Corrosion of cementitious materials under geological disposal conditions with resulting effects on the geochemical stability of clay minerals

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GRS

Abstract: The long-term behaviour of cemented fly ashes and bentonite (MX80) has been investigated in high saline solutions by means of a cascade experiment, batch experiment and by the geochemical modelling of the observed reactions. In contact to IP21 the degradation of CSH phases in the cementitious material could be proposed indicated by the accumulation of Ca in solution. In contact to NaCl brine only a small amount of Ca in solution could be detected indicating a slight dissolution of CSH phases in the cementitious material. Considering the good agreement between the time accelerating laboratory scale cascade experiment and the modelled reaction path using the computer code EQ3/6 we conclude, that it is possible to predict the chemical behaviour of cementitious materials in salt solutions. The degradation experiments with MX80 and cementitious material in NaCl and IP21 solution showed an accumulation of Si and Al in solution and then a remove possibly indicating the formation of new phases. In contact to high saline solutions a reduction of swelling pressure of MX80 at various reduced initial dry densities could be observed in comparison to pure water. Moreover a reduced water-uptake of MX80 in contact to high saline and alkaline solution was obtained.

1. INTRODUCTION

Concepts for the final disposal of radioactive and hazardous waste in salt formations include the use of geological and technical barriers, sealing and backfill materials, which are partly based on cementitious materials and clays. For that reason the safety assessment of the repository system replies detailed knowledge of the geochemical behaviour of cement/clay systems in contact to saline solutions. In case of a brine intrusion into a repository high alkaline interstitial waters will defuse through the clay barrier and affect their properties. This will produce a complex bentonite-cement system, whose evolution with time becomes of great importance to the global performance and safety assessment of the repository.

Cemented waste forms represent a significant part of the inventory material, based on cements and fly ashes, furthermore cementitious materials are considered as sealing and backfill material. In contact to high saline solutions cementitious materials show a significant change in their structure. There are dissolution and precipitation processes observable, resulting in a change of the solution composition and the brine's pH. The degradation mechanisms will result an increase of the hydraulic and mechanical properties.

Bentonites are considered to be favourable as sealing materials because of their swelling capacity. In salt formations however the presence of high saline brines must be considered. This fact poses certain problems concerning the use of bentonites as buffer and sealing materials. Salt solutions tend to reduce the swelling capacity, and no swelling pressure will develop if the swelling capacity is reduced to an extent where the void volume is not filled by the swollen clay. For very high-salt contents, the existing models are not able to predict or reproduce the experimental results. An experimental program was conducted to determine swelling pressures of compacted bentonites, under the special conditions of brine inflow into repositories situated in salt formations.

2. EXPERIMENTAL

2.1. Corrosion experiments

2.1.1. Cascade experiment: Leaching of cementitious material in contact to high saline solution

In order to explain leaching and corrosion processes, a special laboratory scale experiment in several steps (cascades) was developed. It is a fast experimental method for the investigation of the reaction path of the fluid-solid interactions. During the experiment that goes on for several month the temperature is kept constant and evaporation is excluded. In a cascade experiment a weighed mass of a ground down powder is reacted with a certain mass of solution (first cascade). The grinding of the cemented material leads to an increased material surface and thus a time accelerating effect can be obtained. After 2-3 days of equilibration under continuous rotation of the reaction vessel at 25°C, the solution is extruded through a pressure filter onto unreacted solid (second cascade). While these steps are repeated, the effective solid-solution ratio increases. The solid solution ratio will be kept constant for all cascades. The number of steps in the experiment ranges from 10 to 20. The number of steps is limited by the continuously decreasing volume of leachate. The experiment is conducted in several steps towards the thermodynamical equilibrium between the leaching fluid and all involved phases. In each step the resulting chemical composition of the leaching solution is determined as well as the dissolved and precipitated phases. For each cascade the solution is analysed by ICP-MS and ICP-OES, in addition the solid material is analysed by ICP-MS, ICP-OES and XRD. The results of this laboratory experiment are compared with the results of the geochemical modelling.

2.1.2. Batch experiment: Mineral changes of bentonite/cement systems in contact to high saline solutions

In order to understand the mineral changes of bentonite/cement interactions in contact to high saline solutions batch experiments were performed using an IP21 and a saturated NaCl solution. The batch experiment represents one step of the cascade experiment with a certain solid/solution-ratio. In the first attempts 10 g of MX80 were reacted with 10 ml solution at reaction temperatures of 25°C, 90°C and 150°C, respectively. Further experiments were conducted with bentonite and cement in high saline solution. The solution is analysed by ICP-MS and ICP-OES and the reaction products were analysed by XRD, DTA/TG, TEM and atomic force microscopy .

2.1.3. Swelling pressure experiment: Development of swelling pressure of MX80 in contact to different solutions

For the measurements of the swelling pressure two equipment were used. The two methods are described in detail elsewhere [1]. The main difference between these both equipment is that one uses a heavy stable frame (Freiberger method), whereas the other uses pressure chambers (GRS method). In both cases the volume can be kept constant during the measurement. The advantage of the second measuring cells is a moderate price. Many cells can be operated simultaneously and thus many samples can be measured in a relatively short time. In addition the new approach leads to a reduction of the time needed for one measurement from several months to a few days or weeks. These changes allow the collection of much more data. The results can be statistically verified by many repeated measurements under all interesting boundary conditions. Thus it seams possible to quantify the influence of dry density, microstructure, brine composition, sample volume, sample geometry etc.

The swelling pressures of MX80 in contact to solutions of set I (Table 3) were measured by the Freiberger method, whereas the swelling pressure of MX80 with the solution of set II were measured by the method developed by GRS.

