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Comparative study of HTO diffusion on individual and coupled systems of compacted bentonite and fresh ordinary Portland cement paste

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ABSTRACT

The radionuclide transport on the interface of compacted bentonite and cementitious materials has been rarely investigated. The goal of our project is to understand how processes at the interface of bentonite and cementitious materials affect the transport properties of bentonite. The paper describes methodology and evaluation procedure applied on HTO through-diffusion experiments on compacted bentonite/fresh hardened cement paste interface (coupled system). Under the same experimental conditions, HTO through-diffusion experiments were performed on individual materials and compared to experiments in the coupled system. To compare these two types of experiments, samples were saturated separately and coupled before the start of the through-diffusion experiments. An original method of modelling and evaluation of through-diffusion experiments performed in coupled system was applied. The effective diffusion coefficients of HTO in the compacted bentonite in both experimental arrangements, individual and coupled, were found to be in a very good agreement. Based on these finding, the prepared procedure of evaluation of through-diffusion experiments on the coupled system of two porous materials can be considered applicable on further planned studies of bentonite interfaces. A less good agreement, but still satisfactory, was obtained for the fresh hardened cement paste.

1. Introduction

The Czech deep geological repository (DGR) concept emplaced in crystalline rocks assumes disposing of two types of radioactive waste in two separate sections unaffected by each other. The first type represents spent nuclear fuel (SNF) assemblies enclosed in steel-based containers. The deposition tunnels with SNF containers will be backfilled with compacted bentonite and closed with concrete plugs. The second type comes mainly from decommissioning represents the intermediate-level waste (ILW) containing the long-lived radionuclide not being allowed to be disposed of in the near-surface repositories. The ILW will be emplaced in concrete based containers in specially excavated chambers that will be filled with backfill material, likely bentonite based (CEBAMA, 2016). An interface of bentonite and cementitious materials thus will need to be considered in the Czech DGR concept.

The highly alkaline pore fluids from cementitious materials may affect characteristics of bentonite (e.g. cation exchange capacity CEC, cation population on the exchangeable sites, mineralogical composition) that could lead to changes of several qualities of bentonite that are of the great importance for DRG safety, such as low permeability, high swelling pressure, and high sorption capacity for radionuclides.

Much research (Fernández et al., 2008, 2009; 2006; Jenni et al., 2014; Lerouge et al., 2017; Nakayama et al., 2004; Savage and Liu, 2015; Sugiyama and Tsuji, 2008) on clayey-cementitious materials interface has been done in the laboratory, in-situ, or by modelling. Changes in exchangeable cation population, mineralogy, hydraulic conductivity etc. have been widely investigated. To the authors's knowledge, very few publications can be found that address radionuclide transport on the interface of compacted bentonite and cementitious materials. (Karnland et al., 2007) and (Melkior et al., 2004) have used alkaline solutions (e.g. NaOH, $Ca(OH)_2$, or synthetic cement water) to simulate the presence of cementitious material when studying diffusion through compacted bentonite. Another approach is to purify and convert the bentonite to homo-ionic form as presented in (Karnland et al., 2007; Melkior et al., 2009). This approach might represent boundary conditions, in which all exchangeable cations in bentonite are exchanged, e. g. by calcium from cementitious materials. (Albinsson et al., 1996) approached to study radionuclide transport on the interface of compacted bentonite and cementitious materials by coupling saturated sample of compacted MX-80 bentonite with a concrete sample being spiked with a radiotracer. Apparent diffusion coefficients of ^{22}Na, ^{45}Ca and ^{134}Cs were determined from the tracer concentration profiles

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in bentonite (Albinsson et al., 1996). However, when investigating the coupled system of two materials, it is essential to experiment under the same conditions on the individual materials to observe any effects. Otherwise, conclusions based only on the experiments on the coupled system might be misleading.

The goal of our current project is to understand how processes at the interface of bentonite and cement materials affect the transport properties of bentonite. At first, we studied HTO diffusion through individual and coupled materials of compacted bentonite and fresh ordinary Portland hardened cement paste (HCP) under conditions like those expected in the Czech concept of DGR. In the coupled system setup, the materials were in contact only during the diffusion phase leading to none or minimal impact of HCP on the bentonite which was verified by further analysis. The main aim of this paper is to verify whether the same diffusion parameters of materials can be obtained from experiments on materials in coupled system and on individual materials. This verification is also necessary for the demonstration of the validity of the evaluation procedure presented here.

2. Materials and methods

2.1. Solid phases

Bentonite used in this study is the commercial product “Bentonite and Montmorillonite”, here denoted as “BaM″, produced by Keramost Obrnice, a. s. (Černý vrch deposit, NW Bohemia, Czech Republic, 2014). The bentonite characterization in terms of cation exchange capacity and exchangeable cations population is described below.

HCP was prepared from the Portland cement (CEM II/A-S 42.5R) provided by Lafarge Cement, a. s. (Czech Republic) by mixing with distilled water in the water to cement ratio w:c of 0.66. After 28 days of hydration at high humidity level (moulds were placed in the closed vessel above the water level bed), the HCP samples were cut into cylinders of desired dimensions for diffusion study.

