

## **Short and Long Term Behavior of Bentonite under the Boundary Conditions of a Repository for High Level Radioactive Wastes - 9151**

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### **ABSTRACT**

Results of a 3 years study regarding the changes of MX-80 bentonite after reaction with solutions of different ionic strength and pH occurring in repositories in granite, in clay and in salt formations are presented. Each solution reacted differently with the bentonite and affected differently the resulting mineralogy and swelling pressure (SWP). After 3 years of reaction SWP were highest in contact with water (over 4 MPa), significantly lower in contact with low ionic strength solutions (around 3 MPa) and lowest in contact with high saline brines (mostly under 1 MPa). Alteration and partial dissolution of montmorillonite was observed. The Mg, Al and Si contents in the solutions increased with reaction time. Concomitantly in the octahedral layers of montmorillonite Mg was substituted by Al and the interlayer charge decreased. The correlation between the alteration process, the charge reduction and SWP is presented. The key for the observed mineralogical alteration may be the acidity of water in the interlayer space. This may explain why the alteration in compacted bentonite is faster than in the non-compacted. All results can be explained by processes which lead to a kaolinitization/pyrophyllitization and Si-excess of the montmorillonite particles. These processes may lead in the long run to a significant or even total loss of swelling capacity of compacted bentonites, if high saline solutions and cement are involved.

### **INTRODUCTION**

The objective of this study was the investigation of the mineralogical-chemical changes in the buffer material bentonite and their impact on the swelling capacity of bentonite under repository conditions. MX-80 bentonite was reacted with solutions of different chemical composition in a wide range of ionic strengths. For the experiments solutions were used which may occur in repositories in salt formations, in argillaceous formations and in granitic formations. Batch experiments with a low solid liquid ratio as well as experiments with highly compacted bentonite with a high solid-liquid ratio were conducted over a period of 3 years. Samples were analysed after 7 days, 1, 2 and 3 years of reaction.

[1] reported about changes of MX-80 bentonite in contact with saline solutions which led to several working hypotheses. The experiments in the present work aimed at finding new evidence in favor or against the following hypotheses.

- Pore solutions of different ionic strength influence the swelling pressure of bentonite differently.

- The layer charge of montmorillonite affects inversely the swelling pressure of run products.
- In closed reaction systems montmorillonite is undergoing a mineralogical alteration, which is causing a reduction of the interlayer charge in the run products. This reduced charge should lead in the short term to increasing swelling pressures.
- The theoretical end member of the alteration of montmorillonite in closed reaction systems may be kaolinite or pyrophyllite, leading in the long run to strongly reduced swelling pressures.

## **MATERIALS**

### **MX-80 Bentonite**

Commercial MX-80 bentonite (Wyoming, USA) is a highly heterogeneous material composed by 67-88 wt.% of montmorillonite clay particles [2]. The total cation exchange of the montmorillonite is between 0.78 and 0.85 meq/g, which implies a total charge of 0.30; and the cation population at exchange sites is mainly composed by Na (0.624-0.668 meq/g), apart from Ca (0.066-0.074 meq/g), Mg (0.03-0.04 meq/g) and K (0.002-0.013 meq/g) [3]. The MX-80 bentonite used in this study contains 90 wt.-% of montmorillonite, 4 wt.-% quartz, 2 wt.-% albite; and trace amounts of calcite, cristobalite and pyrite. A more detailed mineralogical description of the employed bentonite can be found in [1].

### **Initial Solutions**

The bentonite-water interaction experiments were performed with the following solutions which cover a wide range of pH (5.3 - 13.2) and salinities (with ionic strengths 0 - 15.5):

