5.2
On the short- and long-term behaviour of bentonites as technical barriers material in final repositories for radioactive wastes

The objective of the final disposal of highly radioactive wastes in deep geological formations is it to isolate the pollutants from the biosphere for long periods of time. This objective can be achieved by means of a multi-barrier concept which combines geological and technical barriers. As potential materials for technical barriers, so-called bentonites are being discussed. These are expandable, plastic clay rocks with high sealing potential. Especially in salt formations, but also in other geological host rocks, saline solutions may occur which react with the bentonites and alter their properties. The interactions with the solutions alter the mineralogical composition and thus the swelling and sealing properties of the bentonites.

Within the scope of the EU project NF-PRO, GRS conducted a study with the aim to collect data concerning the relevant interactions between bentonites and saline solutions in a wide ionic strength and pH range and the impacts thereof on the short- and long-term behaviour of the technical barrier. The study was carried out in co-operation with Prof. J. Kasbohm (Greifswald University).
Scientific background

Working hypotheses. Herbert et al. (Long-term behaviour of the Wyoming bentonite MX-80 in high saline solutions, Applied Clay Science 26, 2004) reported on interactions between the Wyoming bentonite MX-80 with saline solutions. For the new GRS study introduced here, this resulted in the following working hypotheses which were to be verified:

1. Saline solutions of varying ionic strength influence the swelling pressure of compacted bentonites to different degrees.
2. When bentonites react with saline solutions, both the mineralogical and the chemical properties of the montmorillonite, an expandable smectitic clay mineral which makes up 70-90% of the bentonite composition, are modified in a way that its interlayer charge is reduced which causes the swelling pressure to decrease and the permeability of the compacted bentonite to increase.
3. The end member of the mineralogical modification of the montmorillonite could be kaolinite or pyrophyllite which in the long run leads to the reduction of swelling capacity and swelling pressure and thus of the scaling effect, too.

Evaluation of research literature. In the relevant scientific literature, information can be found which indicates that these hypotheses are correct; however, some opposing opinions have been expressed as well. According to the so-called DLVO theory, the electrolyte concentration and the layer charge of the clay minerals influence the bentonites' swelling pressure. Savage (The Effects of High Salinity Groundwater on the Performance of Clay Barriers, SKI Report 2005: 54) and Laird (Influence of layer charge on swelling of smectites, Applied Clay Science 34, 2006) described the interrelations between the layer charge of smectites and the swelling pressure of bentonites. According to these authors, the swelling capacity decreases with increasing charge density since a higher charge leads to the integration of more higher-valent cations into the interlayers. At first, this seems to be contradictory to the second working hypothesis. Furthermore - and just like Herbert et al. - the authors found, however, that with the increasing salinity of the solution the swelling capacity decreases. Laird described several different processes which control the swelling of smectites saturated with alkali and alkaline earth metal cations: a) crystalline swelling, b) double-layer swelling, c) internal volume swelling, and d) swelling due to the Brownian motion. A direct impact of the layer charge on the swelling can only be expected for the crystalline swelling. The crystalline swelling degree decreases with an increasing layer charge. Laird further described the appearance and disappearance of so-called quasi-crystals as a dynamic process in an aqueous smectite suspension. With the layer charge increasing, the quasi-crystals become bigger and more stable. Pusch et
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al. (Evolution of clay buffer under repository conditions. Reprints of the contributions to the workshop on long-term performance of smectitic clays, 2007) also developed a concept which describes those parameters which influence the swelling pressure. Pusch’s definition »interlamellar pressure« or »disjoining pressure« can be compared to Laird’s »crystalline swelling«; and Pusch’s »osmotic pressure« corresponds with Laird’s »double-layer swelling«.

**Experimental programme**

*Verifying hypotheses in experiments.* To verify the above-mentioned hypotheses, a three-year experimental programme was set up. MX-80 bentonite was exposed to seven saline solutions of different compositions, ionic strengths and pH values and with two different solid to solution ratios (tests with compacted bentonite with little solution in the pore space and batch tests with non-compacted bentonite with a high excess of solution).

The solutions were as follows:

1. Fissure water out of the granite of the Swedish underground laboratory Äspö,
2. Pore water out of the opalinus clay of the Swiss underground laboratory in Mont Terri,
3. a pure saturated NaCl solution,
4. a carnallite-saturated, Mg-rich IP21 solution as can be found in salt formations in northern Germany,
5. and 6. corrosion solutions which are produced when salt concrete (a special type of concrete with salt as aggregate which is used in salt mines) reacts with NaCl and IP21 solution, and
6. a low saline, but very alkaline young Portland cement pore water (YPC).

