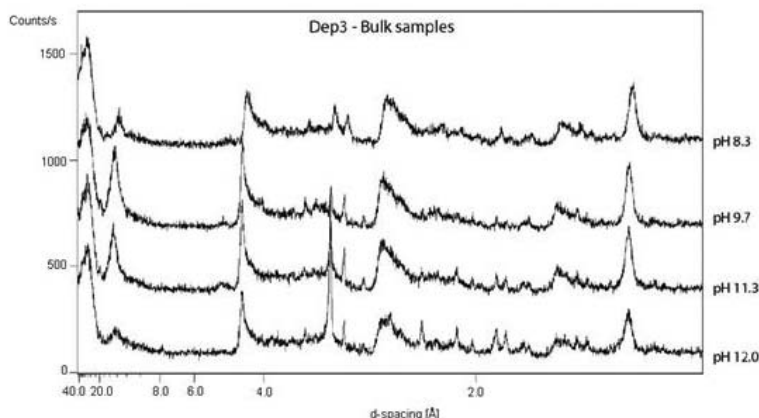


FIG. 4. XRD patterns of bulk Ca-bentonite samples.

Ca-bentonite in the pH 12.0 experiment. A totally new line (or rather humps) appeared at 1.52 Å in the pH 12.0 experiments for both materials (Fig. 5, Table 3). This might indicate the presence of trioctahedral clay minerals such as saponite (Mg-rich smectite). However, carbonates have overlapping lines in that same region, and due to increases in carbonate content in the bentonite samples, it was hypothesized that the more probable reason for the development of the 1.52 Å lines was the presence of carbonates.

XRD: Oriented clay fractions. During the preparation of the oriented XRD mounts, both bentonites in the pH 12.0 experiments were observed to have changed to lighter colours. These samples (both bentonites at pH 12.0) also resisted remaining in dispersion, and they additionally fractured or peeled off during drying, thus preventing the preparation of a proper mount. As proved by chemical analysis and oriented XRD patterns (Fig. 6, Tables 3 and 6), accessory minerals were still present despite the separation of the clay

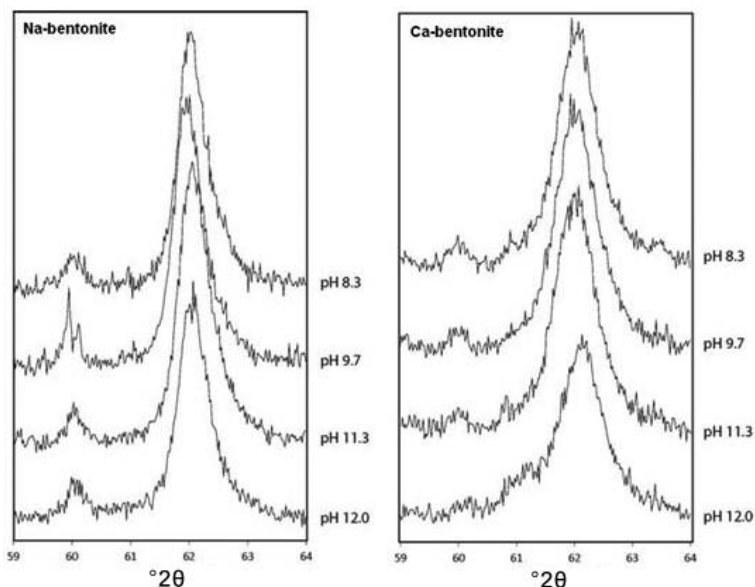


FIG. 5. XRD patterns of Na-bentonite (left) and Ca-bentonite (right) sample series at d_{060} region.

TABLE 3. Positions of important lines (in Å) used in identification of illite/smectite (I/S), and the amount of illite (I) interlayers in I/S calculated using the method of Moore & Reynolds (1989).

Treatment Line/interpretation	Bulk samples		Oriented d_{001}	EG			550°C d_{001}	Interpreted minerals
	Randomly oriented d_{060}	Randomly oriented d_{001}		d_{002}	d_{003}	I% in I/S		
Na-bentonite								
Initial sample*								
pH 8.3	1.497	16.41	13.99	8.35	5.57	0.9	9.56	I/S, Q, Cr
pH 9.7	1.495	16.25	13.75	8.40	5.59	1.4	9.70	I/S, Q, Cr
pH 11.3	1.497	16.71	13.99	8.45	5.60	2.2	9.72	I/S, Q, Cr
pH 12.0	1.492; 1.515	17.57	14.96	8.53	5.64	2.4	9.75	I/S, Q, Cr, Plag.
		16.60	14.52	8.44	5.60	2.3	9.56	I/S, Q
Ca-bentonite								
Initial sample*								
pH 8.3	1.498	16.40	14.38	8.34	5.54	3.8	9.80	I/S
pH 9.7	1.496	17.67	14.93	8.54	5.62	5.6	9.79	I/S, Plag.
pH 11.3	1.497	16.57	14.24	8.41	5.57	5.3	9.59	I/S, Plag.
pH 12.0	1.494; 1.517	16.24	14.18	8.40	5.56	5.3	9.62	I/S, K-Fs, Plag.
		16.94	14.59	8.47	5.60	4.1	9.72	I/S, Q, Plag.