3. GEOCHEMICAL MODELLING

Th Gibbs enthalpy for the formation of a solid phase i from an aqueous solution consisting of species i is given by the following expression:

$$\Delta G = \Delta G^0 + RT \ln \prod_i a_i^{v_i} \tag{1}$$

At equilibrium, $\Delta G = 0$ and the product of activities becomes K, the equilibrium constant:

$$\Delta G^0 = -RT \ln K \tag{2}$$

The activities are a product of the molalities m_i and the activity coefficient γ_i of the species:

$$K = \prod_i a_i^{v_i} = \prod_i m_i^{v_i} \gamma_i^{v_i} \tag{3}$$

The theory of Debye and Hückel is based on the assumption that strong electrolytes are completely dissociated in solution. Following the theoretical considerations of Debye and Hückel the activity coefficient of a strong electrolyte is a function of the solution's ionic strength. For Debye-Hückel the activity coefficient can be expressed:

$$\ln \gamma_i = -A z_i^2 \sqrt{I}\,; \qquad I = \frac{1}{2}\sum_i m_i z_i^2 \tag{4}$$

A Debye-Hückel coefficient; z_i ion charge; m_i molalities of the species

The Debye-Hückel-Theory is valid only for ionic strength less than 10^{-2} - 10^{-3} M. Several extended equations has been established (Güntelberg, Davies). Pitzer and Co-workers developed a model which extends the Debye-Hückel expression for the calculation of ion activity coefficients by terms for the specific interactions between two or three ions. The Pitzer formalism extends the Debye-Hückel expression with a virial expansion to account for binary and ternary ionic interactions between ions of likewise and opposite charge:

$$\ln \gamma_i = f(I) + \sum_I \lambda_{i,j}(I) m_j + \sum_j \sum_k \mu_{i,j,k} m_j m_k \tag{5}$$

$f(I)$ Debye-Hückel expression; $m_{j,k}$ molalities of the species; λ, μ interaction coefficients

The Pitzer expression includes specific parameters which have to be determined for each individual ionic interaction. Further information concerning the Pitzer formalism is given in [2]. For the modelling of the hexary system of salts of the oceanic sea water system (Na-K-Mg-Ca-Cl-SO_4) a set of Pitzer parameters and solubility constants at 298 K has been developed by Harvie et al. [3] with a high degree of precision.

Table 1 Solubility constants of cement phases.

Phase	Formula	Log K_{sp}	Phase	Formula	log K_{sp}
Brucite	MH	17.11	Ettringite	C_3A3CsH_{32}	57.00
Chrysotile	$M_3S_2H_2$	31.13	Friedel's salt	C_3ACcH_{10}	70.72
CSH (0.8)	$C_{0.8}SH$	11.07	Quartz	S	-4.00
CSH (1.1)	$C_{1.1}SH$	16.71	SiO_2 (am)	S	-2.71
CSH (1.8)	$C_{1.8}SH$	32.54	Hydrogarnet	C_3AH_6	80.80
Chabazite	CAS_4H_6	13.21	Si-Hydrogarnet	C_3ASH_4	69.35
Gibbsite	AH_3	7.74	Portlandite	CH	22.80
Gypsum	CsH_2	-4.58	Talc	M_3S_4H	22.41

For the interpretation of the cement corrosion processes, the seawater system of Harvie, Møller and Weare was extended by Pitzer coefficients for Al and Si estimated by Reardon [4]. The solubility data used for cement phases (Table 1) were those published by Revertegat et al. [5], Berner [6] and NEA data listed by Glasser et al. [7].

The experimentally observed reaction path of the degradation of cemented BFA was modelled using the computer code EQ3/6, release 7.2a. The chemical composition of the cemented materials for the main components to be modelled are listed in (Table 2). The cemented BFA contains 54 wt-% of rock salt (94 wt-% of halite and 6% of anhydrite).

Table 2 Main components of the investigated cementitious material (cemented BFA).

Element	Al	Ca	Cl	K	Mg	Na	S	Si
[mol/kg H_2O]	0.619	0.913	13.200	0.285	0.237	13.012	0.218	1.249

The initial composition of the IP21, NaCl and the solutions for swelling pressure measurements are given in Table 3. The solutions were first computed via an EQNR3 run. The reaction path of the materials interaction with the different solutions were modelled in an EQ6 run using the titration model. The steps of the EQ3/6 run (z_i) correspond to the reaction i.e. corrosion progress. For experimental purposes the solutions of set I and set II were slightly diluted by a factor of 0.9.

Table 3 Composition of the IP21, NaCl, set I (#1, #6, #11) and set II (IP9 -IP-24) solution.

	IP21	NaCl	#1	#6	#11	IP-19/10	IP-21/10	IP-9/10	IP-24/10
Element	[mol/kg H_2O]								
Ca	0.001	0.000	0,055	0,056	0,056	0,000	0,013	0,0046	0,0004
Cl	8.873	6.100	5,939	5,940	5,939	8,1067	7,7745	5,6640	5,8904
K	0.547	0.000	0,278	0,278	0,277	0,1730	0,4121	0,8035	1,2841
Mg	4.241	0.000	0,000	1,388	2,775	4,1659	3,7242	0,9019	1,7677
Na	0.462	6.100	5,551	2,776	0,000	0,1347	0,3066	3,8389	2,2770
S	0.309	0.000	0,000	0,000	0,000	0,3424	0,2635	0,3478	0,6681
Density [g/cm^3]	1.292	1.200	-	-	-	1.2800	1.2657	1.2187	1.2543

In order to simulate the corrosion of cementitious materials, the dissolution of portlandite, a main component in cement systems, can be used in a first attempt to predict the solution composition [8-11]. For the prediction of the reaction of complex systems like cementitious materials in contact to saline solutions special reactants were defined by using the chemical composition of the material (Table 2).