- Distilled water (H<sub>2</sub>O), which was used for comparison with the other solutions.
- Äspö granitic ground water (Äspö), which is a Baltic seawater encountered in the crystalline rocks of the Äspö underground laboratory in Sweden.
- Opalinus clay pore water, (Opalinus), which is the pore water of the argillaceous formation Opalinus Clay at Mont Terri Rock Laboratory in Switzerland.
- NaCl solution (NaCl), which is a typical NaCl rich brine encountered in the Zechstein salt formations in Germany and saturated only with halite.
- IP21 solution (IP21), is a MgCl<sub>2</sub>-rich brine which may be encountered in German Zechstein salt formations with potash beds. An IP21 solution is saturated with the salt minerals: halite, carnallite, sylvite, kainite and polyhalite.
- Young Portland cement pore water (YCP), is a solution consisting of water saturated with portlandite. This solution represents the pore water of concretes.
- A solution resulted from the degradation of a salt concrete by a NaCl solution (NaCl+cement), which may occur in the pore space of salt concrete abutments in salt repositories.
- A solution resulted from the degradation of a salt concrete by an IP21 solution (IP21+cement), which may occur in the pore space of concrete abutments in salt repositories with outcrops of potash beds.

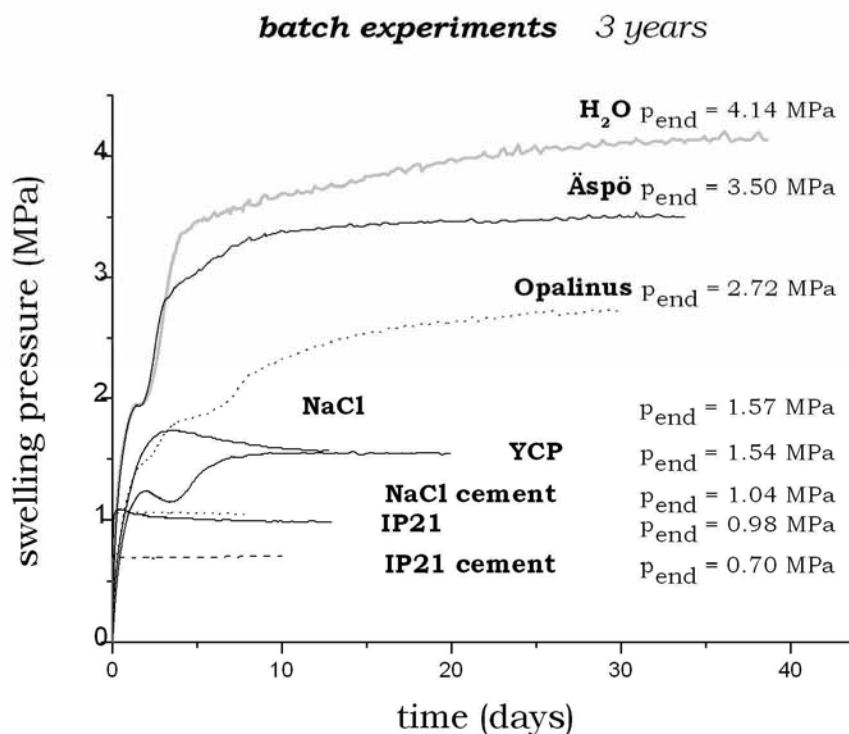
The chemical composition of these solutions is given in [4].

## RESULTS

The most important results are discussed below and presented in Fig. 1 - 4.

### Swelling pressure

With increasing salinity of the solution, the swelling pressure of bentonite decreases. Swelling pressure measurements of untreated original MX-80 bentonite performed a few hours after the first contact with the different solutions showed three groups of SWP values: the high pressure group with an end value of 2.94 MPa for water, a second group with end values between 2.02 and 2.47 MPa related to the medium ionic strength solutions Äspö, Opalinus and YCP; and a third group with very low SWP's between 0.64 and 0.97 MPa related to the high saline solutions IP21, IP21+cement, NaCl and NaCl+cement. The same pattern was observed in all experiments after 7 days, 1 year, 2 years and 3 years of reaction. After 3 years of reaction the SWP values are slightly higher than at the start of the experiments. Fig. 1 shows SWP measurements after 3 years of reaction with the different solutions.