Data from Kiviranta & Kumpulainen (2011).

Abbreviations: I/S = illite/smectite, Cr = cristobalite, Q = quartz, Cl = chlorite, K-Fs = K-feldspar,

Plag. = plagioclase

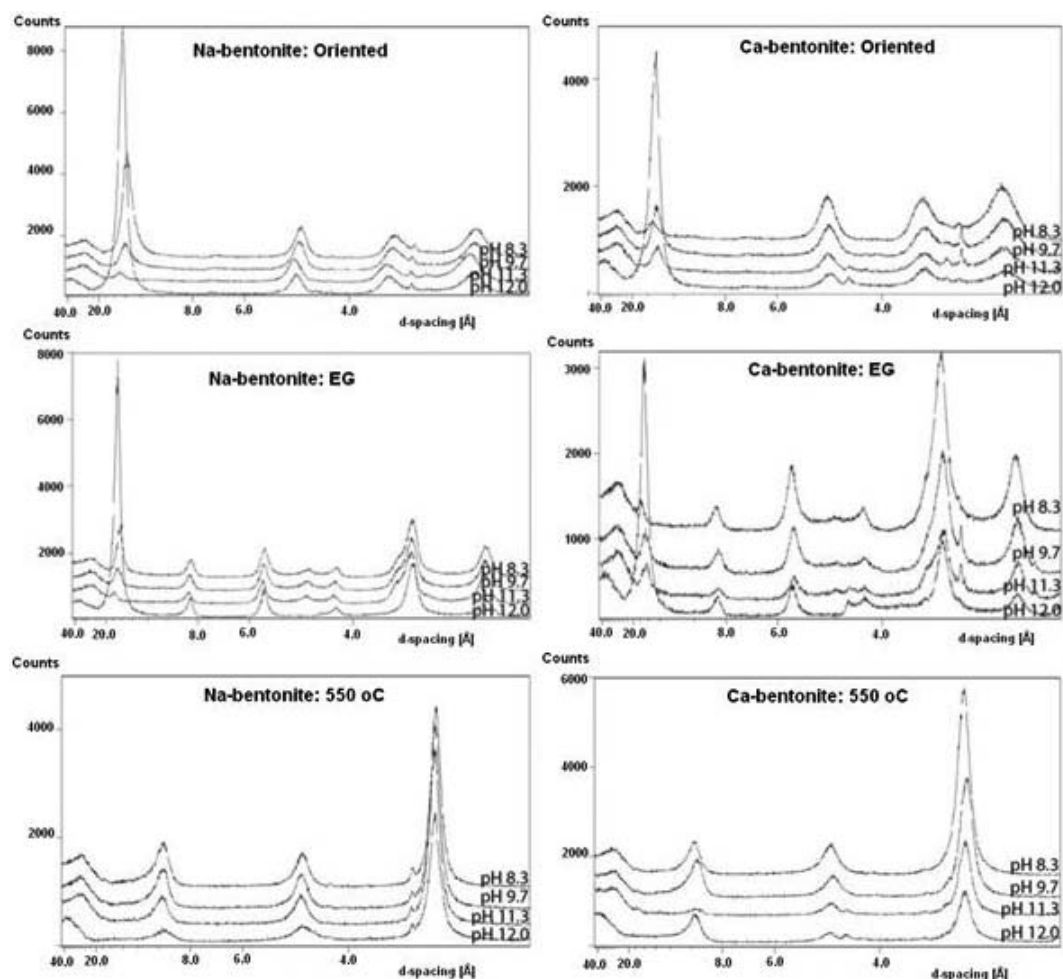


FIG. 6. XRD patterns of clay fractions after different treatments (Na-bentonite left, Ca-bentonite right).

fraction. Carbon analyses showed that the carbon content had increased at pH 12.0, and thus secondary minerals contained carbonates.

FTIR. The results from FTIR analyses are given in Fig. 7 and in Table 4. The results of both bentonite materials (Wyoming and Milos) show four changes in the pH series towards the alkaline samples:

(1) a decrease in smectite OH-bendings over the wavelength region $1000\text{--}500\text{ cm}^{-1}$, especially in samples in the pH 12.0 experiments;

(2) the development of broad bands at 1497 cm^{-1} and 1420 cm^{-1} , and additionally in the Na-bentonite sample in the pH 12.0 experiment a weak band at 958 cm^{-1} was noted, which could

indicate the presence of carbonate and/or CSH phases;

(3) an increase in water absorption bands in the pH 12.0 experiments in both bentonites at 3430 cm^{-1} and 1630 cm^{-1} , and;

(4) a decrease in transmissivity at $3700\text{--}2500\text{ cm}^{-1}$.