4. RESULTS AND DISCUSSION

4.1. Dissolution of cementitious materials in contact to high saline solutions

4.1.1. Cemented BFA in contact to NaCl solution

The degradation experiments were performed using an IP21 and a NaCl solution. For the dissolution reaction of the cemented BFA (M2-4) in contact to NaCl solution an increase of K and an increase of Cl is observed, whereas a slight decrease of Na can be detected. The experimental data as well as the geochemical modelling are in good agreement concerning the elemental concentrations in solution. The concentration of Ca only slightly increases during the leaching experiment. Thus the CSH-phase will only slightly dissolve in NaCl solution. In former experiments after the dissolution of CSH phases a precipitation of newly build CSH/CSAH-phases could be observed *Herbert & Meyer* [8]. The concentration of SO_4 increases during the cascade experiment to 0.15 mol/kg H_2O, the calculated concentrations are in accordance with the experiment.

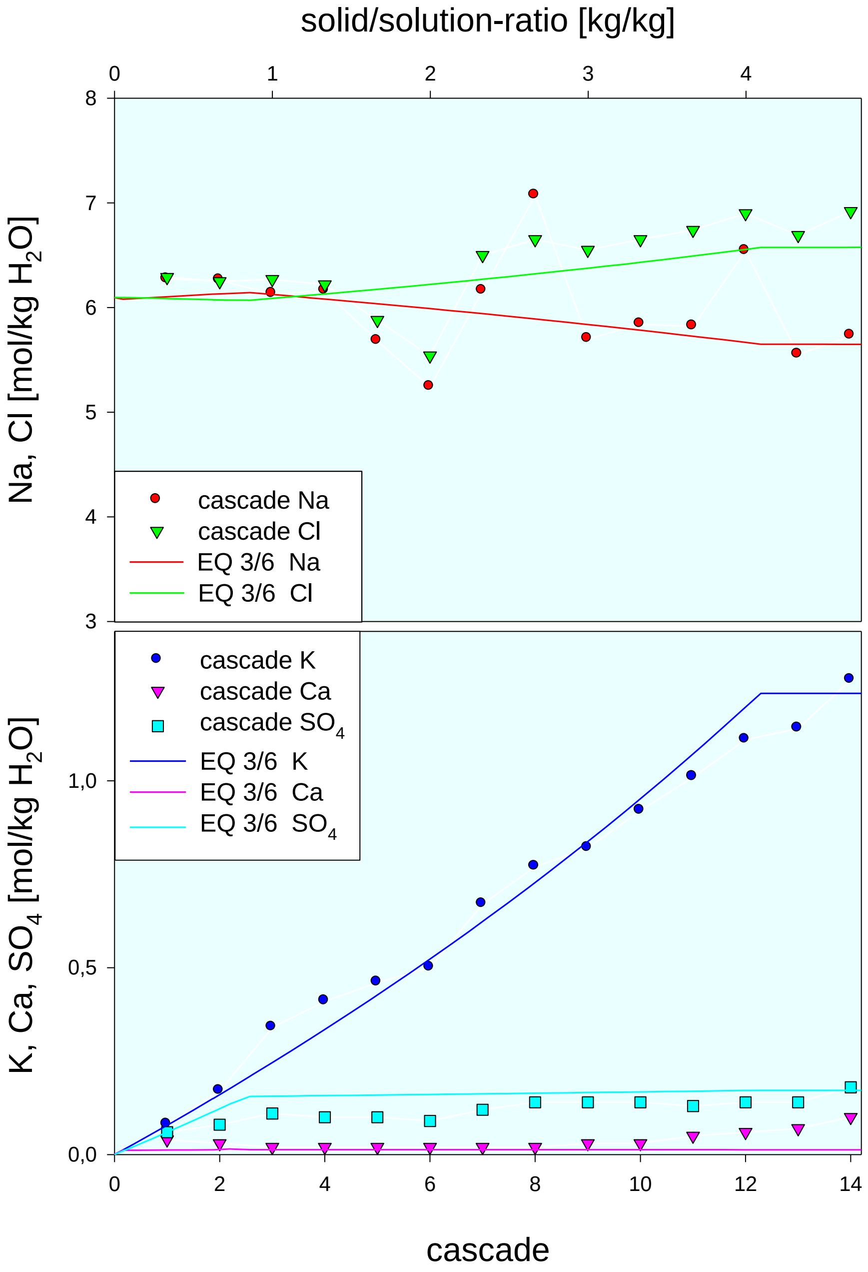

Figure 1 Reaction path of the dissolution of cementitious material (M2-4) in a NaCl-saturated solution; symbols mark the experimental data and lines the calculated results.

Si is calculated to be precipitated in the phases talc, chabazite and quartz, Al is present in the phases gibbsite, chabazite and trichloride. Furthermore the phases anhydrite and halite are modelled (Figure 2). These phases are in good agreement with the results of the experimentally observed phases.