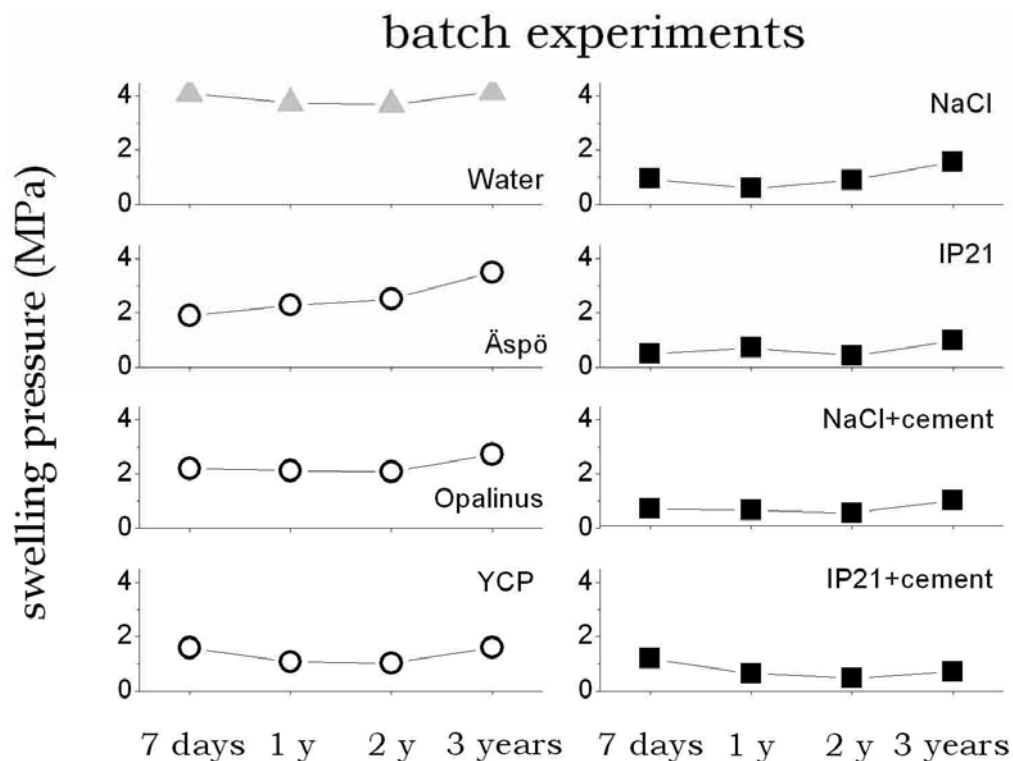
**Fig. 1. Swelling pressure measurements of MX-80 bentonite after 3 years of reaction with solutions of different ionic strength (batch experiments)**

Regarding the evolution in time of the SWP's in the different solutions and in the two types of experiments the following results were obtained (Fig. 2):

- In general the SWP's were slightly higher in the batch experiments than in the compaction experiments;

- Over a reaction period of three years the SWP's of the batch experiments generally increased after passing through a minimum after one or two years;
- In the compaction experiments the SWP's didn't change significantly during the first two years and didn't show a uniform general trend. After the third year however the SWP's increased only in the medium ionic strength solution Opalinus, and decreased significantly in the high saline solutions NaCl and IP21. A similar trend was observed in the YCP sample. The missing values for some of the three years samples in Fig. 2 are caused by lack of enough material for these measurements.

The results show, that the salinity (ionic strength) of the reacting solutions affects the SWP's more than the type of main cation in the exchange sites. All the SWP's of bentonite with high ionic strength solutions belong to the low pressure group regardless if the solutions are Na or Mg dominated. No obvious differences can be recognized between the Na-dominated systems (NaCl, NaCl+cement) and the Mg-dominated systems (IP21, IP21+cement).

