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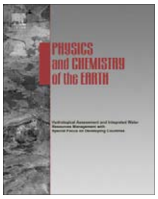

Swelling pressures of MX-80 bentonite in solutions of different ionic strength

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ABSTRACT

Bentonites are part of the engineered barrier system (EBS) of repositories for radioactive wastes. High salinity and high pH of the pore space solutions may cause changes in the mineralogical composition and of the swelling capacity of the bentonites, possibly affecting the long term performance of the EBS. Results of a 3 years study on the changes of MX-80 bentonite properties after reaction with solutions of different ionic strength and pH are presented. The effects of seven characteristic saline solutions potentially occurring in repositories in granite, clay and salt formations were investigated, with comparison with one "pure water" experiment. Each solution reacted differently with the bentonite, resulting in different mineralogy and swelling pressure (SWP). SWP were highest in contact with water (>4 MPa), significantly lower in contact with low ionic strength solutions (~2 MPa) and lowest in contact with high saline brines (mostly under 1 MPa). An alteration and partial dissolution of montmorillonite was observed. 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. Later, a loss of some octahedral layers led to an excess of Si in the montmorillonite particles. The correlation between the alteration process, the charge reduction and SWP is presented. Tentative explanations are given for the activation of bentonites with acids. Key factor for the observed mineralogical alteration may be the acidity of water in the interlayer space. This also may explain that the alteration in compacted experiments with a high solid–liquid ratio (less water, higher acidity) is faster than in batch experiments with a lower solid–liquid ratio.

All results can be explained by processes which lead to a pyrophyllitization/kaolinitization and Si-excess of the montmorillonite particles. An illitization seems less likely. 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 to be answered is not, whether or not bentonites are stable under the conditions of a repository in salt, but rather, what degree of swelling capacity is needed for what length of time.

1. Introduction

This paper presents the results of a study on MX-80 bentonite in contact with electrolyte solutions of different ionic strength. The work was performed in the frame of the Integrated European Project NF-PRO.[1] The near-field of a repository for high-level radioactive waste is an important component of the geological disposal system. It plays an essential role in ensuring the overall safety of geological disposal. In particular, the near-field is made of engineered barriers that should enclose the disposed waste and contain and minimise the release of radionuclides over extended periods of time. Bentonites and concretes are candidate materials for the construction of engineered barrier systems (EBS). Especially, in salt formations but also in other geological host formations saline solutions may occur and can interact with the EBS. It is a known fact that high salinity and high pH in solutions put a high chemical stress on bentonites. These interactions may change the mineralogical composition and especially the swelling capacity of bentonites and thus the long term performance of the EBS.

The objective of this study was to understand and quantify the chemical processes occurring during the interaction of bentonite with solutions of different chemical composition in a wide range of ionic strengths. MX-80 bentonite was reacted with solutions which may occur in repositories in salt formations, argillaceous formations and granitic formations. Batch experiments with a low solid to liquid ratio as well as experiments with highly compacted bentonite with a high solid–liquid ratio were conducted

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[1] Understanding and physical and numerical modelling of the key processes in the near field, and their coupling, for different host rocks and repository strategies.

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over a period of 3 years. Samples were analysed after 7 days, 1, 2 and 3 years of reaction.

2. Working hypothesis

Herbert et al. (2004a) 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.