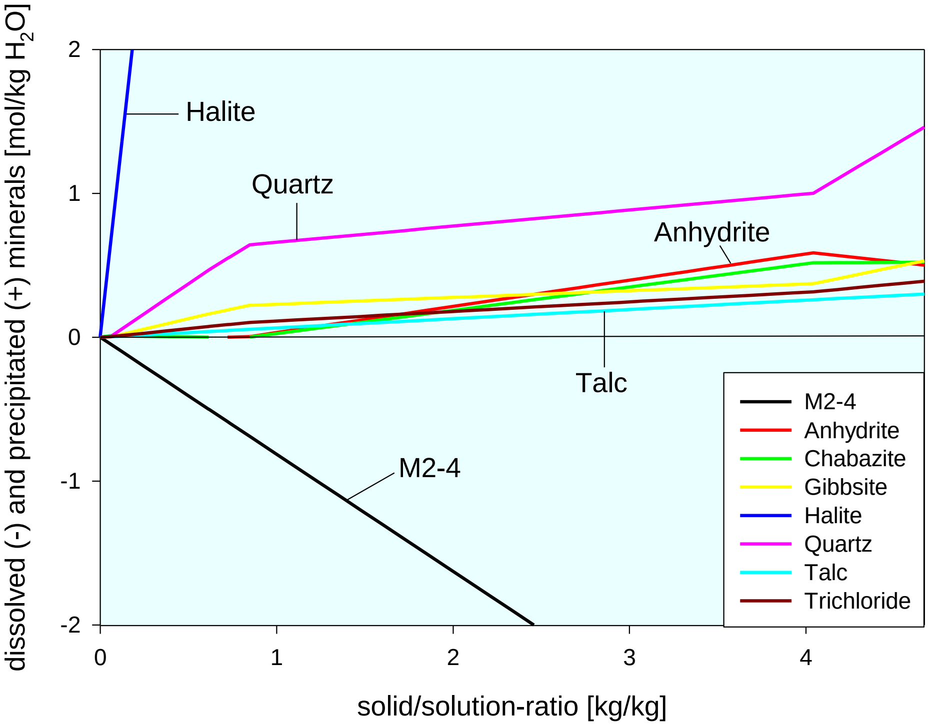

Figure 2 Dissolved and newly formed phases for the calculated reaction path of cementitious material (M2-4) in contact to NaCl saturated solution.

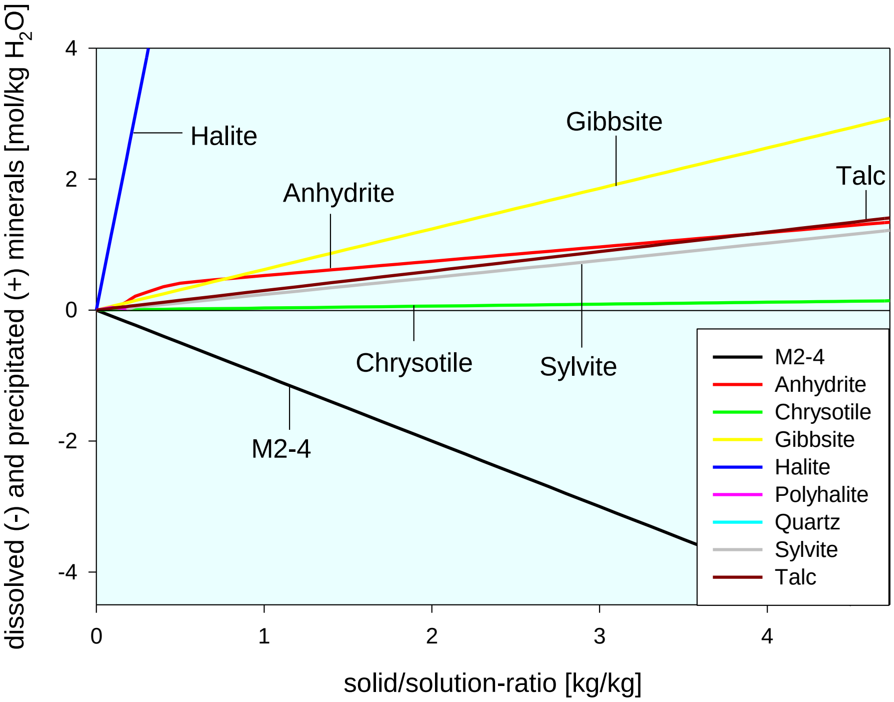

Figure 3 Dissolved and newly formed phases for the calculated reactions of cementitious material (M2-4) in contact to Mg-rich brine (IP21).

4.1.2. Cemented BFA in contact to IP21 solution

In Figure 4 the reaction path of the dissolution of cementitious material in IP21 solution is depicted. During the dissolution of the cementitious material in Mg-rich solution a strong decrease of Mg in solution from 4.25 mol/kg H_2O (IP21) to 2.16 mol/kg H_2O is detected in the reacted brine. We assume the precipitation of $Mg(OH)_2$, because of the absence of further Mg-phases, e.g. Mg-silicate-phases (talc, serpentine etc.). In the modelling talc and chrysotile are calculated as precipitating Mg-phase, which are not observable in our short-term experiment (Figure 3). As well as Mg decreases in solution the concentration of Ca increases. In general, remaining portlandite of the cement hydration will first be dissolved in Ca-unsaturated solutions. In a second step the CSH-phases will be dissolved. Concerning the investigated material no portlandite could be detected in the hardened cement paste. From this follows the Ca increase is founded on the decrease of CSH-phases. In the modelling the increase of Ca is overestimated, depending on an insufficient data base. Si is computed in the phases SiO_2 (quartz), talc, and chabazite. Al occurs in the phases trichloride and gibbsite (Figure 3). The concentrations of K and Na slightly increase to 0.7 mol/kg H_2O and 0.6 mol/kg H_2O, respectively, in the experiments as well as in the geochemical modelling. SO_4 was precipitated as gypsum (anhydrite) during the first two cascades (Figure 4).