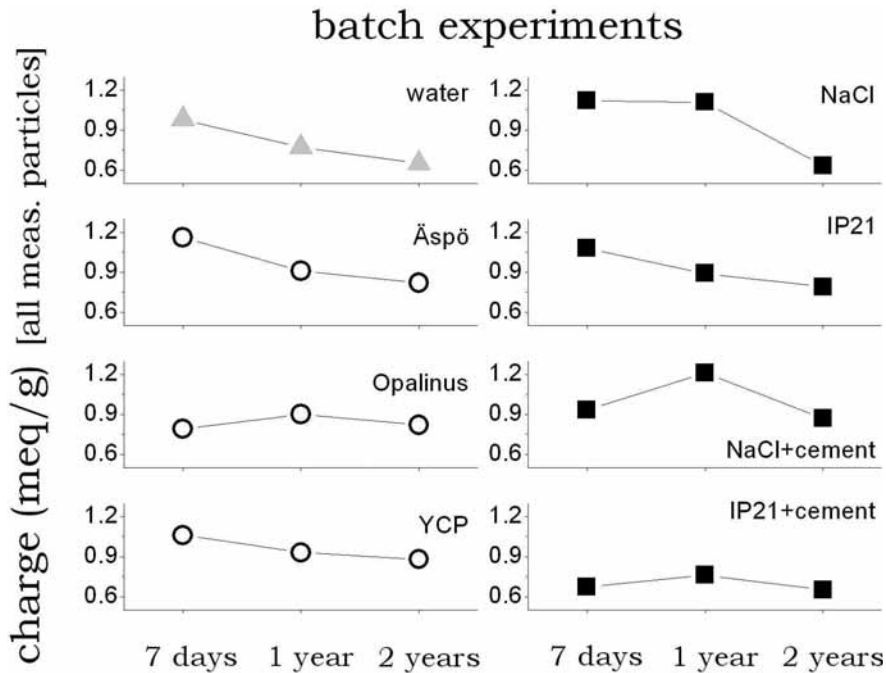


(high ionic strength: NaCl, IP21, NaCl cement, IP21 cement; medium ionic strength: Äspö, Opalinus, YCP; low ionic strength: water)

**Fig. 2. Development of MX-80 swelling pressure due to the interaction with different ionic strength solutions**

**Interlayer charge (ICh) and Total Charge (TCh)**

The chemical composition of several hundreds of clay particles was measured after the reaction of MX-80 bentonite with the 8 fluids by TEM-EDX. The vast majority of the particles were montmorillonite, but not all. Some particles were illite-smectite mixed layers and others dioctahedral vermiculite-smectite mixed layers. For each measured particle the chemical formula was calculated. From the formula the interlayer charge was derived. Mean values of the interlayer charge values were calculated for each investigated bentonite-solution sample. ICh stands for the interlayer charge of the pure montmorillonite particles and TCh for the mean value of all particles measured in a bentonite sample (montmorillonites and mixed layer particles). The interlayer charge (ICh) of pure montmorillonite phases shows in most cases a clear decreasing trend with reaction time (Fig. 3), illustrating the development of montmorillonite into a low charge smectite. The TCh development over time of all measured particles and the correlation with the SWP's (Fig 4 above) shows that not only the ICh of montmorillonite particles but also the TCh of all measured particles decreases with the reaction time.



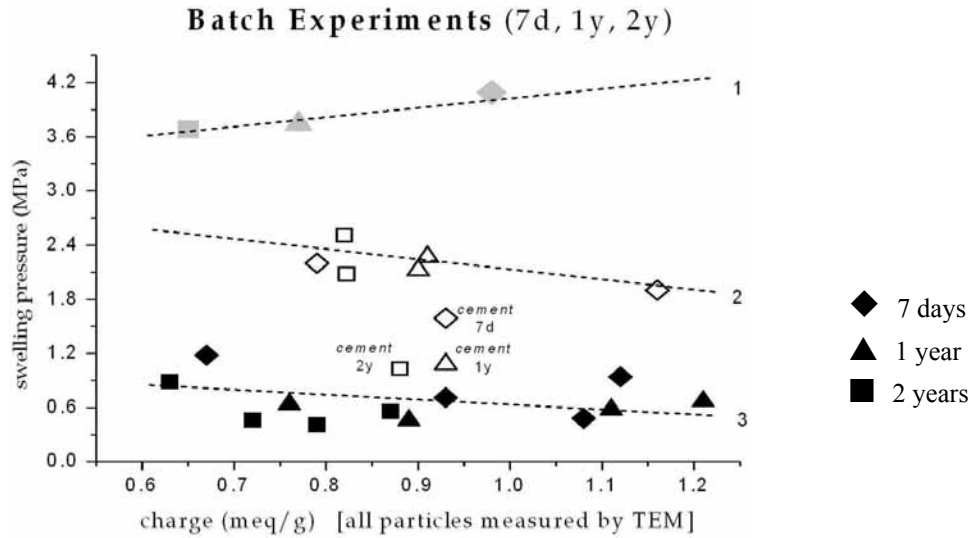
(high ionic strength: NaCl, IP21, NaCl cement, IP21 cement; medium ionic strength: Äspö, Opalinus, YCP; low ionic strength: water)