Most changes that occurred in the pH 12.0 experiments can be explained by the presence of carbonates, which cause bands at 1482 cm^{-1} , 1425 cm^{-1} and 865 cm^{-1} for amorphous calcite (Wilson, 1987) and at 1490 cm^{-1} , 1420 cm^{-1} and 870 cm^{-1} for vaterite (Sato & Matsuda, 1969), or by CSH or a calcium hydroxide (portlandite) phases, which according to Delgado *et al.* (1996)

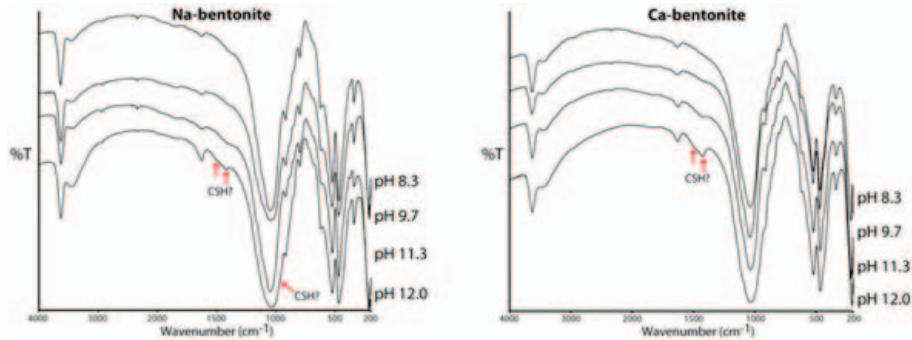


FIG. 7. FTIR patterns of Na- and Ca-bentonite samples leached with different solutions.

induce IR bands at $3640\text{--}3320\text{ cm}^{-1}$, and $460\text{--}450\text{ cm}^{-1}$. Calcite alone does not seem to explain the observed changes in the pH 11.3 and pH 12.0 experiments.

CEC and Greene-Kelly Test. The CECs of the the bulk samples, clay fractions ($<1\text{ }\mu\text{m}$), and clay fractions ($<1\text{ }\mu\text{m}$) after Li-treatment and heating at 250°C , are presented in Table 5.

The results of the CEC determinations indicated a decrease in the bulk sample CEC in Ca-bentonite in the pH 12.0 experiment, which may originate from the decrease in the smectite content. A small increase in the clay fraction CEC in the pH 11.3 and 12.0 experiments of both bentonites was observed. The increase in CEC at high pH could indicate that the smectite layer charge had increased.

Structural calculations. The chemical compositions of the purified clay fractions are shown in Table 6. The structural calculations were made using these values. The chemical compositions of the purified clay fractions ($<1\text{ }\mu\text{m}$) indicated a clear decrease in Fe content that was observed in Ca-bentonite in the pH 12.0 experiment. Both bentonites showed enrichment of Na compared with the initial samples.

Comparison of the structural composition of smectites between the treated samples and the initial sample material (data from Kiviranta & Kumpulainen, 2011) showed that the total charges of smectite were elevated after the batch experiments. This difference can partly be explained by the differences in the analysis methods. The structural compositions calculated from the chemical compositions (Table 7) suggest that the tetrahedral charge, and thereby also the total charge of smectite, increased in the pH 12.0 experiments.

In Na-bentonite this result is in line with the observed increase in CEC of the clay fraction analysed with spectroscopy, as well as with the observed change in the Greene-Kelly test (Table 5). Thus, it can be hypothesised that there was an increase in tetrahedral Al, that is, beidellitization in the pH 12.0 experiments at least in Na-bentonite. In batch experiments Vuorinen *et al.* (2006) also observed beidellitization in Na-bentonite in contact with high-pH saline solution.

Rietveld-analysis. The mineralogical compositions determined after XRD analysis, Rietveld analysis and chemical analyses are shown in Table 8. The results suggested that the smectite content decreased in experiments with both bentonites. Simultaneously, there is a drastic increase in the carbonate contents (Table 8). However, comparison of the mineralogical composition with the chemical analysis shows that the carbonate contents determined by mineralogical analysis (Table 8) were underestimated in the pH 8.3 and 9.7 experiments of both bentonites and the pH 11.3 experiment of the Ca-bentonite samples and overestimated in the pH 12.0 experiments. Overestimation of carbonate content in the mineralogical analysis (both bentonites in the pH 12.0 experiments) may be a result of an error in sample preparation, since acetone was used for grinding and sample mounting. Using acetone may have induced transformation of possible portlandite and CSH phases into carbonates. Furthermore, the carbonate content in all the Na-bentonite samples had increase drastically compared to the initial sample. Possible other explanations of the high carbonate content in the samples may be contamination from the leaching solutions or from the polycarbonate sample vessels. In any case, there are

TABLE 4. The position of FTIR absorption bands in the samples studied (cm^{-1}), and band assignments (S = smectite, Q = quartz).