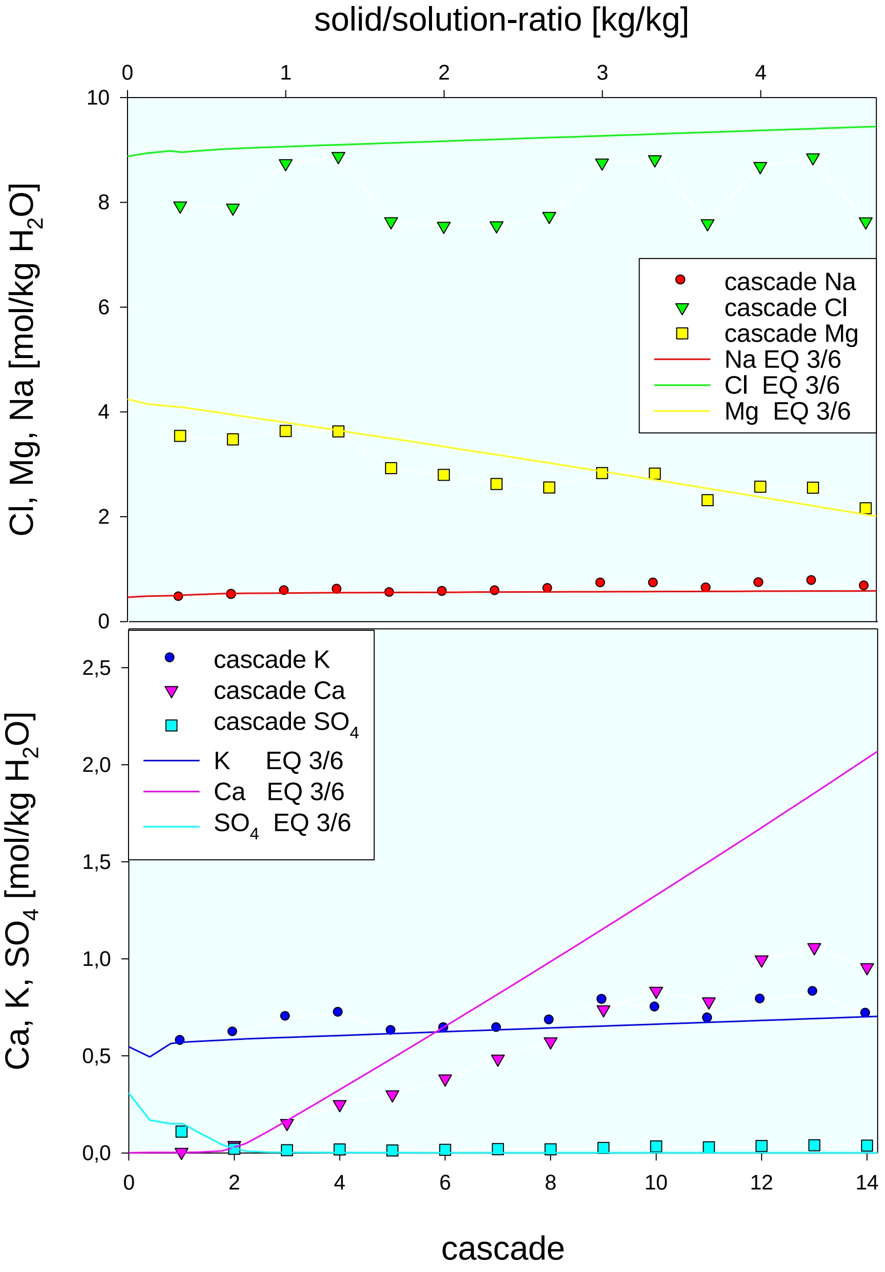

Figure 4 Reaction path of the dissolution of cementitious material (M2-4) in a Mg-rich high saline solution (IP21); symbols mark the experimental data and lines the calculated results.

4.2. Long-term stability of Na-montmorillonite in high saline solutions

In order to understand the mineral changes of bentonite/cement interactions in contact to high saline solutions bentonite and bentonite/cement-systems were reacted in high saline solutions (NaCl, IP21) for 400 d. In Figure 5 the concentrations of Si and Al in the systems MX80/NaCl, MX80/NaCl/cement, MX80/IP21 and MX80/IP21/cement for the temperature range of 25°C to 150°C are depicted.