**Fig. 3. Interlayer charge of all particles measured by TEM-EDX (batch experiments)**

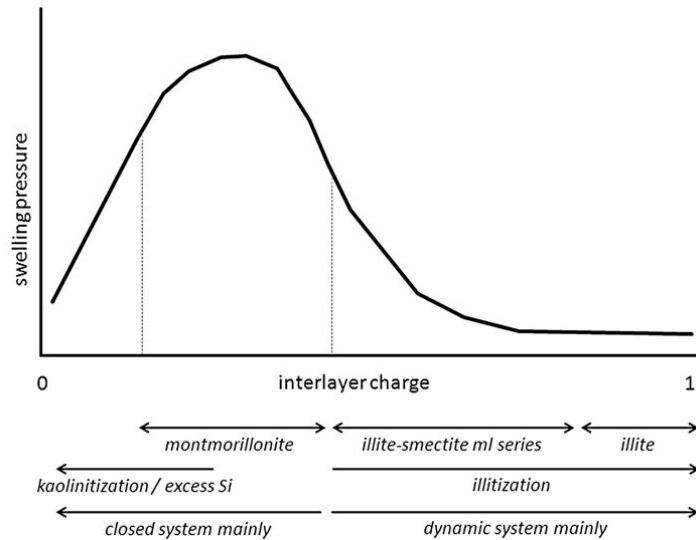
**Interdependence of TCh and SWP**

The correlation between TCh and SWP (Fig. 4 above) shows three groups of samples with high, low and very low swelling pressures as a function of ionic strength of the solutions. The YCP samples occupy an intermediate space between the intermediate and high ionic strength solution samples. Regarding the correlation between TCh and SWP a slightly negative correlation

(increasing SWP with decreasing TCh) seems to exist for the intermediate ionic strength solutions Äspö and Opalinus. A similar trend may also exist for the high ionic strength solutions (NaCl, IP21, NaCl+cement and IP21+cement) even if it is not very pronounced. The working hypothesis that the layer charge affects inversely the swelling pressure of run products seems to be confirmed by the data from the experiments with medium and maybe also with high ionic strength solutions.



1 - low ionic strength: water, 2 - medium ionic strength: Äspö, Opalinus, YCP; 3 - high ionic strength: NaCl, IP21, NaCl cement, IP21 cement;



Interlayer charge per half cell unit = 0 is valid for kaolinite or pyrophyllite as an end member of montmorillonite alteration; interlayer charge per half cell unit = 1 is valid for illite or mica as another end member of montmorillonite alteration

**Fig. 4. (above) Measured correlation between SWP and total charge (TCh)  
 (below) Predicted correlation between interlayer charge (ICh) of clay minerals in bentonites and SWP**

The water samples show an inverse trend, i.e. a direct correlation between TCh and SWP. This may be explained with the very low concentration of electrolytes in this system. The lack of counter ions is probable responsible for the direct correlation between charge and distance of the double diffuse layer.

### **Mineral matter of run products and alteration of montmorillonite**

Over the entire reaction time, montmorillonite remained in all samples the dominating mineralogical phase. Newly formed mineral phases like zeolites have not been identified. XRD measurements showed that the montmorillonite particles maintained their full expandability to 16.9 Å with ethylene-glycol. Nevertheless significant alteration of the montmorillonite became obvious by using transmission electron microscopy (TEM). After the reaction in the different solutions, all smectite particles showed to a different degree a conversion from an initial film like matrix of very thin xenomorphous platy aggregates into discrete well oriented xenomorphous platy particles. The intensity of this process increased with the salinity and pH of solution. Furthermore, in the batch experiments we observed that the original turbostratic layer orientation in the stacks was transformed into 1M polytype. This process was extremely fast with the YCP solution, in which the transformation was completed already after 7 days. The changes in morphology and stack order for all particles were accompanied by a substitution of octahedral Mg by Al. This substitution has caused a substantially lower interlayer charge (partially <0.2 per half unit cell) for smectite. For the Äspö-solution sample the chemical composition of octahedral layer is altered as follows:

untreated MX-80:  $\text{Al}_{1.54} \text{Fe}^{3+}_{0.17} \text{Mg}_{0.26}$ ,  
after 7 days:  $\text{Al}_{1.54} \text{Fe}^{3+}_{0.17} \text{Mg}_{0.25}$ ,  
after 1 year:  $\text{Al}_{1.57} \text{Fe}^{3+}_{0.18} \text{Mg}_{0.22}$ ,  
after 2 years:  $\text{Al}_{1.63} \text{Fe}^{3+}_{0.15} \text{Mg}_{0.20}$ .

