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Research paper

Experimental evaluation of the influence of saturation media on the mineralogical and physicochemical stability of bentonites

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ABSTRACT

Three bentonite buffer materials (Rokle bentonite, FEBEX bentonite, and Mock-Up-CZ mixture composed of 85% Rokle bentonite, 10% silica sand and 5% graphite) interacted with natural water collected from Josef Underground Educational Facility (UEF) Czech Republic, and four different types of artificial groundwater enriched in K^+ and/or Mg^{2+}. The experimental material was prepared in the form of (1) highly compacted samples, (2) dispersion of bentonites (both at temperature of 95 °C), (3) drill hole filling during in situ tests at the Josef UEF (at ordinary temperature), and (4) common batch laboratory experiments (at 20 °C and at 80–90 °C). Partial samples were extracted after 3, 6, 12, and/or 18 months of interaction in the first three set-ups, and after 1 week, 2 weeks, 1 month, 2 months, 3 months, 4 months, 5 months, 7 months, 10 months, and 12 months in the batch experiment. Phase composition and its potential changes were evaluated by X-ray diffraction. In the first three experimental set-ups, no changes were identified. For the batch experiment, formation of illite was detected in FEBEX bentonite saturated with artificial groundwater with K^+ concentration of 1083 mg/L. By using the same saturation medium, gypsum and/or bassanite formed in the Rokle and FEBEX bentonite. Other media did not affect mineralogical composition.

The stability of studied materials was also evaluated by using adsorption and through-diffusion experiments on the basis of migration behaviour of ^{134}Cs. Dispersion of bentonites at laboratory temperature and bentonite samples from in situ test were used as solid phase, and four types of saturation media (artificial groundwater) were used as liquid phase. The distribution coefficient (Kd) is influenced by high concentration of K^+ and Mg^{2+} in saturation media on retention of Cs^+. In Rokle bentonite, the increase concentration of K^+ and Mg^{2+} led to a decrease of Kd. In the case of FEBEX bentonite influence of composition of saturation media was not observed.

The diffusion experiments showed good retardation ability of Rokle and FEBEX bentonites. The values of apparent diffusion coefficient (D_a) of cesium were influenced by composition of saturation media only for Rokle bentonite.

1. Introduction

Bentonites compressed to a given density are considered as the main buffer material used in high-level radioactive waste disposal concepts in many countries (Pusch et al., 2007). The buffer material is expected to fill the spaces between the canisters with the spent fuel and the surrounding geoenvironment (Gens et al., 2002; Komine, 2004). As a part of the engineering barriers, the buffer materials are expected to have the function of both isolation and retardation, i.e. prevention of the flow of groundwater from the surrounding rock to the canisters, as well as adsorbing any potentially released radionuclides from the corroded/corroding canisters. These functions are acquired by the unique properties of smectite-rich materials, which include low hydraulic conductivity, high adsorption capacity, swelling, and/or self-healing potential (Hatano et al., 1995; Kamei et al., 2005; Komine, 2004; Montes-H et al., 2005; Savage et al., 1999). A thorough understanding of the behaviour of the buffer materials in conditions simulating the repository is a necessary prerequisite for ensuring that the bentonite buffer will sustain its properties over the required repository life-time (100,000 years) (e.g., Gibb, 1999).

This paper aims at investigating the mineralogical and physicochemical stability of three materials (two raw bentonites, and one buffer-like mixture) exposed to both hydration (mineralised water) and increased temperatures. To ensure the long-term safety of the engineering barriers of a high-level radioactive waste repository, it is very important to understand the processes of potential transformation of the smectites into non-swelling phases. The transformation of smectites to illite/smectite mixed layer minerals or to non-expandable layer silicates (illite and/or chlorite) reduces the swelling potential of the buffer, and thereby its low hydraulic conductivity and self-sealing potential (Pusch et al., 2007). The composition of the saturation media can play a very important role in such processes, but it has not been experimentally verified (Jakob et al., 2009; Kónya et al., 2005; Missana et al., 2004; Vinšová et al., 2008).

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Table 1
Composition of the saturation media used during experiments.

Component	SGW-K (mg/L)	SGW-K-10 (mg/L)	SGW-Mg (mg/L)	SGW-Mg-10 (mg/L)	Josef (mg/L)
Ca^{2+}	15	148	45	446	85.3
Mg^{2+}	5.1	51	48	476	32.9
K^+	108	1083	0.8	8.1	3
Na^+	5.5	55	10	102	14.7
SO_4^{2-}	133	1333	1.5	15	165
Cl^-	43	425	220	2203	10.5
HCO_3^-	12	118	22	219	233

The composition of the saturation media also has an influence on the retention of radionuclides on the solid phase. The main focus of this work is to study the retention of Cs^+, which is a major radioactive component of high-level nuclear waste. The ion exchange is the dominant mechanism responsible for the retention of Cs^+ on bentonite (Eriksen et al., 1999; Tsai et al., 2001; Vinšová et al., 2008). The presence of complementary cations (K^+, Ca^{2+}, Mg^{2+}, Na^+) in the liquid phase can lead to a decrease in the retention of Cs^+, due to competition between cations and Cs^+ for the ion exchange sites (Khan et al., 1994; Missana et al., 2004; Ochs et al., 2003; Zachara et al., 2002).

2. Materials

The experimental study was performed by using three materials — Rokle bentonite, FEBEX bentonite, and a Mock-Up-CZ buffer-like mixture.