Na-bentonite Init.* pH 8.3 pH 9.7 pH 11.3 pH 12.0	OH-stretching bands (S)	3637	3437	1623	(CSH?), CO_3^{2-} -stretching (Vaterite)	1497	CO_3^{2-} -stretching (Calcite, Vaterite)	1417	1419	1119	1119	1119	1048	(CSH?)	919	885	849	799	Si-O stretching (Quartz, Cristobalite, free Si-O)	Si-O (Quartz)	Si-O bending (Cristobalite)	Si-O bending	Si-O bending Na-bentonite
		3629	3423	1627						916	885	847	800		918	883	843	800	775	774	620	527	468
		3634	3418	1624						918	880	843	800		918	880	843	800	774	774	621	526	469
		3633	3418	1624						913	873	840	800		913	873	840	800	774	774	625	525	469
		3629	3423	1627						916	885	850	800		916	885	850	800	780	780	621	524	468
Ca-bentonite Init.* pH 8.3 pH 9.7 pH 11.3 pH 12.0	OH-stretching bands (S)	3628	3438	1625					919	882	845	801		919	882	845	801	801	780	780	618	525	468
		3629	3423	1627					913	880	843	795		913	880	843	795	795	780	780	623	523	468
		3629	3423	1624					918	878	847	795		918	878	847	795	795	782	782	620	524	470
		3629	3428	1634					916	876	840	795		916	876	840	795	795	780	780	623	523	468
		3625	3437	1630					913	873	840	795		913	873	840	795	795	780	780	623	524	470

* Data from Kiviranta & Kumpulainen (2011).

TABLE 5. Results of the cation exchange capacity determinations and the quantitative Greene-Kelly test. Decrease in CEC after Greene-Kelly test is indicative to montmorillonite content. (Kiviranta & Kumpulainen, 2011)

	Bulk sample CEC (eq/kg)	Clay fraction CEC (eq/kg)	CEC of clay fraction after Li-sat. and 250°C (eq/kg)	Decrease (%)
Na-bentonite				
Initial sample*	0.83	0.89	0.22	75
pH 8.3	0.83	0.93	0.27	74
pH 9.7	0.82	0.94	0.24	74
pH 11.3	0.88	0.99	0.23	77
pH 12.0	0.82	1.05	0.34	68
Ca-bentonite				
Initial sample*	0.91	1.07	0.36	67
pH 8.3	0.89	1.08	0.32	70
pH 9.7	0.89	1.07	0.34	68
pH 11.3	0.94	1.11	0.32	72
pH 12.0	0.78	1.10	0.36	67

* Data from Kiviranta & Kumpulainen (2011).

large uncertainties concerning the origin of the carbonate contents.

Swelling pressure. The swelling pressure data of the pH-treated samples are presented in Table 10 and Figs 8 and 9. For comparison purposes, the swelling pressures of the initial samples from Kiviranta & Kumpulainen (2011), and from other sources of similar materials, are included in Figs 8 and 9.

In contrast to what was initially hypothesized, the swelling pressures of samples treated at pH 12.0 (and also slightly for the pH 11.3 treated Ca-bentonite sample) showed higher swelling pressures than those of the original initial samples (Figs 8 and 9). It was thought that these unexpected results were caused by technical difficulties in sample dismantling due to the very small sample size. Therefore, the measurements of samples treated at pH 12.0

TABLE 6. Chemical composition of purified clay fractions (<1 µm and carbonates removed).

	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	MgO	CaO	Na ₂ O	K ₂ O	Tot. C	LOI
Na-bentonite										
Initial sample*	62.79	20.96	4.04	0.14	2.44	0.01	2.84	0.06	0.30	6.26
pH 8.3	62.04	20.78	4.09	0.13	2.50	0.03	3.03	0.06	0.43	6.28
pH 9.7	63.32	20.97	4.09	0.13	2.54	0.05	3.15	0.06	0.38	6.48
pH 11.3	63.53	21.16	4.17	0.14	2.55	0.06	3.40	0.06	0.71	7.26
pH 12.0	60.97	20.97	4.05	0.14	2.44	0.09	3.80	0.06	0.77	8.87
Ca-bentonite										
Initial sample*	60.41	18.97	4.99	0.75	3.66	0.03	3.17	0.28	1.31	11.29
pH 8.3	63.11	18.55	5.13	0.71	3.70	0.05	3.68	0.27	0.34	6.63
pH 9.7	61.82	18.25	5.05	0.69	3.65	0.07	3.65	0.31	0.27	6.45
pH 11.3	63.11	18.63	5.09	0.67	3.83	0.05	3.75	0.32	0.64	7.90
pH 12.0	60.11	18.63	4.39	0.65	3.57	0.10	3.95	0.23	0.78	9.52

* Data from Kiviranta & Kumpulainen (2011).

TABLE 7. Structural composition of smectite.

