

BEHAVIOR OF SMECTITE IN STRONG SALT BRINES UNDER CONDITIONS RELEVANT TO THE DISPOSAL OF LOW- TO MEDIUM-GRADE NUCLEAR WASTE

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Abstract—Two industrial bentonites, IBECO SEAL-80 and TIXOTON TE, have been proposed as potential backfill material in the German Asse salt dome, a test field for the disposal of low- to medium-grade active nuclear waste. Considering the unlikely but possible case of a barrier breakdown with infiltration of a highly concentrated salt brine, the physicochemical stability and material behavior of these bentonites in a saturated salt brine (predominantly MgCl₂) at 25°C were studied over the time period of 150 days. The results show that no mineral transformations occurred throughout the duration of the experiments and minor dissolution was only active during the first days. Some chemical properties, namely sorption capability and swelling, were reduced during contact with the salt brine, but could be reversed by removing the salt after treatment. Despite restriction of the CEC in the presence of salt solution, interlayer cation exchange reactions are still active in this environment. The long-term chemical stability of smectite in salt brine is predicted under these low-temperature conditions, but the increased permeability during aggregate formation could lead to physical breakdown of the backfill component.

Key Words—Cation Exchange Capacity, Layer Charge, Nuclear Waste, Salt Brine, Smectite.

INTRODUCTION

The secure long-term storage of nuclear waste in underground repositories requires an effective combination of both natural and technical barriers to prevent radionuclides from migrating into the groundwater and finally from coming into contact with the biosphere (Kim *et al.*, 2001). In Germany, deeply buried salt formations are being considered as appropriate host rocks due to their fracture and self-healing properties (Pusch and Alstermark, 1985; Pusch, 1992), and the low groundwater flow over geologically relevant time scales (Schmidt, 1995). This scenario is currently being investigated at the test site of the German Asse salt dome (Gömmel, 1997). Here, 126,000 containers of low- to medium-grade radioactive waste have been stored between 1967 and 1978, and over the past few years, a highly concentrated salt brine has entered the mine. Two bentonites, 'TIXOTON TE' and 'IBECO SEAL-80', are being evaluated for use as backfill which should prevent the waste canisters from coming into contact with the corrosive salt brine and thus prevent radionuclide release.

Although bentonite is a well established sealant used in many disposal sites, its application as a backfill in nuclear waste repositories is not yet fully understood. The main constituent of bentonites, the smectite clays, are considered to be ideal due to their swelling/sealing ability and high cation exchange capacity (CEC) (see Bauer *et al.*, 2001, for review). The high CEC of smectite enables sorption of cations and polar substances

onto particle surfaces and into interlayer spaces (Zachara *et al.*, 2002), and therefore has the potential to retain dangerous radionuclides (Sylwester *et al.*, 2000; Coppin *et al.*, 2002).

Despite the beneficial properties of the smectite group minerals, the stability of these minerals in strong salt solutions is a question of concern. A number of experiments have been conducted to evaluate the stability and behavior of smectite in salt solutions. These experiments show that a number of dissolution and precipitation reactions can occur at elevated temperatures (>50–60°C) and under strong acidic or alkaline conditions (Bauer *et al.*, 2001; Huertas *et al.*, 2001; Cama *et al.*, 2000; Kasbohm *et al.*, 2000; Metz, 2001; Zysset and Schindler, 1996; Eberl *et al.*, 1993; Inoue, 1983; Komarneni and Roy, 1983; Komarneni and White, 1983; Eberl and Hower, 1977). There is, however, a notable lack of experimental data for lower-temperature, near-neutral-pH brines, conditions which are directly relevant to the Asse test site. As the low and medium grade radioactive waste produces no heat, the temperature in the repository chambers at a depth of 510–750 m is not expected to exceed 25°C. Thus to fill this niche, this study evaluates the stability and behavior of the bentonite backfill under conditions specific to this repository and also examines the influence of the salt brine on the CEC and layer-charge properties of the clays.

MATERIALS AND EXPERIMENTAL SETUP

The two industrial bentonites used for experimental work are described as follows: 'IBECO SEAL-80' is a Na-activated bentonite distributed by IBECO Bentonit-

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Technologie GmbH* and contains 8–12% calcite and traces of feldspar as accessory mineral phases. 'TIXOTON TE' provided by Süd-Chemie AG† is a Ca-activated bentonite, with mica, chlorite, quartz and feldspar as accessory mineral phases. Both bentonites are very fine grained with 80% of the volume <0.063 mm in size. These two bentonites are referred to as IBECO and TIXOTON throughout this text. The mineralogical and chemical compositions of both starting materials are listed in Table 1. Both bulk materials are distributed in powder form and shipped as bagged cargo. Whole powder fractions were used for experiments in the same form as applied for backfill.

Experiments were conducted in batch reactors using a saturated salt brine ('Q-brine') with a typical composition expected in the Asse mine. The solution was prepared using analytical-grade chemicals and Milli-Q deionized water with a resistivity of $>18.2 \text{ M}\Omega \text{ cm}^{-1}$ (Kienzler and Loida, 2001). The solution chemistry and composition of the Q-brine at room temperature (25°C) is listed as follows: pH 6.6, Eh -108.9 , K^+ 0.4, Na^+ 0.43, Mg^{2+} 4.42, SO_4^{2-} 0.4 (element concentrations given in mol L^{-1}). Batch experiments were prepared in a glovebox in Ar atmosphere to avoid CO_2 contamination and a reduction in solution pH not caused by the mineral reactions being investigated. Samples were prepared by weighing 4 g of the bulk bentonite material and adding 40 mL of salt brine into 50 mL Oak Ridge polypropylene centrifuge vessels. During the experiment the suspensions were shaken twice a week. At the end of the experiments, the samples were removed from the glove box and the solids separated from the brine by centrifugation. Afterwards, the samples were returned to the glove box for pH measurements. 10 mL of the supernatant solution were separated and filtered through a 0.45 μm filter membrane. Appropriate dilutions of the filtered salt solutions were prepared for chemical analyses. Remaining salt was removed from the solids by washing them at least eight times with 40 mL of deionized water. After each washing step the solids were separated by centrifugation and re-suspended by ultrasonic treatment. In a final step, traces of remaining salt were removed by dialysis. Following the first two washing steps, small amounts of clay material were separated to test changes in CEC as a function of washing degree. No additional ultrasonic treatment was used. All washed samples were freeze dried and stored for further analysis.