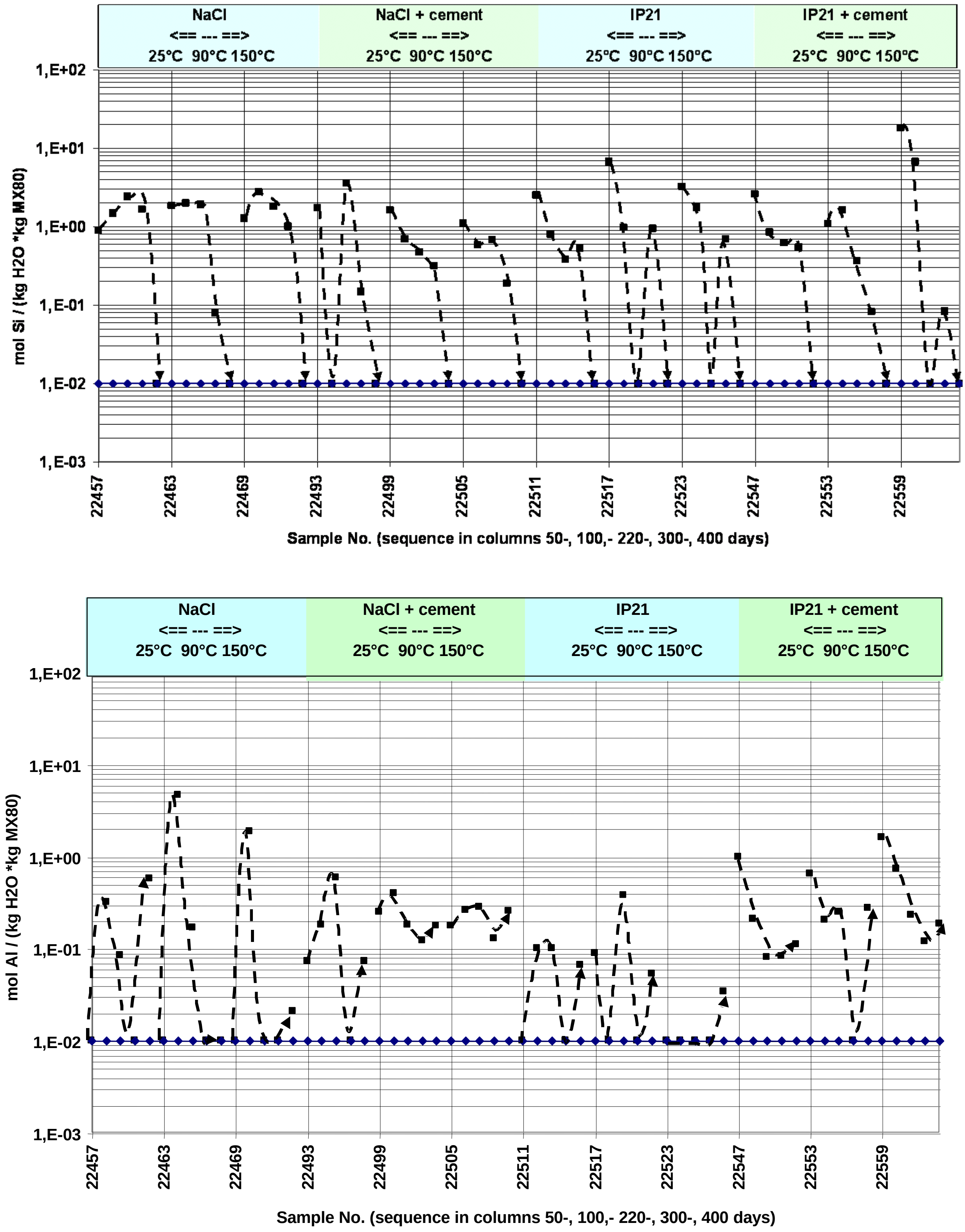

Figure 5 Concentration of Si (upper part) and Al (lower part) in solution in the system of bentonite in contact to NaCl and IP21 solution with and without addition of cement.

For each temperature in the investigated systems five measured concentrations are displayed with respect to the reaction times of 50, 100, 220, 300 and 400 days.

The degradation experiments of bentonite and bentonite/cement systems in high saline solution indicate a concentration increase of Si and Al in solution in short terms (50d). Thereafter it is found a strong decrease (400 d) of Si in solution to concentrations below the limit of detection (Figure 5, upper part). This increase to a maximum and the following decrease can be obtained for all systems (MX80/NaCl, MX80/IP21, MX80/cement/NaCl as well as MX80/cement/IP21). The concentration of Al in solution varies for the investigated systems and reaction times. It seems that the Al concentration will be more stable in the systems with cement addition, but exceptions (MX80/NaCl/cement, 300d; MX80/IP21/cement, 300 d) can be observed. Also measurement errors can not be excluded. Si and Al do not occur in the same stoichiometric ratio in solution then in montmorillonite. That could indicate a different amount of dissolution of octahedral and tetrahedral layers. The decrease of Si and Al is due to the precipitation of newly build phases which has to be determined in further experiments.

4.3. Influence of high saline solutions of the swelling pressure and the water-uptake

The investigations were performed with two sets of high saline solutions [12]. In order to limit the variables in the experiments, we kept the K and Ca content constant and varied Na/Mg ratio within the first set. The second set of solutions comprised four geochemically relevant solutions, each of which was NaCl-saturated and in equilibrium with typical mineral assemblages encountered in the German Zechstein salt formations. For experimental purposes these solutions were slightly diluted by a factor of 0,9. In these solutions the K content varies.

The performed experiments indicate that Bentonites develop swelling pressures not only in contact to water, but also in contact to high saline brines. The swelling pressures in contact to brines however are considerably lower than those with pure water. The brine composition influences the resulting swelling pressure. Pressures obtained with synthetic brines containing very low (and constant) K but varying amounts of Na and Mg (solutions 1,6,11) increase with increasing Mg in solution.