Sample	Na-bentonite					Ca-bentonite				
	Init.*	pH 8.3	pH 9.7	pH 11.3	pH 12.0	Init.*	pH 8.3	pH 9.7	pH 11.3	pH 12.0
Tetrahedral positions										
-Si ⁴⁺	7.949	7.933	7.954	7.930	7.848	7.900	8.000	7.994	7.990	7.919
-Al ³⁺	0.051	0.067	0.046	0.070	0.152	0.100	0.000	0.006	0.010	0.081
-Sum	8.000	8.000	8.000	8.000	8.000	8.000	8.000	8.000	8.000	8.000
Octahedral positions										
-Al ³⁺	3.106	3.054	3.048	3.032	3.019	2.800	8.712	2.703	2.697	2.759
-Fe ³⁺	0.348	0.396	0.389	0.394	0.394	0.461	0.502	0.506	0.500	0.445
-Fe ²⁺	0.022	—	—	—	—	0.014	—	—	—	—
-Mg ²⁺	0.466	0.477	0.475	0.475	0.467	0.727	0.702	0.707	0.728	0.703
-Sum	3.943	3.926	3.912	3.901	3.880	4.002	3.917	3.916	3.925	3.908
Interlayer positions										
-Ca ²⁺	0.000	0.004	0.006	0.008	0.012	0.000	0.008	0.010	0.007	0.014
-Mg ²⁺	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
-K ⁺	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
-Na ⁺	0.711	0.756	0.773	0.827	0.954	0.836	0.928	0.944	0.949	1.033
-Sum	0.711	0.760	0.779	0.835	0.966	0.836	0.936	0.955	0.955	1.047
O	24	24	24	24	24	24	24	24	24	24
H	4	4	4	4	4	4	4	4	4	4
Unit cell weight	745	746	746	747	750	752	753	753	753	753
Charges										
-tetrahedral charge	-0.051	-0.067	-0.046	-0.070	-0.152	-0.100	-0.000	-0.006	-0.010	-0.081
-Octahedral charge	-0.660	-0.697	-0.739	-0.772	-0.826	-0.736	-0.953	-0.959	-0.952	-0.980
-Total charge	-0.711	-0.764	-0.785	-0.842	-0.978	-0.836	-0.953	-0.965	-0.962	-1.062
-Beidellite content (%) from structural composition	7	9	6	8	16	12	0	1	1	8
CEC (for S) calc from structural compos. (eq/kg)	0.95	1.02	1.05	1.13	1.30	1.11	1.27	1.28	1.28	1.41

* Data from Kiviranta & Kumpulainen (2011).

S = smectite

were repeated, but the result obtained was still an increase in swelling pressure in both bentonite materials of the pH 12.0 experiment.

As swelling pressure is a function of density and montmorillonite content, the effective montmorillonite dry densities (EMDD) were calculated on the basis of the Rietveld analysis (Table 6) and are presented in Table 10 and Fig. 10. As seen in Fig. 10, a change in montmorillonite content does not explain the increase in swelling pressure in the pH 12 experiment. One probable explanation could be the observed increase in the layer charge of smectite.

DISCUSSION

Buffering against alkaline solutions was observed in both bentonites as the initial alkaline leachate pH values of 9.7, 11.3 and 12.0 were not reached after 554 days. However, a slight reduction of the buffering capacity was observed in the pH 11.3 and pH 12 experiments of both bentonites. According to Ramirez *et al.* (2002) such a pH decrease may be due to the deprotonation of aqueous silica ($\text{H}_4\text{SiO}_4 \rightarrow \text{H}_2\text{SiO}_4^{2-} + 2\text{H}^+$), to the incorporation of OH^- in the structure of formed minerals or to the retention of OH^- in the external surface of smectite. However,

TABLE 8. Mineralogical composition (wt.%). Values shown in parentheses are based on chemical compositions assuming that all carbonates are calcite, all sulfides and all titanium rutile or anatase.

Minerals	Init.*	Na-bentonite			Ca-bentonite		
		pH 8.3	pH 9.7	pH 11.3	pH 8.3	pH 9.7	pH 11.3
Smectite	87.6	90.2	88.6	88.6	84.1	84.2	86.8
Illite/mica	0.1	0.7	0.7	0.7	2.9	3.4	3.5
Plagioclase	4.2	1.4	1.9	1.6	0.8	1.7	0.0
K-feldspar	1.8	0.8	1.8	1.4	0.9	1.3	0.2
Quartz	4.1	3.0	3.3	2.3	0.1	0.2	0.0
Cristoballite	tr	0.4	0.2	0.0			
Calcite	0.6 (1.7)	2.3 (8.4)	1.9 (10.0)	2.6 (3.4*)	3.3 (8.9**) 2.3	2.5 (10.0**) 2.3	4.4 (11.9**) 1.9
Dolomite							
Vaterite							
Hematite	tr	0.7	0.5	0.8	1.2	0.9	1.1
Magnetite	tr			0.6			
Pyrite	0.6 (0.3)	0.5 (0.3)	0.7 (0.4)	1.1 (0.3)	1.5 (0.4)	1.4 (0.4)	1.5 (0.8)
Rutile	0.9 (0.1)	0.1 (0.2)	0.3 (0.2)	0.7 (0.1)			
Anatase							
Tridymite/opal							
Laumontite							
Zircon	tr			tr	0.5 (0.7) 1.1	0.3 (0.7) 1.2	0.3 (0.7) 0.4
Apatite							
Pyroxene				tr		tr	tr

* Data from Kiviranta & Kumpulainen (2011).
tr: trace, *: includes both calcite and vaterite, **: includes both calcite and dolomite

TABLE 9. Comparison of observed chemical compositions (wt.%) and chemical compositions (wt.%) calculated from the mineralogical compositions.