The averaged mineral formula of all measured and calculated montmorillonite particles in all experiments shows a trend to higher Al and lower Mg values in the octahedral layer compared to the montmorillonite in the original MX-80 bentonite. This trend increases with reaction time. This alteration of octahedral layer, the substitution of Mg by Al is the cause for the development of montmorillonite into low charge smectite. The alteration rate of morphology and the change of stack order of particles are controlled by salinity. It seems to be possible to detect an order of alteration rate: water < Äspö, Opalinus << NaCl, NaCl+cement < IP21, IP21+cement << young cement.

### **DISCUSSION**

The discussion concentrates on the parameters which influence the swelling pressure. The initially postulated working hypotheses are discussed in the light of these results.

### **Pore Solutions of Different Ionic Strength influence the Swelling Pressure of Bentonite differently**

This working hypothesis is confirmed by all the experiments (Fig.1 – Fig.4). The dependence of SWP from the salinity of solution is caused mainly by the double-layer swelling (in the sense of [5]). Higher concentrations of counter ions between quasi crystals reduce the volume of aggregates.

### **Montmorillonite Layer Charge affects inversely the Swelling Pressure of Bentonite**

The layer charge of montmorillonite affects inversely the swelling pressure of run products. This hypothesis seems to be confirmed by the majority of the batch experiments. The trend of slightly rising swelling pressures with decreasing TCh is clear for the medium ionic strength solutions (Fig. 4). This trend may also exist for all the high ionic strength solutions although it is less pronounced. An inverse trend was obtained only for the experiments with de-ionized water. In the water system the concentration of counter ions between the quasi crystals is extremely low. Thus the charge of the clay mineral surface determines directly the extension of the double layers. With an extremely low electrolyte concentration a high charge requires a large volume in order to obtain enough counter ions for electrical balance.

SWP rise in the time interval from 2 to 3 years (Fig. 2). According to our working hypothesis the TCh should decrease continuously in the samples from 7 days, 1 year, 2 years and 3 years. This trend has been proved by the NaCl samples where the following TCh's were determined: 7 d = 1.12 meq/g, 1 year = 1.11 meq/g, 2 years = 0.63 meq/g and 3 years < 0.5 meq/g. Whereas in the first 2 years primarily the substitution of Mg by Al in the octahedral layers causes the decreasing charge values, in the third year dissolution processes seem to become more important. Over 60% of the analyzed particles in the 3 years sample have excess Si in the EDX-analysis. We have strong indications that some of the 2:1 sheets within a single particle have lost in some sheets their octahedral layers.

### **Montmorillonite Alteration in Closed Systems – Reduction of Interlayer Charge**

In closed reaction systems montmorillonite is undergoing a mineralogical alteration, which is causing a reduction of the interlayer charge in the run products. This reduced charge should lead in the short run to increasing swelling pressures and in the long run to a loss of swelling pressure. The setup used in our experiments can be considered, at least from a macroscopic point of view, as a closed system. Dissolution and precipitation processes have been observed in the interlayer spaces. While the mass of particles must not yet be totally dissolved, a reorientation of the single montmorillonite particles and a change from the turbostratic to the 1M ploytyp structure takes place. This process is accompanied by the substitution of Mg by Al in the octahedral layers, which in turn is responsible for the reduction of the interlayer charge of montmorillonite and of the total charge of all measured particles. Kaolinite structures in the run products have already been observed. Kaolinite or pyrophyllite may represent end members of the documented trends towards lower charges (Fig. 4 below).