Rokle bentonite is a Ca-bentonite, commercially available from Keramost, a.s., Czech Republic in a non-activated state. It is predominantly composed of Fe-montmorillonite (60–65 mass%), accompanied by illite (5–10 mass%) and kaolinite (2–5 mass%) (Kolaříková et al., 2010; Přikryl et al., 2003). Non-clay minerals include quartz (15–20 mass%), K-feldspar (1–2 mass%), and anatase (<1 mass%) and in places calcite (2 mass%). Among the accessory phases, heavy minerals including rutile, titanite, pyrite, zircon, augite, and pyrolusite have been detected by separation techniques using heavy liquids (Přikryl et al., 2006). The suitability of this bentonite for potential use in engineering barriers of nuclear waste repositories has been thoroughly studied during the last decade (Kolaříková et al., 2005; Přikryl and Weishauptová, 2010; Přikryl et al., 2003; Vejsada et al., 2005; Vinšová et al., 2008, among others).

FEBEX bentonite is the material used in the FEBEX (Full-scale Engineered Barrier EXperiment) Project (ENRESA, 2000), which was selected by ENRESA (Empresa Nacional de Residuos Radioactivos — the Spanish Agency for Radioactive Waste Management) as a suitable material to backfill and seal high-level radioactive waste repositories. It was extracted from the Cortijo de Archidona deposit, in the Cabo de Gata region, Almería, Spain (Fernández et al., 2004; García-Gutiérrez et al., 2001; Villar, 2007; Villar and Lloret, 2007).

A detailed description of FEBEX bentonite can be found elsewhere (ENRESA, 2000; Fernández et al., 2004; Lloret et al., 2004; Villar, 2002, 2007; Villar and Lloret, 2007). The major mineral phase (90–92 mass%) of the FEBEX bentonite is the mixed layer of montmorillonite–illite with 10–15% of illite layers (Villar, 2007; Villar and Lloret, 2007) or with 11% illite layers ($^\circ\Delta 2\theta = 5.502$) according to Fernández et al. (2004). The FEBEX bentonite contains variable amounts of quartz (2 ± 1 mass%), plagioclase (2 ± 1 mass%), K-feldspar, calcite and opal-CT (cristobalite–trydimite, 2 ± 1 mass%), as well as numerous accessory minerals (dolomite, gypsum, pyrite, barite, celestite, halite, mica, chlorite) (ENRESA, 2000; Fernández et al., 2004; Villar, 2002; Villar and Lloret, 2004, 2007; Villar and Lloret, 2007).

Mock-Up-CZ is an artificially-prepared buffer-like mixture composed of Rokle bentonite (85 vol.%), quartz sand (10 vol.%, PR33 type glass raw material of narrow grain sizes 0.1–0.6 mm, from the Provodín area, Czech Republic), and graphite (5 vol.%, with 94–96 vol.% carbon content provided by Grafit Netolice, a.s., Czech Republic). The Mock-Up-CZ experiment was performed at the Centre of Experimental Geotechnics (CEG), Czech Technical University, with the objective to simulate the vertical placement of a canister with radioactive waste according to the Swedish KBS-3 system (Pacovský et al., 2007; Svoboda and Vašíček, 2008). Samples used in this study were extracted from the central part of the experimental set-up, where they had been exposed to: a combination of increased temperature (60–70 °C) and hydration through artificially prepared groundwater for a period of 45 months. Its use in this test extends the time for interaction of the material components with the fluids at given temperature.

3. Experimental procedures

3.1. Composition of saturation media

The experimental materials described in the previous section were subjected to interactions with five types of saturation media (see Table 1), which either represent natural groundwater (Josef) or simulate artificial groundwater with an increase primarily in K^+ and Mg^{2+} content. Natural groundwater was collected from the drill holes in the Josef Underground Educational Facility (the Josef UEF; located near the Slapy Reservoir by the village of Čelina in the Příbram district, southern part of Central Bohemia, Czech Republic).

3.2. Test conditions

The experiments were performed using the study material (Table 2) in (1) highly compacted blocks, (2) in dispersions and (3) as a hole-filling during an in situ experiment. In the case of the highly compacted blocks, only the Rokle bentonite was pressed to achieve a dry density of $\rho_d = 1600$ to ~2000 kg/m^3. The blocks were placed in small physical models, and were saturated with SGW-K and Josef saturation media at 95 °C. To avoid drying during the thermal loading which included a period of 13 days at 95 °C and 1 day at 25 °C, with a break for water level monitoring/water refilling, the samples were placed in pressure vessels. For further testing, individual samples were extracted after 3, 6, 12, and 18 months of interaction.

In experiments with dispersions, 4 kg of wet experimental material was mixed with 3 L of the saturation media (SGW-K and Josef type) into the intended dispersion. Pressure vessels were also used to avoid drying during thermal loading, which also included a period of 13 days at 95 °C and 1 day at 25 °C. Individual samples were extracted after 3, 6, 12, and 18 months of interaction.

Table 2
Tests specification. Explanation to abbreviations: Ro = Rokle bentonite, CEG = Centre of Experimental Geotechnics, ICT = Institute of Chemical Technology.

Test no.	Test purpose	Material	Saturation media	Test technique
1.	Mineralogical stability	Ro	SGW-K, Josef	CEG, highly compacted blocks, 95 °C
2.	Mineralogical stability	Ro, Feb, Mock-Up-CZ	SGW-K, Josef	CEG, suspension, 95 °C
3.	Mineralogical stability	Ro, Feb, Mock-Up-CZ	Josef	CEG, in situ procedure, Josef UEF
4.	Mineralogical stability	Ro, Feb, Mock-up-CZ	SGW-K, SGWK-10, SGW-Mg, SGW-Mg-10, Josef	ICT laboratories, 25 °C/80–90 °C
5.	Retention behaviour	Ro, Feb	SGW-K, SGWK-10, SGW-Mg, SGW-Mg-10	ICT laboratories, 25 °C
6.	Diffusion behaviour	Ro, Feb	SGW-K, SGWK-10	ICT laboratories, 25 °C