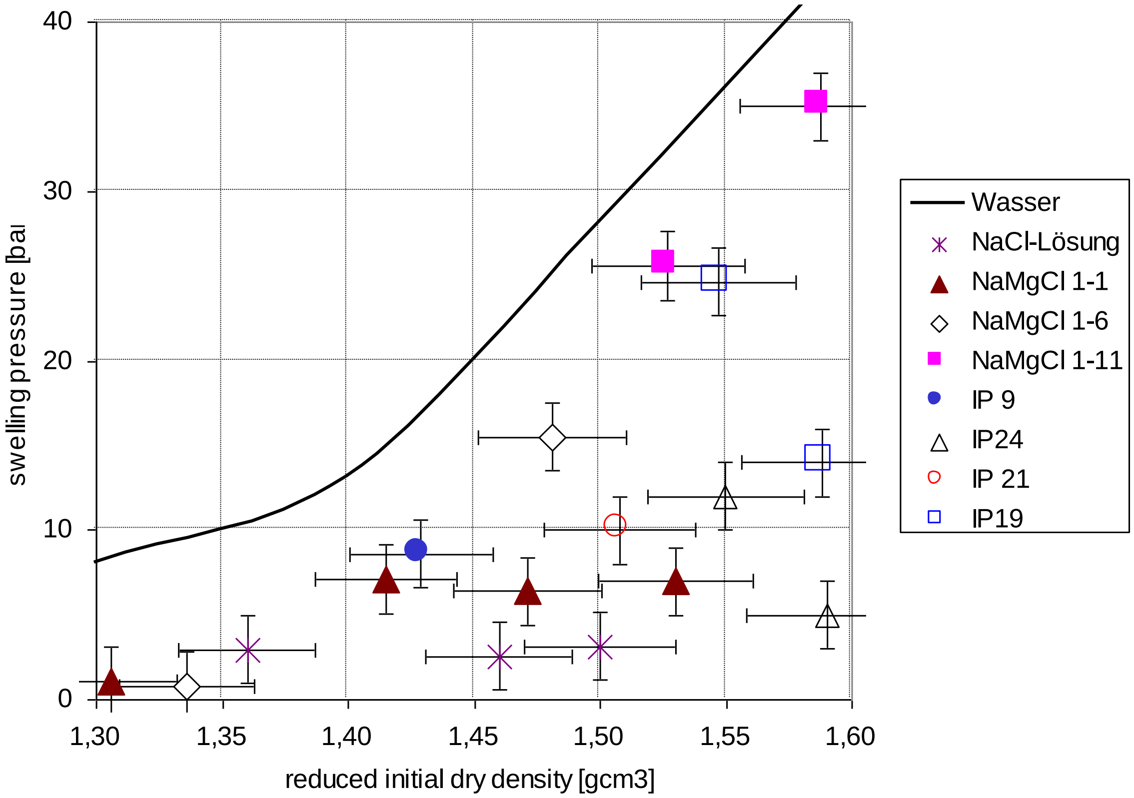

Figure 6 Swelling pressure of MX-80 bentonite in contact to salt solutions as a function of the reduced dry density compared to the swelling pressure with water

Mg with its bigger hydration sphere leads to much higher swelling pressures than Na. Mg increases and K decreases the swelling pressures, i.e. K counteracts the effect of Mg. The impact of K on the swelling pressure is higher than that of Mg. Because of these opposite effects of K and Mg the swelling pressures obtained with naturally occurring brines with varying K and Mg contents do not differ as much as expected (Figure 6).

The few results obtained so far can not be extrapolated to other boundary conditions. We are of the opinion, that this is true not only for our own experiments. Therefor we conclude that at the time being the existing knowledge on swelling pressures in contact with brines is not complete nor consistent enough for a successful modelling. Factors like dry density, microstructure, flooding regime, sample dimensions seem to have a much bigger influence on the swelling pressure than brine composition. The comparison of the two procedures employed for the measurement of swelling pressures reveals that not only the swelling pressure itself is important. The flooding regime of the compacted bentonites has a decisive influence on the resulting permeability and thus on the sealing capacity of the bentonites. With the same solution a very similar swelling pressure can be obtained under different brine inflow rates. Under certain conditions the build-up of a pore pressure is faster than the closure of the pores by the swelling and a relative high permeability is maintained despite a high swelling pressure. Therefore in order to obtain data which can be used for the practical purposes future swelling pressure experiments should be conducted under boundary conditions as close as possible to the expected in-situ conditions. The new GRS procedure seems to be a suitable tool for the systematic investigation of all the boundary conditions identified to have a major influence on the swelling pressure of bentonite in salt formations. Further measurements will include also the investigation of the influence of the clay particle orientation and the influence of elevated temperatures on the swelling pressure of compacted bentonites.

The water-uptake of the MX80 was strongly reduced for the experiments performed in NaCl in comparison to the water-uptake of bentonite in pure water. In Figure 7 the water-uptake within the first 150 min. of the different cured samples is depicted. It will be reduced by time of curing as well as the curing temperature. The water-uptake of the bentonite material after 150 min. in pure water is about twice of that in NaCl solution cured at temperatures of 25°C - 150°C.

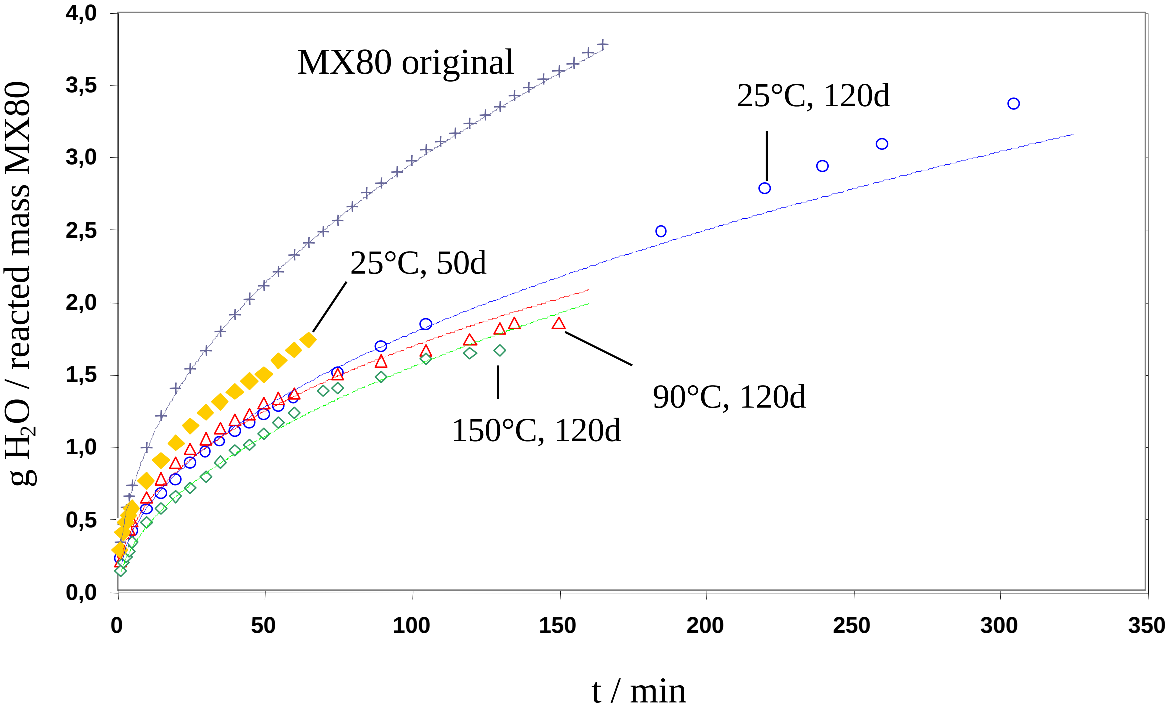

Figure 7 Water-uptake of bentonite after curing for 120 d at 25°C, 90°C and 150°C in comparison to the original MX80 and a sample cured at 25°C for 50 d.

