



## 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 findings, 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' 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)<sub>2</sub>, 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 <sup>22</sup>Na, <sup>45</sup>Ca and <sup>134</sup>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

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

Species	Na <sup>+</sup>	K <sup>+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Cl <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	HCO <sub>3</sub> <sup>-</sup>	pH
mmol·L <sup>-1</sup>	0.45	0.05	0.47	0.29	0.95	0.29	0.50	7.8

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.

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  $22 \pm 3$  °C. Reservoirs were filled with fresh SGW water, the inlet reservoir was spiked with HTO tracer to initial activity concentration of 2000–3500 Bq·mL<sup>-1</sup> (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

was analysed. 8 mL of 0.01 mol·L<sup>-1</sup> Cu(II)-trien was added to 200 mg of milled and dried bentonite samples. After the interaction, the suspensions were centrifuged and concentration of Cu, Na, K, Mg, and Ca was determined by AAS. CEC-sum and the cation population on the exchangeable sites and was calculated from the sum of Na, K, Mg, and Ca exchanged by Cu.

### 3. Modelling of diffusion on individual and coupled systems

A compartmental model was developed in the GoldSim environment, that was used for simulation and evaluation of diffusion experiments performed under different configurations and boundary conditions (Baborová et al., 2016; Havlová and Vopálka, 2010; Vopálka et al., 2006), mostly for 1D-through-diffusion configuration, i.e. inlet/(filter)/sample/(filter)/outlet. Parentheses illustrate the option of including separating filters in the simulation.

The presented experiments on the coupled system include two adjacent samples with different diffusion properties. Therefore, an update of the model was executed. Each sample (compartment) in the model is now characterized by its thickness, dry density, porosity, geometrical factor, and sorption characteristics (which were not considered for HTO). The model considered 1D-diffusion through the same diameters of both samples and filters. The real experimental arrangement described in Section 2.4 does not meet this geometry because of the different diameters of materials ( $d(\text{HCP}) = 36 \text{ mm}$ ,  $d(\text{BaM}) = d(\text{filter}) = 30 \text{ mm}$ ). It represents rather a 2D layout (axial diffusion in the whole system and radial diffusion at the interface of material with different cross-sections). The way of the approximation of experiment by the simplified model of 1D-through-diffusion experiment is presented in the following model example.

Numerical simulations were performed for HTO tracer to test effects of different configuration and samples diameters on the through-diffusion datasets (i.e. depletion and breakthrough curves and tracer concentration profile in the layers of both materials). No HTO sorption on both materials was assumed neither in the modelling study nor in the evaluating of real experiments. The reference diffusivity of HTO in free water  $D_w = 2.44 \cdot 10^{-9} \text{ m}^2 \text{ s}^{-1}$  was taken according to (Melkior et al., 2009). The other input parameters of the simulations were selected from similar materials (bentonite dry density, water to cement ratio w:c = 0.66, except of filters) but using the geometric dimensions of our experiments (Table 2). We have considered four cases:

- both materials have the same diameter of 30 mm;
- both materials have the same diameter of 36 mm;
- both materials have the same diameter  $d_c$  of 33 mm as a weighted arithmetic mean value for the total volume of coupled system in the real configuration:

**Table 2**

Selection of input parameters for modelling study.

parameter	Filter F	bentonite (1600 kg m <sup>-3</sup> ) B	hardened cement paste C
thickness $L$ (mm)	0.75	15.50	10.50
porosity $\varepsilon$ (-)	0.35 <sup>a</sup>	0.41 <sup>a,b</sup>	0.50 <sup>c</sup>
geometrical factor $G$ (-)	$FF/\varepsilon$	$FF/\varepsilon$	$FF/\varepsilon$
formation factor $FF$ (-)	0.19 <sup>a</sup>	$D_e/D_w$	$D_e/D_w$
$D_e \cdot 10^{11}$ (m <sup>2</sup> s <sup>-1</sup> )	$FF \cdot D_w$	5.8 <sup>a</sup>	2.0 <sup>d</sup>

<sup>a</sup> (Melkior et al., 2009).