Indications that these working hypotheses might be confirmed, were found in the literature. Following the DLVO-theory concentration of electrolyte and layer charge of clay minerals affect the swelling pressure in bentonites. Savage (2005) and Laird (2006) described the interaction between the interlayer charge of bentonite and the resulting swelling pressure. Swelling decreases with increasing charge density, because a higher charge density will prefer more cations in the interlayer with higher valences. Swelling decreases also with increasing salinity of the contacting solution. Laird (2006) distinguished several separate processes, which control the swelling of smectites saturated with alkali and alkaline earth cations in aqueous systems – crystalline swelling, double diffuse layer swelling, co-volume swelling and Brownian swelling. A direct influence by layer charge can only be expected for the crystalline swelling. The extent of crystalline swelling decreases with increasing layer charge. Laird (2006) characterized the break up and formation of quasicrystals as a dynamic process that controls the average size of quasicrystals in an aqueous smectite suspension. As layer charge increases, quasicrystals tend to become larger and more stable. Also demixing of interlayer cations influences the breakup and formation of quasicrystals because quasicrystals preferentially cleave along interlayers dominated by alkali cations. Increasing layer charge increases the selectivity for alkaline earth cations relative to Na or Li, and hence reduces the breakup of quasicrystals. Pusch et al. (2007), have developed a concept which describes the parameters which influence the swelling pressure (SWP). Push's term "interlamellar pressure" or "disjoining pressure" is comparable with the Laird's "crystalline swelling" and Pusch's "osmotic pressure" is the "double-layer swelling" of Laird (2006).

Following these hypotheses and the described interaction between charges and swelling the authors expected to find in the new experiments presented here decreasing interlayer charges in the run products and increasing crystalline swelling.

3. Materials

3.1. MX-80 bentonite

Commercial MX-80 bentonite (Wyoming, USA) is a highly heterogeneous material composed by 67–88 wt.% of montmorillonite clay particles (Grauer, 1986; Madsen, 1998). Total cation exchange of the montmorillonite is between 0.78 and 0.85 meq/g, which implies a total charge of 0.30. The cation population at exchange sites is mainly composed by Na (0.624–0.668 meq/g), Ca (0.066–0.074 meq/g), Mg (0.03–0.04 meq/g) and K (0.002–0.013 meq/g) (Müller-Vonmoos and Kahr, 1985; Bradbury and Baeyens, 2002; Wieland et al., 1994). The MX-80 bentonite used in this work contains 90 wt.% of montmorillonite, 4 wt.% quartz, 2 wt.% albite; and trace amounts of calcite, cristobalite and pyrite (Table 1). A more detailed mineralogical description of the employed bentonite can be found in Herbert et al. (2004a,b). In this study, MX-80 bentonite was saturated with sodium in order to gain reproducible results in the experiments.

3.2. Initial solutions

The bentonite-water interaction experiments were performed with eight different solutions (Table 2) covering a wide range of pH (5.3–13.2) and salinities (ionic strengths 0–15.5 M):

- Distilled water (H_2O), which was used as diluted solution for comparison with the other saline solutions.
- Äspö granitic ground water (Äspö), which is seawater solution encountered in the crystalline rocks of the Äspö underground laboratory in Sweden (Kärnbränslehantering, 2004).
- Opalinus clay pore water, (Opalinus), which is the pore water composition of the argillaceous formation Opalinus Clay at Mont Terri Rock Laboratory in Switzerland (Pearson et al., 2003).
- Saturated NaCl solution (NaCl), which is a typical brine encountered in the Zechstein salt formations in Germany (Herbert et al., 1991).
- IP21solution (IP21) is a $MgCl_2$-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 (Herbert et al., 1991).
- Young Portland cement pore water (YCP), is a solution consisting of water saturated with portlandite. This solution represents the pore water of the 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.

Table 1
Chemical composition and mineral formula of montmorillonite in MX-80 bentonite.

Interlayer					Octahedral layer				Tetrahedral layer IS[a]				S% (IS)	S% (diVS)	Total charge
Ca	Mg	Na	K	charge	Al	Fe^{3+}	Mg	Ti	nVI	Al	Si	(IS + diVS)			
0.02	0.03	0.11	0.02	0.23	1.62	0.17	0.19	0.02	1.99	0.02	3.98	38	89	91	0.29

[a] IS: illite-smectite mixed layers; diVS: dioctahedral vermiculite-smectite mixed layers; S (IS): % of smectite layers in IS mixed layers; S(diVS): % of smectite layers in diVS mixed layers; IS/(IS + diVS): portion of IS mixed layer phases. Total charge here is the average of interlayer charge for all TEM-measured particles.