For comparison, the tests were also carried out with pure water as the knowledge about interactions of bentonites with water is the greatest. Samples were analysed after reaction times of seven days, one, two and three years. The composition of the solution, the mineralogical composition of the bentonite, the chemical changes of the montmorillonites and the swelling pressure of the bentonite were measured. Fig. 54 »SWELLING PRESSURE MEASURING CELLS« shows the setup of swelling pressure measuring cells and the data collection in the laboratory.

**Results**

*Swelling capacity of the montmorillonites.* Overall, both in the compacted and in the non-compacted bentonite samples, the swelling capacity of the montmorillonites persisted for all solutions they were in contact with over the entire observation period of three years. This was demonstrated through the expansion of the montmorillonite interlayers by means of ethylene-glycol. At the beginning and at the end of the experiments, the maximum interlayer distance at glycol saturation was reached and consistently amounted to 17 Å. Nevertheless, each of the eight solutions caused distinct mineralogical and chemical alterations of the montmorillonites albeit to different extents.

*Changed swelling pressure.* These alterations are also reflected by the changes of the swelling pressures. As expected, the measured swelling pressures were highest for water and declined with increasing salinity (and increasing pH value) of the solutions (see Fig. 55 »SWELLING PRESSURE«). Although the drop in swelling pressure of compacted bentonite in contact with water compared to the swelling pressure with low-saline solutions is clear, it is still moderate compared to the strong decline during reaction with high saline solutions. In respect of the swelling pressures, the Young Portland cement pore water (YCP) takes a middle position: It does indeed show low salinity, but in turn, it also shows a high pH value. This observation, too, confirmed the working hypotheses described at the beginning. A surprising observation was, however,
Experimental Results

Fig. 55–57
Swelling pressures with different solutions
Batch experiments with excess solution

that with progressing reaction time the swelling pressures did not drop but, on the contrary, increased (see Fig. 56 and 57). This led – for a short time at least – to an improved sealing effect of the bentonite in contact with the examined solutions.

Partial dissolution of clay particles. At the same time, a partial dissolution of clay particles was observed which caused the Al content of the solution to increase. In the montmorillonite particles which were maintained, an increasing Si excess and a reduction of the total charge and the interlayer charge were observed with progressing reaction time. This is due to the exchange of Mg and Al in the octahedron layers. In addition, it was observed that the alterations of the montmorillonites in the compacted bentonite samples proceed faster than in the batch experiments with excess solution. One possible explanation for this is the acidity of the interlayer water which is higher compared to the pore water. Yariv & Michaelian (Surface acidity of clay minerals. Industrial examples—Angewandte Geowissenschaften 1, 181-190, 1997) discovered that the amount of dissociated water in the interlayers of the montmorillonite is 107 times higher than in the pore space of the bentonite because the dielectric constant of the interlayer water is lower than the one of the free water in the pore space.

Formation of new clay minerals. The expected kaolinisation/pyrophyllitisation (working hypothesis 3) and the Si excess in the modified montmorillonites were actually observed in several samples at an incipient stage (see Fig. 58 «TEM-PICTURE»).

Confirmation and explanation of the hypotheses. The evaluation of these own results and of the data collected from literature which supposedly contradict the working hypotheses led to new findings all of which do not only confirm these observations, but also consistently explain them. Increasing interlayer charges lead – as Savage and Laird reported – to declining swelling pressures. As far as we can see, this is on account of the transformation of montmorillonite into illite, a clay mineral which
is not expandable anymore. The illitisation is a widespread process in open, natural systems with exchange of solutions. This process, however, does not take place under test and thus reservoir conditions. In our tests under repository conditions, i.e. in a closed system, in all samples we detected no increase of the interlayer charge but a significant decline thereof. Such a sequence cannot lead to illitisation. In literature, however, an illitisation has so far been generally assumed for repositories, too. A decline in charge leads – as observed – to a kaolinitisation/pyrophyllitisation. As the clay minerals kaolinite and pyrophyllite are – similar to illite – not expandable anymore either, the apparent contradiction to the literature data is resolved. Both an increase and a decline of the charge can cause a loss of the swelling capacity. 

Fig. 59 »SWELLING PRESSURE/INTERLAYER CHARGE« schematically represents the interrelation between the mineralogical alterations of the montmorillonites and the change of the interlayer charge and swelling pressure of the bentonite in case of reactions with solutions in open and closed systems.