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ANALYTICAL METHODS

Starting materials and reactant products were characterized using scanning electron microscopy (SEM), X-ray diffraction (XRD), X-ray fluorescence (XRF) and ICP-AES techniques in order to determine the mineralogy and compositions of both solids and solutions. The CEC and layer-charge characteristics of the bentonite samples were analyzed using Cu-triethylenetetramine and alkylammonium methods (Lagaly and Weiss, 1971; Meier and Kahr, 1999).

For SEM investigation, a small amount of bentonite material was separated after salt removal and before re-dispersion by ultrasonic techniques. The dry material was mounted onto aluminum sample holders using self-sticking carbon pads and coated with gold. For comparison with untreated material, small amounts of dry bulk bentonite powder were also prepared. The samples were then imaged using a LEO SEM instrument under high vacuum with a secondary electron detector and tungsten filament.

The XRD analyses were conducted using a Siemens D500 or Bruker AXS D8 diffractometer. Oriented samples were prepared by dispersing 45 mg of the solids in 1.5 mL of deionized water and pipetting the dispersion onto glass slides. The samples were treated ultrasonically using a micro tip for a few seconds before drying under atmospheric conditions overnight at room temperature. All XRD analyses were conducted between relative humidities of 30 and 35%. For calibration of the IBECO XRD patterns, the 001 reflection of the accessory mica

Table 1. Mineralogical composition of the starting materials, IBECO and TIXOTON, as given by the suppliers and chemical composition measured by XRF (wt.% oxide).

	TIXOTON	IBECO
Mineralogy (%)		
Montmorillonite	>80	>80
Mica	1–2	<3
Calcite	1	8–12
Feldspar	5–6	<3
Quartz	8–9	–
Other	–	2
Composition (% oxide)		
SiO_2	53.8	52.9
Al_2O_3	17.5	16.6
Fe_2O_3	5.1	4.6
MnO	0.1	0.1
CaO	3.7	6.1
MgO	3.9	3.0
K_2O	1.3	0.5
Na_2O	2.2	2.6
TiO_2	0.3	0.8
P_2O_5	0.1	0.1
SO_3	–	2.9
LOI*	12.0	9.8

* LOI: loss on ignition

was used as an internal standard, whereas for TIXOTON, the 104 calcite peak (3.03 Å) was used.

The XRF analyses were conducted using pressed dry pellets and measured with a Siemens SRS 3000 sequential X-ray spectrometer. The concentration of dissolved Na, K, Mg, Ca, Al, Si and Fe in solution was determined by using a Plasma 400 ICP-AES (Perkin-Elmer) after appropriate dilution. The measurement precision determined on known standards ranged between 2 and 6%. The pH and Eh were measured using an Orion ROSS combination electrode (type 8102) and an Orion 920A pH-meter. Aliquots of the untreated bulk material of TIXOTON and IBECO and salt-treated samples after 3 and 150 days were microwave digested for ICP-AES analyses of the chemical composition.

The CEC was determined using the Cu(II)-triethylenetetramine method described by Meier and Kahr (1999). The CEC was measured twice for all samples, the first time following two washing steps, and a second time after eight washing steps with additional dialysis and ultrasonic treatment. Determination of layer charge (*i.e.* charge density) and layer-charge distribution was performed using the alkylammonium method of Lagaly and Weiss (1971). Layer-charge characteristics were determined for untreated original material and the samples treated with salt solution for 3, 80 and 150 days at room temperature (25°C). A detailed description of the sample- and alkylammonium-chloride solution preparation procedure can be found in Lagaly (1991), Lagaly (1994) and Mermut and Lagaly (2001).

From each of the freeze-dried bentonites, a further 15 samples were prepared by weighing 0.1 g of bentonite powder and placing them in 10 mL Oak Ridge PP centrifugal tubes. 4 mL of alkylammonium chloride solution with carbon chain lengths from $n_C = 3$ to $n_C = 18$ (except $n_C = 17$) were then added to the samples of each series. The exchange procedure was performed twice in order to ensure a complete interlayer exchange of the tenside molecules. After washing the samples at least eight times with 5 mL of pure ethanol, 10% talc (<2 µm fraction) was added as an internal standard for calibration. Oriented samples were prepared for XRD analysis by pipetting 1 mL of the dispersion onto a 3 × 3 cm glass slide. The slides were air dried overnight at 60°C and afterwards dehydrated under vacuum conditions over P₂O₅ in a desiccator for a further 24 h.

For layer-charge determination, oriented samples were measured using either a Siemens D500 or Bruker AXS D8 diffractometer (θθ). To reduce water uptake and swelling caused by humidity, the samples were measured individually, while other samples were stored under vacuum conditions. The *d* values were plotted as a function of the number of carbon atoms in the alkyl chain and the average charge density and layer-charge distribution were calculated using the computer program XCharge (Hofmann *et al.*, 2002), following the calculation procedure of Lagaly (1994).

RESULTS

Solution chemistry and pH

The Ca concentration in TIXOTON salt brine initially increased from 0 to 2.2×10^{-3} mol L⁻¹ during the first days and then was more or less constant for the remaining duration of the experiment (Figure 1a). IBECO released similar concentrations of Ca (up to 3.9×10^{-3} mol L⁻¹) into the solution during the first days of the experimental run (Figure 1b), but after 80 days this value decreased by 40% before remaining constant. As this smectite is Na-saturated, the likely source of Ca is the accessory calcite, which makes up 8–12% of the starting material.