<sup>b</sup> Bentonite porosity was estimated as  $\varepsilon = (1 - \rho_d/\rho_s)$ , where  $\rho_s = 2700 \text{ kg m}^{-3}$ .

<sup>c</sup> HCP porosity was estimated by extrapolation on the ratio w:c = 0.66 in (Gallé, 2001).

<sup>d</sup>  $D_e$  was estimated from Fig. 1 in Bejaoui and Bary (2007).

$$d_c = (V_{\text{BaM}} d_{\text{BaM}} + V_{\text{HCP}} d_{\text{BaM}}) / (V_{\text{BaM}} + V_{\text{HCP}}); \quad (1)$$

- individual materials (bentonite or HCP) of total thickness of 26 mm and diameter of 33 mm.

The first two cases set the estimated range at which all three experimental datasets should occur. The case c) demonstrates a simplified approach for conversion of real conditions to 1D layout. The case d) serves for monitoring the effect of coupled system of two different diffusion sets of parameters on transport.

Both experimental configurations, “F/B/C” (filter/bentonite/HCP) and “C/B/F” (HCP/bentonite/filter), were examined. Finally, the updated model was used for evaluation of experiments on individual and coupled systems. Our approach in the evaluation of real experiments on coupled system was based on the case c).

## 4. Results and discussion

### 4.1. HTO diffusion on coupled system – modelling study

Results of simulated HTO diffusion on individual and coupled systems of bentonite and hardened cement paste using input parameters from Table 2 are displayed in Figs. 1–3. According to the formulation of the first Fick's law, the sample diameter clearly affects the tracer evolution in both reservoirs. The larger the diameter; the faster the diffusion flow for a given diffusion coefficient, which implicates the faster changes in modelled activity concentrations in both reservoirs (compare case a) and b) in Fig. 1 and Fig. 2). A change of 3 mm on the samples diameter had a slight effect on HTO break-through curve. On the other hand, the depletion curves are quite different for different sample diameters as well for different configurations (compare difference between case c) and cases a) or b) in Fig. 1 and Fig. 2). The initial drop of HTO activity in the inlet reservoir is larger in case of configuration “F/B/C” due to the presence of separating filter which has a low diffusive resistivity. Particularly in Fig. 2, by comparing cases c) and d) of the series “F/B/C” and “F/B/F” it is evident that hardened cement paste reduces diffusion flow. Conversely, the bentonite and separating filter in the “C/B/F” series enlarges diffusion flow in comparison to configuration “-/C/-”. These two effects interfere with each other that can be seen on the equality of break-through curves for both experimental configuration of coupled system (“F/B/C” and “C/B/F”).

### 4.2. Experimental study of HTO diffusion on individual materials - BaM

Six through-diffusion experiments were performed on compacted bentonite of different dry densities. Concentration profiles revealed a significant diffusive resistance of separating filter membranes compared to the diffusive resistance of compacted bentonite. A large drop in HTO activity concentration was observed on the inlet/bentonite interface (see Fig. 4) and the slope of the profile data was low.

To evaluate these experiments, it was necessary to find formation factors ( $FF$ ) for bentonite and for filters. In case of  $FF_{\text{BaM}}$ , total porosity  $\varepsilon_{\text{BaM}}$  was determined gravimetrically so only geometrical factor  $G_{\text{BaM}}$  was unknown. While no parameter defining  $FF_{\text{F}}$  was known for separating filters. Best fit parameters were found based on simultaneous fitting of the break-through curve and the concentration profile.  $FF_{\text{F}} = 0.008 \pm 0.001$  was determined for this series. Fig. 5 shows effective diffusion coefficients calculated for the interval of  $FF_{\text{F}}$ . The uncertainty of the filter parameters has a significant effect on the uncertainty of the effective diffusion coefficient, especially at low dry densities. The presented asymmetric interval of the effective diffusion coefficient is caused by a disproportionate change of  $G_{\text{BaM}}$  to  $FF_{\text{F}}$ .