Kaolinite and pyrophyllite with the interlayer charge of zero/half cell (left) and illite with the interlayer charge one/half cell (right) are end members of the montmorillonite transformation with different developments due to different boundary conditions.
Summary and conclusions

Significant differences between closed repository systems and open geological systems. The three working hypotheses established at the beginning of the R+D project were confirmed by new tests. Apparent contradictions with data from the literature could be satisfyingly clarified. The new understanding which has developed explains both the short- and the long-term behaviour of bentonites and makes clear that there are significant differences between a closed repository system and an open geological system. In a final repository in salt formations which can be considered practically closed and where no fast removal of Al can be assumed, no illitisation of expandable smectites, but a kaolinisation/pyrophyllitisation can be expected. In the long run, however, both directions of transformation lead to a decreasing swelling capacity of the bentonites, even though a short-term swelling pressure increase can be observed. This means that in the long term a permeability increase of the technical barrier bentonite is to be assumed.

The question which thus has to be answered in the context of bentonite barrier stability is not if, but how long the bentonite will maintain its sealing effect under final repository/underground waste disposal site conditions. In the long-term safety analysis it thus has to be clarified which degree of swelling capacity is required and over which period of time a certain permeability has to be maintained.
EXPERIMENTAL RESULTS

Fig. 55 (from 55-57)
Swelling pressures with different solutions (Batch experiments with excess solution)

55 SWELLING PRESSURE
of original, untreated MX-80 bentonite immediately after first exposure

Fig. 55  Master file

batch experiments - first contact

H₂O  $P_{\text{end}} = 2.94$ MPa

Äspö  $P_{\text{end}} = 2.47$ MPa

Opalinus  $P_{\text{end}} = 2.34$ MPa

YCP  $P_{\text{end}} = 2.02$ MPa

IP21  $P_{\text{end}} = 0.97$ MPa

IP21 cement  $P_{\text{end}} = 0.86$ MPa

NaCl  $P_{\text{end}} = 0.83$ MPa

NaCl cement  $P_{\text{end}} = 0.64$ MPa

time (days)  swelling pressure (MPa)
EXPERIMENTAL RESULTS

Fig. 56 (von 55-57)
Swelling pressures with different solutions (Batch experiments with excess solution)

Fig. 56 SWELLING PRESSURE
of MX-80 bentonite after a three-year reaction time

**Experimental Results**

**Fig. 56**

*Batch experiments - 3 years*

<table>
<thead>
<tr>
<th>Solution</th>
<th>Swelling Pressure $P_{end}$ (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$O</td>
<td>$P_{end} =$ 4.14 MPa</td>
</tr>
<tr>
<td>Åspö</td>
<td>$P_{end} =$ 3.50 MPa</td>
</tr>
<tr>
<td>Opalinus</td>
<td>$P_{end} =$ 2.72 MPa</td>
</tr>
<tr>
<td>NaCl</td>
<td>$P_{end} =$ 1.57 MPa</td>
</tr>
<tr>
<td>YCP</td>
<td>$P_{end} =$ 1.54 MPa</td>
</tr>
<tr>
<td>NaCl cement</td>
<td>$P_{end} =$ 1.04 MPa</td>
</tr>
<tr>
<td>IP21</td>
<td>$P_{end} =$ 0.98 MPa</td>
</tr>
<tr>
<td>IP21 cement</td>
<td>$P_{end} =$ 0.70 MPa</td>
</tr>
</tbody>
</table>
**EXPERIMENTAL RESULTS**

Fig. 57 (from 55-57)
Swelling pressures with different solutions (Batch experiments with excess solution)

57 INTERRELATION OF SWELLING PRESSURE AND CHARGE OF THE MONTMORILLONITE in contact with:
1 – water,
2 – solutions of medium ionic strength
3 – solutions of high ionic strength
after
◆ – 7 days, ■ – 1 year, ▲ – 2 years

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**Fig. 57** Master file
Fig. 58
Newly-formed hypidiomorphic kaolinite crystals in a bentonite sample after a 2-year reaction time with a Mg-rich IP21 solution.
Fig. 59
Schematic interrelation between montmorillonite transformation, interlayer charge and swelling pressure in open and closed systems.

Kaolinite and pyrophyllite with the interlayer charge of zero/half cell (left) and illite with the interlayer charge one/half cell (right) are end members of the montmorillonite transformation with different developments due to different boundary conditions.

**SWELLING PRESSURE/INTERLAYER CHARGE**

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**Fig. 59**
Master file