The measured concentrations of Mg, Na and K show no significant variation in solution chemistry during the duration of both experiments (Figure 1a,b). Within the accuracy of the measurement method (error range ±5%), end concentrations do not vary from the original composition of the Q-brine. Although pH determination in strong salt solutions is complex due to the varying diffusion potential between the reference electrolyte and the sample solution, corrections can be made following

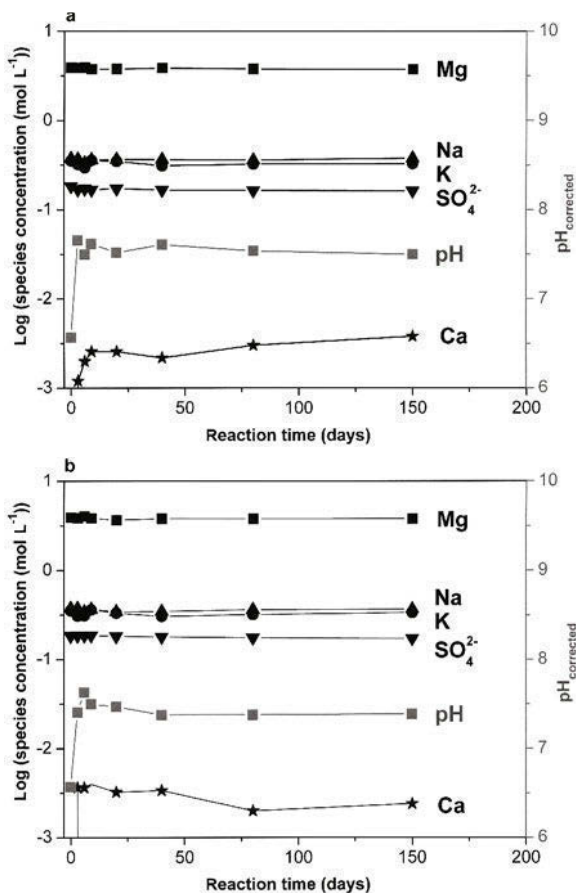


Figure 1. Solution chemistry and corrected pH values as a function of reaction time for (a) TIXOTON and (b) IBECO experiments.

the procedure proposed by Grambow and Müller (1990). This technique uses the EQ3/6 convention (Wolery, 1992), which yields a ΔpH of 1.53 for the applied Q-brine. The corrected pH here represents the proton activity in solution. In both cases, the corrected pH of the initial salt brine increased slightly within the first 3 days, changing from 6.6 to 7.6, and reflects the expected and well known proton sorption of smectites (Bauer *et al.*, 2001). After 3 days no further change in pH was recorded.

In contrast to Mg, Na and K, a slight increase in Al and Si concentrations in solution could be observed for both starting materials within the initial days of the experiment (Figure 2). As for Ca, an initial increase can be recognized during the first 3 days. The Si concentrations increased from 0 to $3 \times 10^{-5} \text{ mol L}^{-1}$, whereas Al concentration reached $7 \times 10^{-6} \text{ mol L}^{-1}$. The calculated Al/Si ratios of the whole sample material were 0.20 and 0.24 for TIXOTON and IBECO, respectively. Following this initial period, no significant changes in Al and Si concentrations were detected and a 'steady state' system was reached where the Al/Si ratio remains constant.

Mineral chemistry

Chemical analyses of the two bentonite samples by ICP-AES, conducted on initial material and after 3 and 150 days' reaction time, show similar changes in composition for both materials (Table 2). The concentrations of Al and Fe remain nearly constant at $90 \text{ mg of Al (g solid)}^{-1}$ and $20 \text{ mg Fe (g solid)}^{-1}$. In contrast, a notable decrease can be observed in Ca and Na concentrations, whereas Mg and K increased during the time span of the experiment. As recorded in the solution chemistry, most changes occurred during the first 3 days of reaction time.

The decrease in Ca content for the TIXOTON bentonite by $8 \text{ mg of Ca (g solid)}^{-1}$ reflects the replacement of interlayer Ca by Mg and K, and its release into solution. Although the exact elemental compositions differ for the two bentonite samples, *e.g.* TIXOTON has three times as much K as IBECO, both experimental runs show notably similar patterns. Consequently, the Mg and K concentrations are slightly enriched by $5 \text{ mg of Mg (g solid)}^{-1}$ and $4 \text{ mg of K (g solid)}^{-1}$, respectively. Similarly, the decrease in Na,

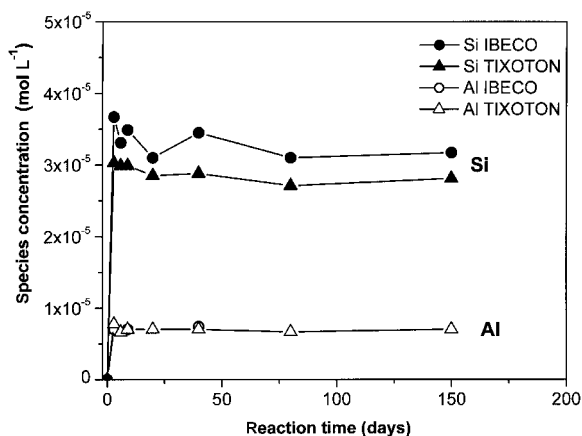


Figure 2. Element concentrations of Al and Si in the salt brine as a function of reaction time.

depleted by $11 \text{ mg Na (g solid)}^{-1}$ for TIXOTON and by $14 \text{ mg Na (g solid)}^{-1}$ for IBECO, can be attributed to cation replacement. The fact that K replaces Ca reflects the preferred selectivity of this small, monovalent cation, which fits almost perfectly into the pseudohexagonal ring structure within tetrahedral sheets in smectite (Lagaly, 1993).