	Na-bentonite								Ca-bentonite							
	pH 8.3		pH 9.7		pH 11.3		pH 12.0		pH 8.3		pH 9.7		pH 11.3		pH 12.0	
	obs	calc	obs	calc	obs	calc	obs	calc	obs	calc	obs	calc	obs	calc	obs	calc
Na ₂ O	0.78	0.55	0.80	0.53	0.75	0.63	0.73	0.40	0.55	0.45	0.45	0.45	0.44	0.35	0.45	0.37
CaO	2.76	3.49	2.81	3.37	4.40	4.31	10.76	10.60	5.34	5.74	5.98	4.91	8.17	5.73	13.42	12.95
Al ₂ O ₃	19.08	19.83	18.74	19.65	18.58	19.35	16.69	18.48	16.53	16.55	16.38	17.10	15.42	16.81	14.00	14.91
Fe ₂ O ₃	3.87	4.87	3.84	4.66	3.74	4.88	3.38	4.26	4.63	6.47	4.48	6.29	4.79	6.60	4.41	5.60
MgO	2.26	2.37	2.20	2.31	2.40	2.29	2.20	2.16	4.20	3.71	4.15	3.74	4.37	3.85	4.05	3.14
SiO ₂	62.44	62.58	62.26	62.75	61.2	60.42	55.66	52.83	57.3	57.12	56.42	58.59	53.56	53.56	49.61	48.55
H ₂ O	4.07	4.36	3.63	4.29	6.43	4.25	8.14	3.84	5.91	4.05	5.95	4.08	5.81	4.18	6.94	3.46
CO ₂	3.71	1.01	4.38	0.83	1.50	1.48	1.48	6.35	3.91	2.99	4.38	2.16	5.25	2.79	5.04	8.57
K ₂ O	0.49	0.20	0.68	0.37	0.48	0.25	0.46	0.29	0.34	0.45	0.62	0.56	0.41	0.36	0.31	0.46
TiO ₂	0.15	0.10	0.15	0.30	0.14	0.69	0.13	0.40	0.71	0.49	0.69	0.29	0.68	0.30	0.63	0.30
SO ₃	0.40	0.66	0.50	0.93	0.38	1.45	0.37	0.40	0.59	1.97	0.50	1.84	1.10	1.97	1.14	1.71

the carbonate content also contributes to the buffering capacity of the bentonite material.

Chemical analyses of both leachates and bentonite materials agree rather well. The evolution of the elements (e.g. Ca, Na, K, Mg) in the solution can be explained by ion-exchange reactions on the clay surfaces and also the interlayer space by the dissolution/precipitation reactions. XRD analysis revealed the presence of calcite (CaCO₃) and vaterite (CaCO₃), which may be a result of contamination by atmospheric CO₂ during the experiment or sample preparation despite the

efforts of avoiding air contact. One source could be the atmosphere inside the glove-box, which contains trace amounts of CO₂ (~0.01 ppm). During the clay purification process, when the clay batches were dried in the glove-box, they were in contact with the atmosphere without any further protection.

SiO₂ was released from the bentonite material. It is assumed that the concentration of Si in the solution might be controlled by the dissolution of quartz, which is reported to have higher dissolution rates compared to other silicates (Knauss & Wolery, 1988). Mineralogical analysis showed a decrease in

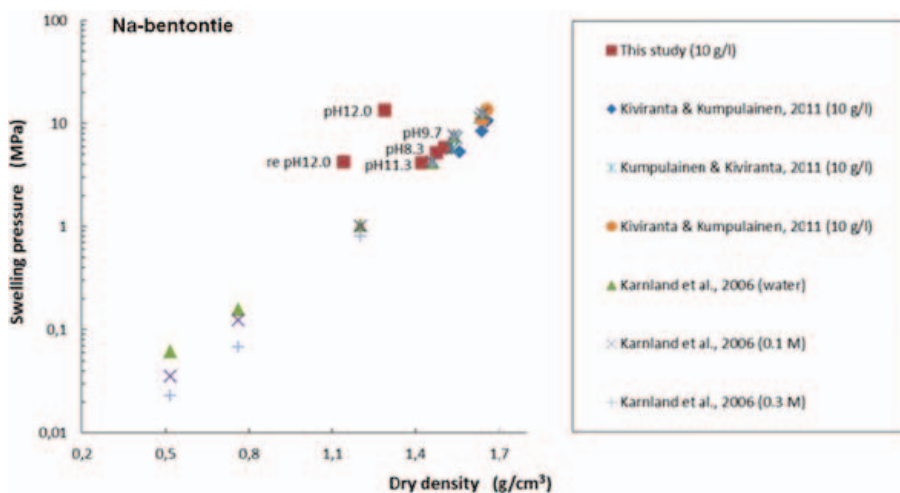


FIG. 8. Swelling pressures of pH-treated Na-bentonite samples compared to swelling pressures of initial MX80 materials from Kiviranta & Kumpulainen (2011), Kumpulainen & Kiviranta (2011) and Karnland *et al.* (2006).