The decrease of the water-uptake indicates the decrease of the swelling pressure. These results are in good agreement with the results of the swelling pressure measurements observing a decreased swelling pressure of MX80 in contact to brines in comparison to the swelling pressure of the bentonite/water system.
In a second attempt the water-uptake of a cured bentonite/cement-system was investigated. The results show a significant decrease of the water-uptake after 70 min. for all cured samples in comparison to the water-uptake of the of MX80 in pure water.

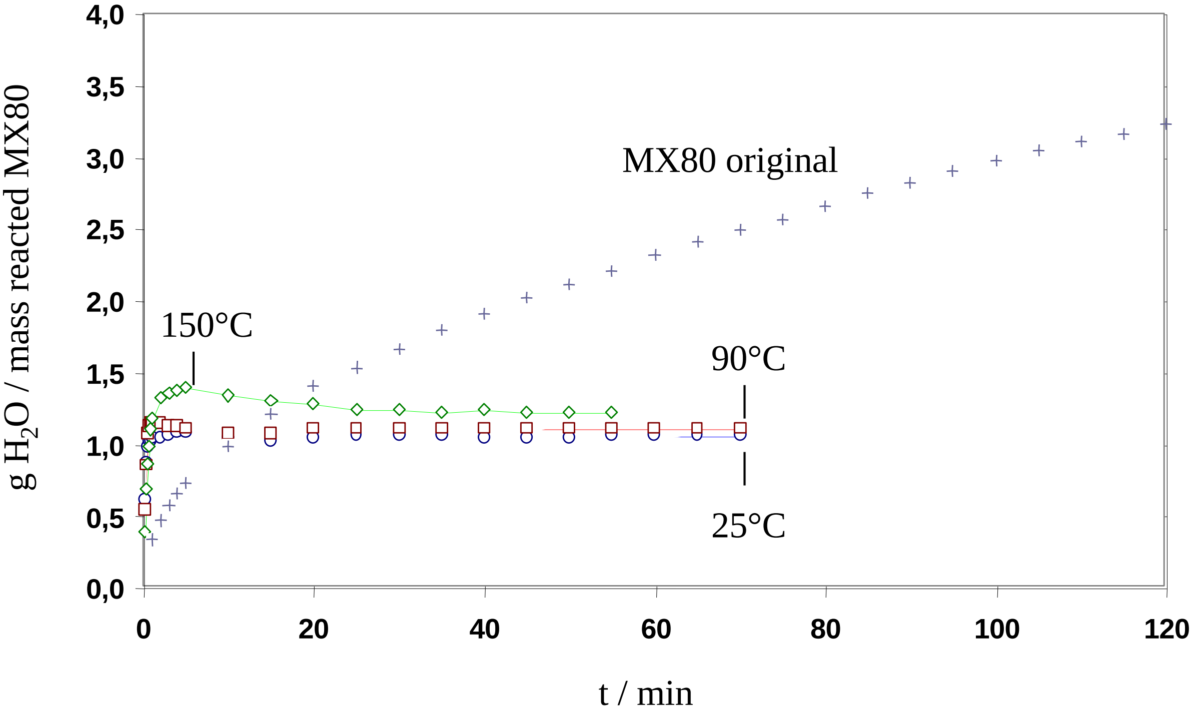

Figure 8 Water up-take of the a bentonite/cement system after curing for 120 d at 25°C, 90°C and 150°C in comparison to the original MX80.

Within the first minutes the maximum water-uptake will be reached. In the following time the mass of water per mass bentonite decreases for the cured samples to a maximum water-uptake of about 1.2 g H_2O / mass MX80 (Figure 8). Provided that the water-uptake indicates the extent of swelling pressure a further reduction of swelling pressure will be expected for bentonite in contact to high saline and alkaline solution.

5. CONCLUSIONS

Considering the good agreement between the time accelerating laboratory scale cascade experiments and the geochemical modelling we conclude, that it is possible to predict the chemical behaviour of cementitious materials in salt solutions. The cascade experiment is a rapid method, that enables the prediction of the chemical changes in solution during the cement corrosion processes. For the investigated materials in contact to brines a good agreement between the experimental data and the modelling results was obtained. The existing thermodynamic database for the geochemical modelling however is still incomplete. Solubility data and dissolution models for CSH phases are incomplete or missing. The Pitzer coefficients of Si and Al still need to determined more accurately. However the present state of the geochemical modelling possible with the existing database allows a valuable insight into the processes taking place along the reaction path in the extremely complex system.

The employed experimental and modelling tools have proved to be suitable for a prediction of the long-term chemical behaviour of cementitious materials.

The degradation experiments of bentonite and bentonite/cement in high saline solution indicate an increase of Si in solution and then after a decrease can be interpreted as a dissolution of the fine-grained clay fraction. Si and Al do not occur in the same stoichiometric ratio in solution then in montmorillonite. That may be indicate a different amount of dissolution of octahedral and tetrahedral layers. The decrease of Si and Al could be due to the precipitation of newly build phases which has to be determined in further experiments.

The swelling pressure is largely dependant on the degree of compaction and the applied fluid pressure. Therefore most of the experiments were conducted using raw densities around 1.6 g/cm^3. All swelling pressure with brines were much lower than those obtained with pure water, but higher as with saturated NaCl-solution. K and Mg tend to decrease or increase swelling pressure, respectively.

The water-uptake of the MX80 was strongly reduced for the experiments performed in NaCl in comparison to the water-uptake of the bentonite/water system. A further decrease could be detected in the bentonite/cement/NaCl system. Provided that the water-uptake indicates the extent of swelling pressure a further reduction of swelling pressure will be expected for bentonite in contact to high saline and alkaline solution.

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