Physical characteristics and mineralogy

The SEM and XRD investigations of the salt-treated bentonite reveal no new mineral phases formed during the time period of the experiment. Additionally, no dissolution of smectite particle edges, such as etch pits or sutured edges, could be identified by SEM examination. Untreated IBECO samples show small, irregularly shaped flaky smectite particles with clusters of varying sizes (Figure 3a). However, notable and expected changes in particle behavior occur immediately on addition of the salt solution, with formation of sub-spherical aggregates, commonly 0.1–0.2 mm in diameter, producing a sand-like texture (Figure 3b). The resultant large pore-volume becomes rapidly saturated during the first seconds of the experiment. In our tests, 4 g of bentonite powder were saturated by the Q-brine within 2 s, driven by capillary forces. The enhanced permeability reflects the inhibiting effect of the salt solution on particle swelling (Studds *et al.*, 1998). These aggregates remained stable even after removal of excess

Table 2. Chemical composition of TIXOTON and IBECO as a function of reaction time (wt.% oxide).

% oxide	starting	IBECO		TIXOTON		
		3 days	150 days	starting	3 days	150 days
Al ₂ O ₃	17.76	15.49	16.43	17.50	17.76	16.81
Fe ₂ O ₃	4.72	4.15	4.43	5.10	5.15	5.00
CaO	6.02	4.76	4.90	3.70	2.80	2.52
MgO	2.99	3.81	3.98	3.90	4.98	4.64
K ₂ O	0.48	0.72	0.96	1.30	1.93	1.81
Na ₂ O	2.56	0.54	0.67	2.20	0.81	0.67

salt by washing the samples. Re-dispersion was only possible by ultrasonic probe treatment.

Whereas IBECO shows a typical XRD pattern for a Na-activated smectite, the TIXOTON starting material revealed unexpected XRD results. The d value of the 001 reflection lies at 12.7 Å (at 30% relative humidity) characteristic of a 1 H₂O layer structure, and the broadening of the low-angle peak shoulder indicates that a few 2 H₂O layers are present. It is therefore suspected that a mixture of monovalent and bivalent cations occupies the interlayer spaces, and that the bulk TIXOTON material has not been well Ca saturated.

The XRD patterns of the salt-treated smectite material show an increase in the d_{001} values from 12.6 Å to 15.4 Å, reflecting the typical exchange of monovalent cations by bivalent cations, responsible for building 2 H₂O layer structures (Figure 4a,b). These interlayer exchange reactions correspond well with the documented changes in solution composition and the chemical composition of the solid material. For both salt-treated smectites, the d values fluctuate between 14.9 Å and 15.4 Å without showing any time-dependent trend. As the humidity was held constant during XRD measurements, this behavior is considered to reflect insufficient cation exchange. Similar fluctuations can be

observed for the full-width-at-half-maximum (FWHM) data. Consistent differences in values are notable when comparing the different materials, whereby TIXOTON shows generally broader reflections (mean = 1.4°Δθ) than IBECO (mean = 0.74°Δθ), indicating thinner particle and smaller scattering domain sizes for the latter. No major changes in the accessory mineral phases were detected in the XRD data of the bentonite materials and no newly formed secondary mineral phases could be observed.

Cation exchange capacity

The CEC results give different values (72 meq/100 g⁻¹ and 82 meq/100 g⁻¹ for IBECO and TIXOTON, respectively) for the untreated, original starting materials (Figure 5). As IBECO contains 2.9% SO₃, the higher CEC values may relate to the precipitation of CuS. Despite these differences, both bentonite samples

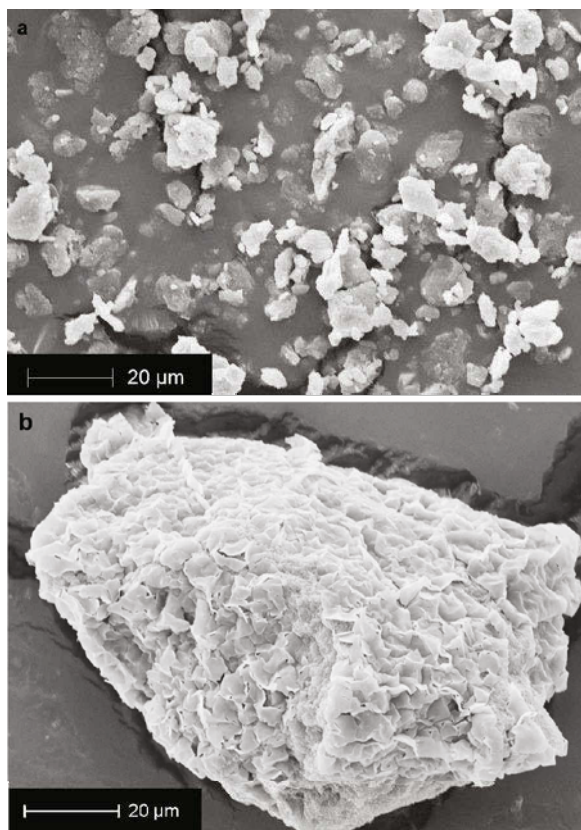


Figure 3. SEM image of (a) untreated bulk bentonite particles of IBECO and (b) aggregate induced after contact with salt brine.