Some HCP samples were used in addition to diffusion experiments for the porosity determination using mercury intrusion porosimetry (MIP) and gravimetry.

2.2. Aqueous phase

All experiments were performed in synthetic granitic groundwater, named SGW-UOS (Table 1, further denoted as “SGW″). It represents a simplified groundwater from boundary of shallow and deeper groundwater circulation (depths 20–100 m) in the granitic rocks of the Bohemian Massif (Červinka et al., 2016). SGW was prepared by mixing chemicals of analytical purity and the composition was controlled by atomic absorption spectroscopy (AAS) for cations, alkalimetry for alkalinity and ion chromatography (IC) for anions.

2.3. Sample preparation, saturation and equilibration

Bentonite was compacted in the cylindrical space of a diffusion cell body (a diameter of 30 mm, a thickness of 15.0–15.5 mm) to different dry densities and closed with end-plates composed from stainless steel filter membranes (thickness of 0.75 mm) placed on the carbon composite strainer. The diffusion cell was described in detail by (Gondolli and Večerník, 2014).

The process of preparing a saturated and equilibrated bentonite sample was identical for experiments on individual bentonite and on bentonite coupled with HCP. Following procedure was applied following the equilibration procedure used in e.g. (Melkior et al., 2007; Motellier et al., 2007). One reservoir with 30 mL of SGW was connected to the first side of the diffusion cell and vacuumed in the desiccator, the procedure was repeated with fresh 30 mL of SGW water after 3–5 days from the second side of the diffusion cell and thereafter again from the first side. Then, the equilibration phase was terminated by connecting both reservoirs to the cell filled with 60 mL of SGW water, solutions in both reservoirs were replaced by 60 mL of fresh SGW water at the regular intervals.

Table 1
Composition and pH of synthetic granitic water SGW-UOS.

Species	Na^+	K^+	Ca^{2+}	Mg^{2+}	Cl^-	SO_4^{2-}	HCO_3^-	pH
$mmol{\cdot}L^{-1}$	0.45	0.05	0.47	0.29	0.95	0.29	0.50	7.8

The HCP samples (on the individual system with a diameter of 45.8–45.9 mm and thickness of 10.5–12.3 mm; on the coupled system with a diameter of 36.0–36.4 mm and thickness of 10.3–10.5 mm) were kept immersed in vacuumed desiccator filled with SGW water for six weeks; SGW water was replaced by fresh one twice during the whole period. The HCP samples intended for experiments on the coupled system were firstly sealed into the end-plates of the diffusion cell for compacted clays by silicone glue before their saturation.

After six weeks of separated equilibration of both samples with SGW, one of two end-plates of diffusion cell (adjacent to saturated bentonite) was interchanged by end-plate with saturated HCP sample two days before the start of the through-diffusion experiment. Both reservoirs (60 mL) were connected to the cell.

The diffusion cell for rock samples, presented by (Havlová and Vopálka, 2010), was used for the through-diffusion experiments on the individual HCP samples.

2.4. Through-diffusion and profile analysis

The through-diffusion experiments were performed under controlled laboratory temperature 22 ± 3 °C. Reservoirs were filled with fresh SGW water, the inlet reservoir was spiked with HTO tracer to initial activity concentration of 2000–3500 $Bq{\cdot}mL^{-1}$ (SGW-HTO). HTO activity concentration was monitored in both reservoirs regularly by taking 0.25 mL for liquid scintillation counting analysis. To keep the constant volume of the solution the taken volume was replaced by the same volume of SGW into the outlet and the initial solution (SGW-HTO of initial activity concentration) into the inlet, respectively.

Through-diffusion experiments in coupled system of compacted BaM and HCP was performed in two configurations:

A inlet/filter/BaM/HCP/outlet ("BaM/HCP″),
B inlet/HCP/BaM/filter/outlet ("HCP/BaM″).

The through-diffusion experiments lasted 28 days except for experiments on individual bentonite that lasted 14 days. After this period, the bentonite sample was extruded and sliced into thin slices. Slices were weighed, and half of the slices was dried at 105 °C to a constant weight with the aim to determinate the bentonite porosity necessary for the evaluation of experiments and further analysis of CEC and cation population on the exchangeable sites. The second half of slices was leached with the known volume of SGW water and shaken. After a week, suspensions were separated by centrifugation. HTO activity concentration was determined in the supernatant to obtain concentration profile of HTO in the compacted bentonite.

We attempted also to determine the HTO profiles in HCP samples using the hand-sawing method. The results are discussed in Section 4.4.

2.5. CEC and cation population on the exchangeable sites

The saturated compacted bentonite and fresh hardened cement paste in the coupled system were in contact for 30 days. A possible change of CEC and cation population on the exchangeable sites due coupling both materials was determined by the Cu(II)-trien method based on (Bergaya and Vayer, 1997; Meier and Kahr, 1999). In addition, the raw bentonite and bentonite after the contact with SGW water