TABLE 10. Swelling pressures.

Sample	Grain density (g/cm ³)	SP (MPa) in Olkihuoto ref. water	SP (MPa) in test water	Ratio of non- swelling material	W (%)	Calculated from w		Sample thickness (mm)	
						ρ_d (g/cm ³)	ρ_d (g/cm ³)		
Na-bentonite									
Initial 1*	2.78	8.44	—	0.115	25.1	1.64	2.05	1.55	10.0
Initial 2*	2.78	10.49	—	0.115	24.4	1.66	2.06	1.57	10.0
Initial 3*	2.78	5.31	—	0.133	28.3	1.56	2.00	1.46	10.0
pH 8.3	2.78	5.86	5.55	0.098	30.5	1.50	1.96	1.43	6.70
pH 9.7	2.78	5.25	4.91	0.114	31.8	1.47	1.94	1.39	6.70
pH 11.3	2.78	4.16	3.85	0.114	34.3	1.42	1.91	1.34	6.70
pH 12.0	2.78	13.38	13.16	0.205	41.7	1.29	1.82	1.13	6.70
re- pH 12.0	2.78	4.22	4.06	0.205	51.8	1.14	1.73	0.99	6.70
Ca-bentonite									
Initial 1*	2.81	11.47	—	0.225	29.3	1.54	1.99	1.36	10.0
Initial 2*	2.81	9.66	—	0.197	29.5	1.54	1.99	1.38	10.0
Initial 3*	2.80	10.76	—	0.196	29.3	1.54	1.99	1.39	10.0
pH 8.3	2.81	6.42	6.17	0.159	32.6	1.47	1.95	1.35	6.70
pH 9.7	2.81	6.42	6.15	0.158	33.7	1.44	1.93	1.32	6.70
pH 11.3	2.81	6.00	5.81	0.132	38.9	1.34	1.86	1.24	6.70
pH 2.0	2.81	12.53	12.34	0.288	44.8	1.24	1.80	1.02	6.70
re- pH 12.0	2.81	6.03	5.84	0.288	49.9	1.17	1.75	0.95	6.70

* Data from Kiviranta & Kumpulainen (2011).

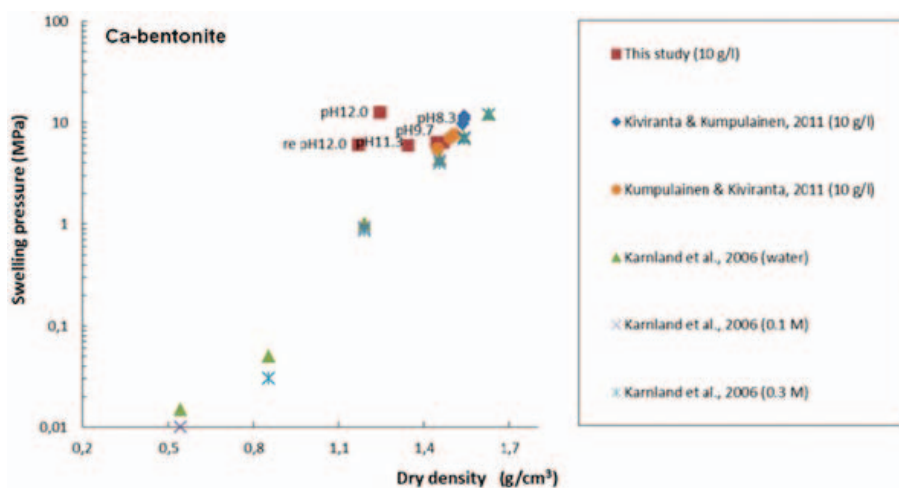


FIG. 9. Swelling pressures of pH-treated Ca-bentonite samples compared to swelling pressures of initial Na-bentonite materials from Kiviranta & Kumpulainen (2011), Kumpulainen & Kiviranta (2011) and Karlund *et al.* (2006).

the quartz content after the experiment in all the tests, but especially in those carried out at pH 12.0.

Magnesium release was more prominent in Ca-bentonite samples and occurred in the beginning of the experiment. Both bentonites released more Mg in the lower pH experiments (8.3 and 9.7). This was rather to be expected since the solubility of Mg is sensitive to pH and temperature; a decrease in pH increases the dissolution. Lesser amount of Mg observed in the higher pH leachates may also be a

result of precipitation of brucite, $Mg(OH)_2$, as it occurs between pH 9 and 10 (Baes & Mesmer, 1976). Only very small amounts of Al and Fe were released in the pH 12.0 experiments (both bentonites), and in other experiments the levels were below detection limit. The chemical compositions of the purified clay fractions showed an enrichment of Na compared to the initial samples. It was considered that this increase was not related to excess salts since the purified clay fractions were