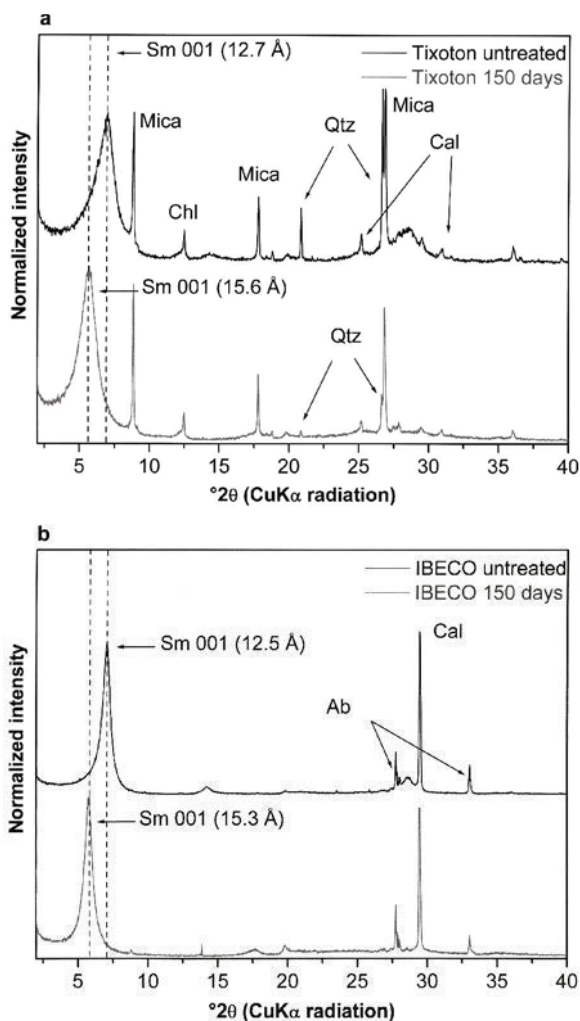


Figure 4. XRD patterns of (a) TIXOTON and (b) IBECO in original, untreated form and after 150 days of salt treatment. Ab = albite; Cal = calcite; Chl = chlorite; Qtz = quartz; Sm = smectite.

show similar CEC behavior throughout the duration of salt treatment. Statistical analyses of the data indicate that only small variations occur, ranging between 4 and 8% (σ_1 confidence level). These results indicate that no significant changes in the CEC of smectite were caused by salt treatment over the reaction time of 150 days. However, a slight decrease can be observed, compared to values of the original starting material during the first days of the experiment. The CEC values of TIXOTON decrease from 72 to 66 meq 100 g⁻¹ and IBECO decreases from 82 to 80 meq 100 g⁻¹.

In contrast to these minor changes, significant differences in the CEC do occur between aggregated and ultrasonically dispersed material (Figure 5). The undispersed smectite samples produced, on average, 20% lower CEC values than the disaggregated material. This effect is independent of reaction time and coincides with the formation of aggregate particles observed by SEM. Despite this reduction, the overall trend with time remains consistent.

Layer charge and layer-charge distribution

The permanent mean layer charge (charge density) of the original material for both bentonites ranges between 0.29 and 0.33 eq/(Si,Al)₄O₁₀ (Figure 6). That for IBECO is slightly higher than that of TIXOTON and the layer charge does not change significantly during exposure to the salt brine over the period of 150 days. However, a slight decrease in layer charge is evident for both smectites within the initial days of the experiment, similar to that described for the CEC, followed by an increase after 150 days towards the layer-charge values of the original starting material.

Differences in the shape of layer-charge distributions are evident when comparing original bentonite material before contact with salt solution (Figure 7 and 8). TIXOTON has a characteristic asymmetric distribution, with a well defined maximum skewed towards lower

layer charges (Figure 7a). In contrast, the layer-charge distribution of IBECO smectite is more symmetrical, with a poorly defined maximum, which is divided into a number of 'sub-peaks' (Figure 8a). This distribution may reflect a greater layer-charge heterogeneity and particle-size variations (Lagaly, 1994). Despite these differences in mean layer charge and layer-charge distributions between the two materials, no significant changes occurred during treatment with the salt brine at 3, 80 or 150 days (Figures 7b–d and 8b–d). That more complex distributions occur after 3 and 80 days for TIXOTON probably reflects artifacts in the measurement method. Similarly, the complex distribution patterns of IBECO appear to show no consistent time-dependent trends, although after 150 days of salt treatment, the distribution does appear more homogeneous in nature.

DISCUSSION

Interlayer exchange reactions and mineral dissolution

The results of our controlled 'short-term' experiments, conducted over 150 days under constant starting system variables (temperature, solution composition and solid/solution ratio), indicate that no detrimental reactions occurred after an initial time period of 3 days. During the first days of reaction, slight variations in solution chemistry were detectable, reflecting typical interlayer cation exchange behavior, where preferentially bivalent cations replace monovalent ones (Lagaly, 1993). For TIXOTON, exchange is marked by the notable substitution of Ca²⁺ and Na⁺ by Mg²⁺, derived from solution. As this material does not contain accessory calcite, it is assumed that the source of Ca²⁺ here lies in the interlayer sites of the smectite. Although Ca²⁺ is usually preferred over Mg²⁺, the opposite replacement of Ca²⁺ for Mg²⁺ within the interlayers is probably the result of the high Mg²⁺ concentration in

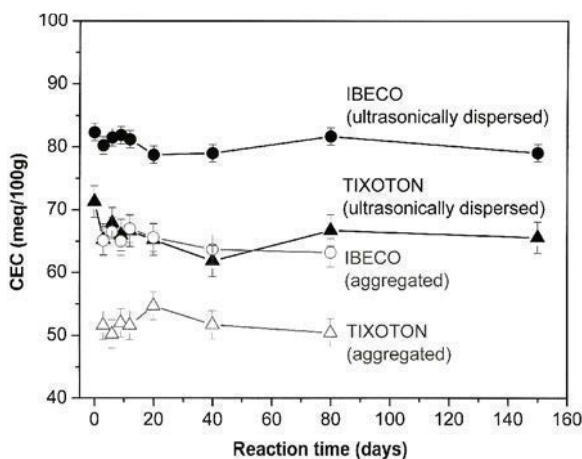


Figure 5. CEC of ultrasonically dispersed and aggregated IBECO and TIXOTON smectite.