[6] have already described a „solid state transformation“ in the interlayer space. [7] too have used this process to explain their experimental results. They also have found low charge and high charge smectites in their reaction products. Comparable phases have been found in our experiments as well in the form of IS (= high charge type) and diVS (= low charge type) mixed



layers structures. The higher charge of these particles (as a result of their higher number of mica sheets) increases sometimes the TCh of the sample and overlap sometimes the obvious trend of decreasing charge over time. But even these phases show decreasing charges over time.

As protons penetrate into clay layers and attack the OH groups, the resulting dehydroxylation connected with successive dissolution of the octahedral sheet can be readily followed by intensity decreases in the hydroxyl-bending vibrations of  $\text{Al}_2\text{OH}$  and  $\text{AlMgOH}$  at  $915$  and  $842\text{ cm}^{-1}$ , respectively by IR spectroscopy [8]. There also exists an order in which bindings are attacked. Because of the isoelectric points the  $-\text{Mg}-\text{O}-$  surface functional group is the first site to be protonated, followed by octahedral  $-\text{Al}-\text{O}-$ , tetrahedral  $-\text{Al}-\text{O}-$  and  $\text{Si}-\text{O}-$  groups [9]. This explains why in a closed system Mg is exchanged by Al.

The smectite alteration increases with higher Mg and Fe contents [10]. This behavior can be deduced from the binding energies respectively from the solubilities of the respective metal oxides. The succession of solubilities is:  $\text{Mg}^{2+} > \text{Fe}^{2+} > \text{Fe}^{3+} > \text{Al}^{3+}$ . That means that stresses in the lattice due to the presence of different cations in the octahedral layer would lead to an accelerated alteration [11]. In [8] an approach can be found for the discussion of the alteration as a function of the cations in the reacting solutions. [8] found that freshly protonized smectites showed strong and weak sites at the surface, the number of strongest acid sites (60 – 90% of the total acidity) decreased by ageing, while the number of all weaker acid sites increased with auto transformation. The strongest acid sites were connected with free protons present in the dispersion, while the weaker acid sites were connected with  $\text{Al}^{3+}$ ,  $\text{Fe}^{3+}$  and  $\text{Mg}^{2+}$  cations released from the structure [12] Auto transformation decreased the mean layer charge, suggesting that protons attack preferentially the  $\text{Mg}(\text{O},\text{OH})_6$  octahedra [13].

The observed enrichment of Si in the samples can now be explained. Infrared spectrometric investigations have shown that Al-O-Al bindings are broken and Si-OH-H bindings are closed. That means that this reaction in the interlayers is characterized not just by a pure dissolution process but also by a rearrangement of parts of the relictic tetrahedral sheets [10]. The samples of the compacted experiments seem to undergo the described processes faster than the samples in the batch experiments. [14] have evaluated papers which proved that the relative permittivity of the water phase decreases with decreasing water contents. This in turn raises the acidity of the interlayer water (which now can be penetrated easier by  $\text{H}^+$  protons). In this way it seems logic that the smaller pore space of the compacted samples accelerates the alteration.

### **Alteration Product of Montmorillonite - Kaolinite or Pyrophyllite**

The theoretical end member of the alteration of montmorillonite in closed reaction systems may be kaolinite or pyrophyllite, leading in the long run to strongly reduced swelling pressures.

According to our experimental results two different ways of alteration can be distinguished: (i) normal charge montmorillonite via low charge montmorillonite into a kaolinite–montmorillonite–dioctahedral vermiculite mixed layer (KSV-ml) phase and (ii) normal charge montmorillonite via IS-ml via VS-ml into KSV-ml. Both processes can occur concomitantly but in different particles.

- *Why do emerge from montmorillonite-tetrahedral layers ( $\text{Si} \sim 4$ ), mica like tetrahedral layers ( $\text{Si} = 3.0 \dots 3.2$ )?*

At the time being we have only guesses about the mechanism of the formation of mixed layers. Essentially two mechanisms seem possible, but they must be proved in the future. First it seems possible that equilibrium reactions take place between the interlayer space and the neighboring

pore solution. On a submicroscopic scale this would be an open system. A Si-surplus in the interlayer would be reduced by this equilibrium reaction. In this situation only mica-like tetrahedral layers could recrystallize. On the other hand [8] described alteration mechanisms of bentonites treated with acids. He pointed out that freshly protonized smectites showed strong and weak sites at surface, the number of strongest acid sites (60 – 90% of the total acidity) decreased on ageing, while the number of all weaker acid sites increased with auto transformation. The occurrence of IS-ml in our experiments and their successive transformation could correspond to [8] observation. Whereas the aging process was observed by [8] during the acid activation within a few days, it took much longer time in our experiments with solutions of weaker acidity. Komadel's mechanisms could explain the development of lower charges.