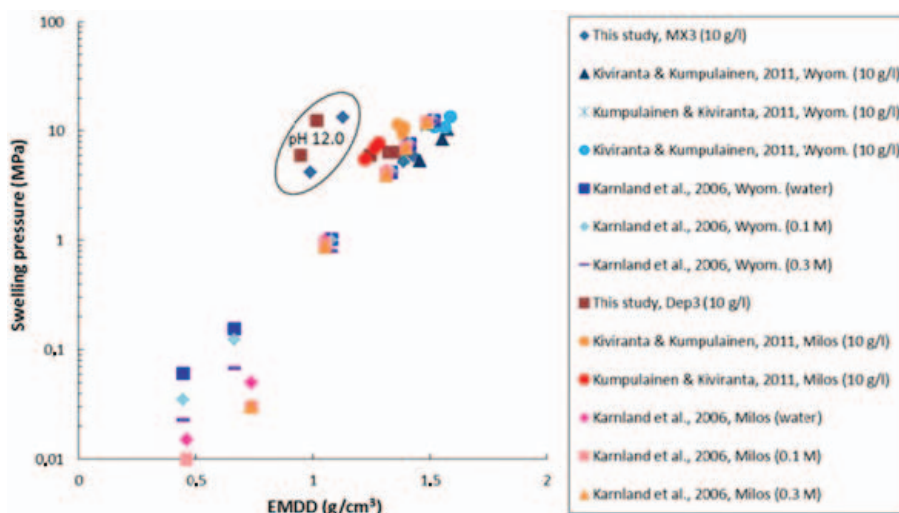


FIG. 10. Dependency of swelling pressure on EMDD.

washed with dialysis before chemical analysis using a similar protocol to that of the initial samples (Kiviranta & Kumpulainen, 2011). The increase in Na content may be partly related to the increase in layer charge at high pH, but does not fully explain it, since the Na content also increased in pH 8.3 and 9.7 experiments.

In their experiment Karland *et al.* (2007) did not observe major changes in mineralogy/chemical composition or in swelling pressure of bentonite material in contact with 0.1 M NaOH (pH 12.9) and saturated Ca(OH)₂ solutions (pH 12.4). Whereas the bentonite in contact with 0.3 M (pH 13.3) and 1.0 M (pH 13.8) NaOH underwent significant loss of swelling pressure. Their solution data as well as chemical and mineralogical data on the bentonite composition indicated that the interaction between bentonite and solution was minimal. Similar results were also obtained in our experiments. Only small alterations were detected in the mineralogy and chemical composition of the bentonites, and they concentrated mainly on samples in the pH 11.3 and 12.0 experiments. Precipitation of vaterite and calcite was observed and possibly also the presence of CSH-phases. This is in agreement with the findings of e.g. Claret *et al.* (2002) and Savage *et al.* (2002), as they have noted that CSH phases are common phases obtained in alkaline experiments with bentonites at low temperatures. Both bentonites showed an overall increase in the carbonate content and decrease in the smectite content (in the pH 12.0 experiment).

Some changes in the smectite structure were detected, such as an increase in CEC. Similar results were found by Sánchez *et al.* (2006) in experiments conducted at 75–25°C. They concluded that the formation of CSH gels or tobermorite-like minerals contribute to the higher CEC values.

The increase in the layer charge and in the tetrahedral charges together with the tetrahedral aluminium that is beidellitization was also observed. According to Mosser-Ruck & Cathelineau (2004) the coexistence of different types of expandable or collapsed layers (in particular high-charge and low-charge smectite), which may be formed during the first step of the illitization process and are related to a solid-state transformation, complicate the interpretation of the evolution of smectite.

In contrast to what was initially hypothesized, the swelling pressure in the pH 12.0 experiments

showed a higher value than in the initial samples. The increase was thought to result at least partly from an increase in the layer charge of smectite. No notable changes were seen in the other experiments on both bentonites.

CONCLUSIONS

The effect of three alkaline solutions on two selected bentonites was investigated experimentally at 25°C. After leaching the bentonites with the alkaline solutions (1 g bentonite/145 ml solution) for 554 days no significant changes were observed. The time for major alterations to occur may have been too short, however, and experiments with two parallel sets of samples are still being continued to provide further results.

The main processes observed were cation exchange (Na⁺ and Mg⁺ by Ca²⁺) and pH buffering. The swelling clay component is unstable at high pH, reflected by the results – the higher the initial pH of the solution, the stronger its interaction with the bentonite material. The most significant changes in the mineralogy were observed in the pH 12.0 experiments. Overall, the bentonite minerals were rather stable under alkaline attack within the duration of our tests. Some changes in the smectite structure were detected, such as an increase in CEC and in the layer charge. These developments are not fully understood since the dissolution of the clay minerals is usually accompanied by an overall decrease of the layer charge followed by a decrease in the cation-exchange capacity.

The effect of the interaction between the alkaline solutions and bentonite materials is dependent on the strength of alkalinity, concentration and nature of the dissolved ions, as well as on the temperature of the reaction. Therefore similar experiments at 60°C were started in order to investigate the effect of temperature. Results from these experiments will be published later.

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