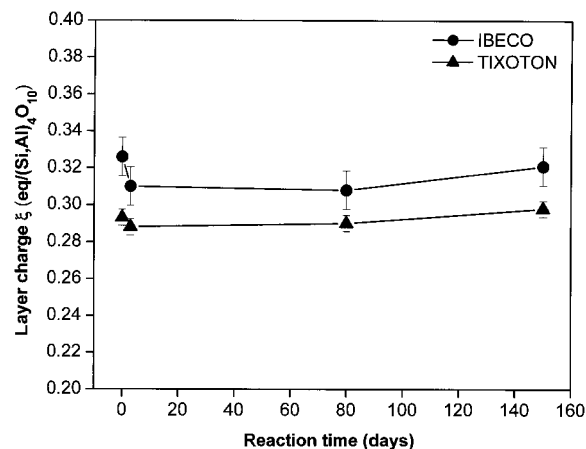


Figure 6. Mean layer charge of IBECO and TIXOTON smectite as a function of reaction time.

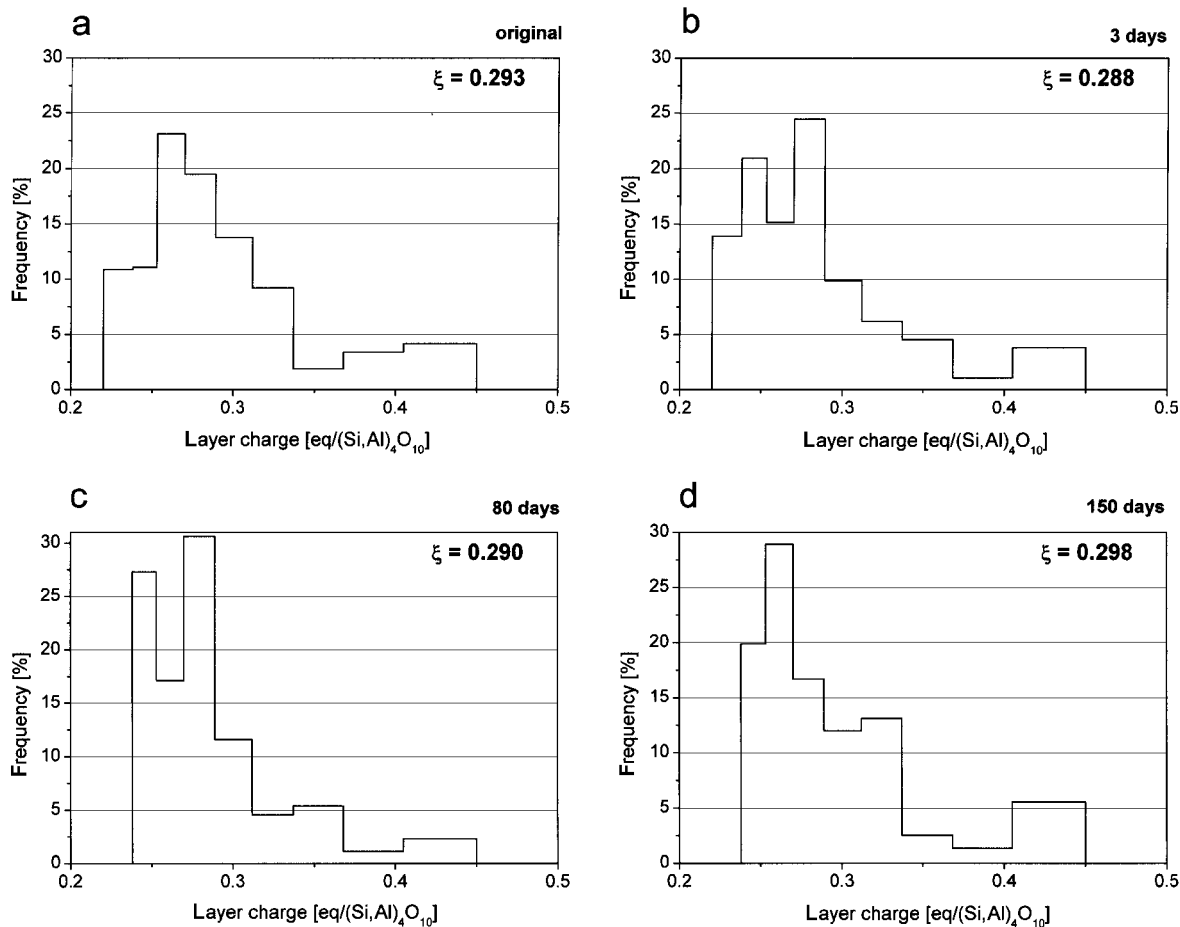


Figure 7. Layer-charge distributions of TIXOTON smectite as a function of reaction time.

solution (Lagaly, 1993). That minor amounts of K^+ were also sorbed into the smectite interlayers, indicates that preferred K^+ selectivity is maintained under these conditions and probably indicates that monovalent radionuclides (*i.e.* Cs^+) could be retained. In the IBECO bentonite sample, which has significant amounts of calcite, sorption of Ca^{2+} into the interlayer spaces was also detected, leading to decreasing concentrations in solution by up to 50%. This behavior also corresponds to the short-term changes in bentonite composition and indicates that the important sorption ability of smectite is not lost when coming into contact with the salt brine.

The dominant substitution of monovalent by bivalent cations in smectite interlayers can also be deduced from the XRD patterns. This exchange increases the basal spacings by forming 2 H_2O layer hydration states (Lagaly, 1993). The significant decrease in the number of expandable layers, attributed to layer 'collapse', as described by Bauer *et al.* (2001) and Kasbohm *et al.* (2000), during salt treatment was not observed in this study. Additionally, no changes in FWHM values reflecting differences in coherent particle thicknesses were detected.