- *How does the kaolinitization/pyrophyllitization happen?*

[1] described already in previous experiments in closed systems the charge reduction of montmorillonite over time in the reaction products. If the underlying process, the substitution of Mg by Al, continues kaolinite or pyrophyllite could be expected as end members of the montmorillonite transformation. KSV mixed layers appeared already after 2 years in the compaction experiments and after three years in the batch experiments. Also [15] have described the occurrence of KSV-ml phases in long term experiments with compacted MX-80 bentonite. On the other hand we also observed in the compaction experiments that more and more montmorillonite particles show a surplus of Si. In accordance with the findings of the activation mechanisms, the alteration of the octahedral layers continues until they are totally dissolved. Afterwards only the crystalline Si tetrahedral layers persist. How can this process be explained? Due to the gradual decomposition of the octahedral layers according to [16]  $Al^{3+}$  acts in the interlayer more and more also as counter ion. In particular the weak charge sites bind the cations which have been liberated previously [8]. In this way the acidity in the interlayers increases, because the higher polarizing ability of the interlayer cations increases both the strength and number of acid sites per surface and area – decreasing strength from Al, Fe, Mg, Ca, Li, Na, K to Cs [9]. In addition the substitution of Si by Al in the tetrahedral layer (formation of IS-ml) increases the acidity. This substitution leads according to [9] to an increase in both types of surface acidity, acceptance and donation of electron pairs (the Si atom uses vacant d orbitals to form  $\pi$  bonds with O atoms).

- *Why appear KSV-ml first in the compaction experiments?*

Water donation tendency increases as the water content of the interlayer space decreases [9]. This is in accordance with the observation of [14] who have described a reduced remittivity of water molecules with reduced water volume. As a consequence of the smaller pore space and the higher acidity of the water molecules the alteration occurs faster in the compacted experiments than in the batch experiments.

Both processes, the kaolinitization/pyrophyllitization and the appearance of surplus Si reduce the charge of the particles to a minimum. Thus, if the charge reduction continues a critical point can be expected, at which the previously rising SWP collapses. Fig. 4 below illustrates this hypothetic correlation between charge and swelling pressure. A charge reduction as a result of illitization processes (formation of IS) reduces the SWP (see the first 2 years of the batch experiments, Fig. 2). As long as the charge reduction has not yet passed a critical point the SWP rises (see SWP raises in the third year of the batch experiments, Fig. 2). If this critical point is

passed and the charge reduction continues the SWP collapses (see Fig. 2, the decrease of SWP in the third year of the compacted experiments with high ionic strength solutions NaCl and IP21). This point has not yet been reached in the sample with the lower ionic strength solutions Opalinus. This sample shows still the same behavior (rising SWP as in the corresponding batch experiment).

## CONCLUSIONS

Taking into account the acidity of the interlayer water and regarding the known mechanisms of the acid activation of bentonites tentative explanations have been given for the mechanisms of the montmorillonite alteration processes observed in our experiments. This opens new approaches for the quantification of the alteration processes and for the verification of the existing information on the long term stability of bentonite. High ionic strength solutions seem to accelerate (because of the higher acidity of the interlayer water) the transformation rate. In compacted bentonites the amount of water with higher acidity is higher which increases the transformation rate even more. The expected kaolinitization/pyrophyllitization and Si-excess may lead in the long run to a significant or even total loss of swelling capacity of compacted bentonites, if high saline solutions and cement are involved. Therefore the question which must be answered is not, whether or not bentonites are stable under the conditions of a repository in salt, but rather, how much swelling capacity is needed and for how long.

So far the practical relevance of the possible collapse of the SWP due to long term mineral transformation is not yet clear. Still open is also the quantitative relationship: alteration–SWP–permeability.

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