In addition to the rapid exchange reactions described, our results also indicate that minor amounts of mineral dissolution occur within the first 3 days of the experiment. The initial increase in Al and Si concentrations in solutions could be related to dissolution of accessory mineral phases, such as aluminosilicates and SiO_2 phases. On the other hand, the increase of these elements could also indicate that some initial dissolution of smectite takes place, as reported in the experiments of Zysset and Schindler (1996), Schlabach (2000) and Metz (2001). In this study, a time-dependent increase in Al and Si concentrations was observed, albeit at lower solution concentrations and lower pH. The calculated Al/Si ratios of 0.20 and 0.24 in solution for TIXOTON and IBECO, respectively, as observed in our experiments, are significantly lower than the ratios calculated from the bulk compositions of the bentonite samples. Moreover, these low Al/Si ratios lie significantly below the Al/Si range of montmorillonitic smectites. Thus, the observed Al/Si in solution indicates non-stoichiometric dissolution at the onset of our experiments. Cama *et al.* (2000) and Metz (2001) studied smectite dissolution in both acidic and basic solutions, using flow-through

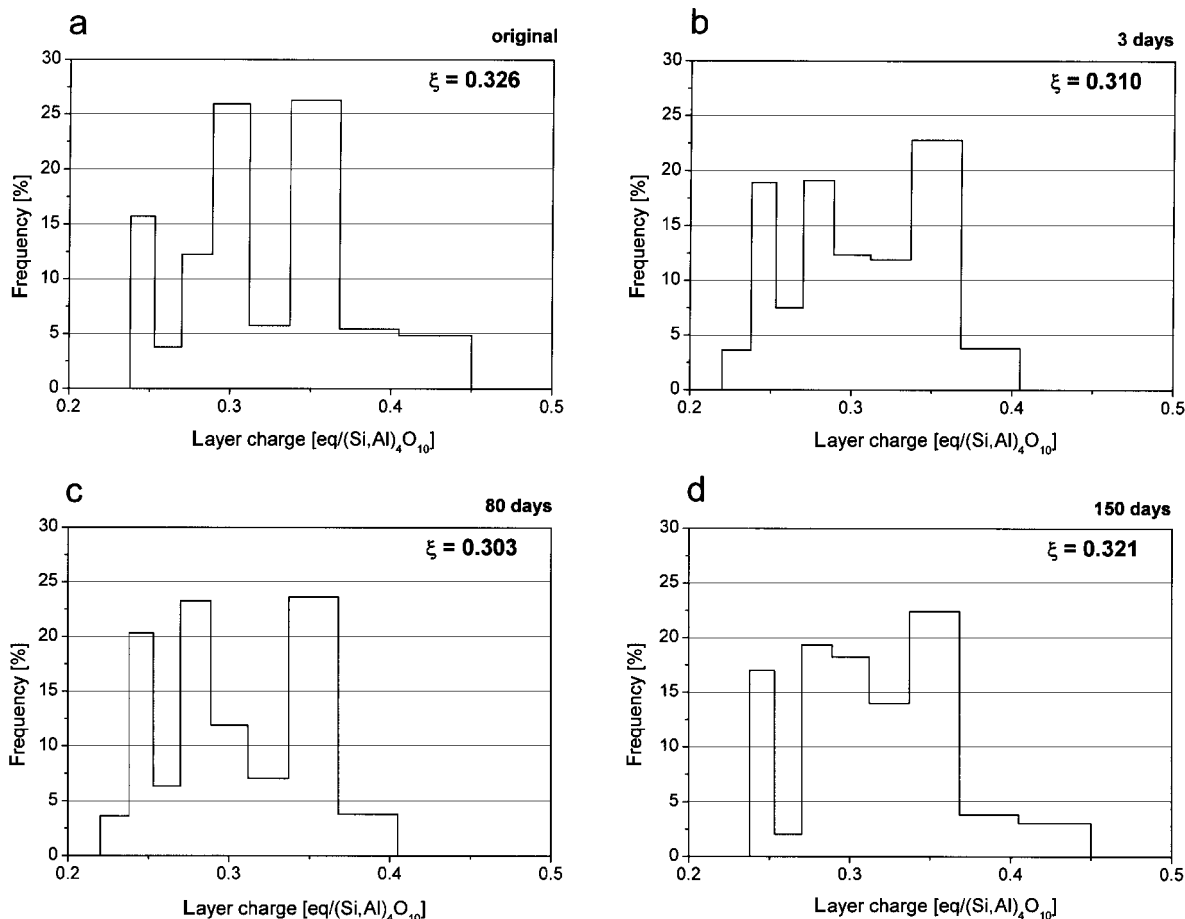


Figure 8. Layer-charge distributions of IBECO smectite as a function of reaction time.

experiments. Based on the release of Al, Si and Mg at steady state, they interpreted their results as reflecting stoichiometric smectite dissolution. However, Metz (2001) reported lower Al/Si ratios during the initial period of their experiments and suggested initial hydrolysis of accessory silica-rich phases which dissolve faster than smectite. The preferred release of Si over Al in our experiments therefore suggests that smectite is not the only mineral phase included in the dissolution process and probably involves accessory amorphous and crystalline phases (such as feldspar and amorphous silica).

That the pH reaches a steady state concentration after 3 days of reaction time, and no further Al and Si is released into the solution, implies that no further dissolution occurred during the remaining reaction time of the experiments. This can be attributed to the combination of high salt concentrations and neutral pH conditions, which have been shown experimentally to produce the lowest dissolution rates at 25°C. For example, Huertas *et al.* (2001) obtained the lowest rates of smectite dissolution at pH 8 using granitic solutions, and Zysset and Schindler (1996) reported the

lowest dissolution rates of Si and Al within brines of higher salt concentrations and pH 7–8. Although the slight change in solution chemistry does not conflict with the measured pH values and the chemical composition of the solids, it must be taken into account that the amount of consumed protons ($2.25 \times 10^{-7} \text{ mol L}^{-1} \text{ H}^+$) is much less than the amount of released Al ($7 \times 10^{-6} \text{ mol L}^{-1}$) and Si ($3 \times 10^{-5} \text{ mol L}^{-1} \text{ Si}$). If mineral dissolution occurs during the initial period of our experiments and the smectite is the main source for Al and Si, this source of dissolution can be considered as negligible.

Additional dissolution in the IBECO bentonite can be recognized during the first days of the experimental run, whereby calcite, the only carbonate-bearing mineral in the sample, dissolved to release Ca into solution. Calcite dissolution being strongly pH-dependent and being inhibited under neutral to alkaline conditions (Sjoberg and Rickard, 1984) implies that the availability of protons is the limiting factor. This explains the correlation between the increase of Ca in solution and increasing pH before reaching a steady state.

Particle aggregation, cation exchange and layer-charge characteristics

When the bentonite came into contact with the salt brine, strong aggregate formation was observed. This is accompanied by an increase in permeability, as indicated by the very fast, almost instantaneous, wetting of the material. The formation of smectite aggregates (coagulation) in contact with salt solutions is a well known phenomenon and can be explained by the DLVO theory (Lagaly, 1993). Here, the high cation concentration in solution prevents the formation of a colloidal dispersion by reducing the thickness of the electrostatic double layer, enabling the particles to stick together by van der Waals forces (Lagaly, 1993; Lagaly *et al.*, 1997). Investigation by SEM (Figure 4) shows clearly the small (<0.2 mm) and spherical shape and size of the formed aggregates, with properties typical of a sandy sediment. It appears that the void spaces between the particles are connected forming a micro-network which allows for migration of solution (Studds *et al.*, 1998).

The effect of aggregate formation on the chemical properties of the smectite is significant and can be seen in the CEC results. Ultrasonically dispersed samples, with the salt removed by a larger number of washing steps and additional dialysis, yield CEC values more than 20% higher than the undispersed, less-washed samples. This applies to both of the bentonites tested here, despite the presence of sulfide within IBECO. The inhibiting effect of salt solution on the CEC can be attributed to the reduction of the specific reactive particle surface area during aggregate formation (Hofmann, 2003). That aggregate formation inhibits complete cation exchange is also seen by the variation in *d* values of the 001 XRD peaks of the salt-treated samples, whereby monovalent interlayer cations are exchanged insufficiently by Mg^{2+} from solution. As aggregates can be broken up during dispersive treatment and additional washing, the CEC increases towards the values of the untreated material.

The slightly lower CEC values of the salt-treated samples suggests that the aggregates, although extensively washed, do not completely retain their dispersed state and thus the reactive particle surface remains slightly reduced. This behavior also implies that the CEC will be more significantly reduced in the presence of strong salt solutions due to the strong aggregate formation. That this effect is more evident in TIXOTON is considered to reflect the stronger tendency of Ca-activated smectite to coagulate (Brindley and Brown, 1980; Lagaly, 1993; Grace *et al.*, 1997). As variations in the CEC and thus sorption capability of the smectite are temporary effects that can be reversed by dispersion and washing, permanent changes do not occur over the experimental time scale of 150 days.

That the important chemical and mineralogical properties of the smectites remained preserved during

exposure to the salt brine is also evident in the measurement of mean layer charge and layer-charge distribution. No changes were detected indicating no cation substitutions within the crystal structure in vacant tetrahedral and/or octahedral sites. That there is a general correlation between the layer charge and the CEC values for both the bentonites suggests that layer-charge variations are the primary cause for CEC variations and not the presence or absence of sulfide. Any collapse of expandable layers, as described by Bauer *et al.* (2001), would be recognizable by an increase in layer charge or by a shift in the layer-charge distribution towards higher charges (*i.e.* by substitution of octahedral Al^{3+} for Mg^{2+}), which is not the case here.

Implications for the disposal of low- to medium-grade nuclear waste in salt repositories

Based on our experiments conducted under conditions relevant to the Asse test site, a number of aspects become apparent. That no significant mineral alteration took place within 150 days is an indication that the bentonite can remain stable over a long period of time, as long as the environmental conditions remain unchanged. Additional support for the long-term stability of smectite in saline environments can be obtained from the geological record. Many of the world's important bentonite deposits are often found in the Na-saturated state, where much of the Na originates from sea water during the alteration of volcanic ashes in marine to evaporitic environments (Moll, 2001; Vallés *et al.*, 1989). Bentonites may be preserved over significant periods of many millions of years without further alteration, as long as they do not significantly depart from the conditions under which they were formed and the temperature does not increase significantly over 60°C (Eberl *et al.*, 1993).

Another positive aspect of the experimental results was the persistence of exchange reactions within smectite interlayers, properties that were not lost during the salt treatment. Such exchange mechanisms are important if radionuclides are to be retained in the backfill material. However, it is also apparent that the salt solution has a detrimental effect on the CEC, which is reduced during contact of the smectite with the salt brine. As the CEC appears to be dependent on salt concentration, the exchange capacity of the smectite could be further reduced onsite in the salt repository if coming into contact with strong salt solutions. This problem is also coupled with the significant loss of swelling and an undesired increase in permeability that constitutes barrier breakdown.

CONCLUSIONS

(1) Under conditions selected to simulate the access of groundwater into the Asse salt dome test field, the two bentonites investigated (IBECO and TIXOTON)

remained chemically stable over the period of 150 days when treated with a saturated Mg-rich salt brine at 25°C.

(2) No new mineral products were formed during the experimental run and mineral dissolution was only active during the first days of contact with the salt brine. Furthermore, no modifications of the layer charge and layer-charge distribution of smectite occurred. Based on these results, a long-term chemical stability of smectite in salt brine is predicted, as long as the conditions do not vary significantly from those applied in this study.

(3) The physicochemical properties of smectite, namely sorption capability and swelling, were negatively influenced during contact with the salt brine, but not permanently destroyed. The CEC is probably reduced in the presence of salt solution, although interlayer cation exchange reactions continue to occur in this environment.

(4) The most significant problem of using bentonite in salt repositories is the formation of aggregates and the increasing permeability when coming into contact with the salt solution. This effect could lead to the physical breakdown of the backfill component.

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