As can be seen from Fig. 5, very similar HTO effective diffusion coefficients were obtained on the bentonite BaM compared to other bentonites (CEC in meq/100 g, dominant cations): MX-80 (70–80, Na/

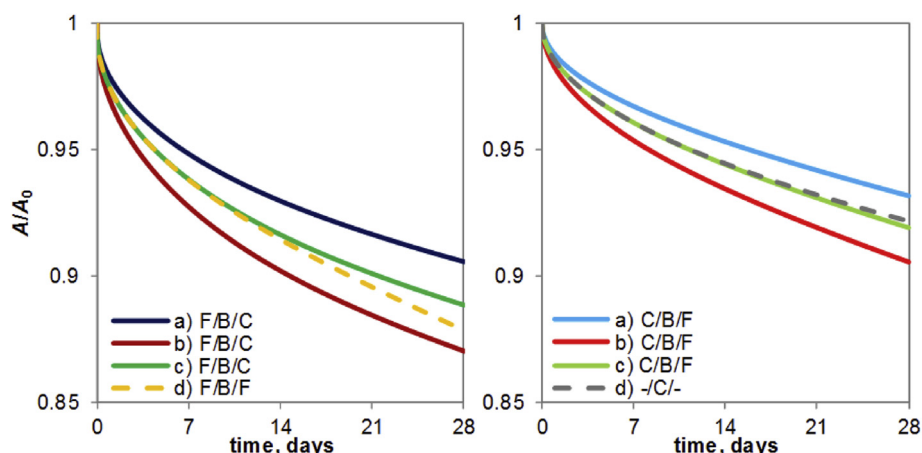


Fig. 1. Modelled depletion curves of HTO relative activity concentrations in the reservoirs (60 mL) for four different cases where the both materials have the same diameter of: a) 30 mm; b) 36 mm; c) 33 mm (as a 1D approximation of the real case); or d) where the individual materials have the same diameter of 33 mm.

Ca); FEBEX (100, Ca/Mg); and Kunigel-V1(60, Na/Ca).

#### 4.3. Experimental study of HTO diffusion on individual materials - HCP

Over 28 days, 9% of the initial HTO activity concentration had diffused into HCP samples, of which 4% of initial activity concentration had diffused out into the outlet reservoirs. The experiments were evaluated by fitting the experimental concentration data from both reservoirs, geometrical factor and total porosity being fitted. The best fitted porosity (or capacity factor) values were in the range of 0.67–0.71. Porosity values from obtained by gravimetry and MIP were 0.50–0.52 and 0.37–0.40, respectively. The large discrepancy in porosity values determined by different methods is often discussed, e.g. (Aligizaki, 2006; Gallé, 2001). To shed more light on this issue, the addition of the third dataset, i.e. HTO concentration profile in the HCP sample would narrow the uncertainty range of porosity values. However, the range of effective diffusion coefficients obtained was acceptable,  $(2\text{--}3)\cdot 10^{-11} \text{ m}^2 \text{ s}^{-1}$ .

#### 4.4. HTO diffusion on coupled system

The evaluation procedure consisted of fitting the experiments (using least-squares method) on coupled system by simulation of the diffusion experiment by the prepared model, in which we started from data previously obtained on individual materials.

The input data ( $\epsilon_{\text{BaM}}$ ,  $G_{\text{BaM}}$ ) for the actual dry density had to be

estimated for the predictive modelling. The total porosity  $\epsilon_{\text{BaM}}$  was determined gravimetrically and the relevant  $G_{\text{BaM}}$  was interpolated from the data presented in Section 4.2. To simplify the evaluation procedure, the  $FF_F$  of 0.008 (mean filter formation factor) was fixed as the input parameter.

The measured depletion curves and the concentration profiles of HTO relative activity concentration are shown in Fig. 6 and Fig. 7. Model predictions based on data from individual materials have provided good agreement only with “F/B/C” series - dataset from the inlet reservoir. In case of the same dataset in “C/B/F” series, a smaller decrease of HTO activity concentration was observed than expected. These observations lead us to the conclusion that the diffusion parameters of BaM and filters were set correctly, unlike HCP. The diffusive resistance of HCP samples with the diameter of 36 mm appears to be greater than those of 46 mm in diameter. Higher predicted parameters of HCP also greatly influence concentration profile in bentonite. Although we attempted to determine the HTO profile in HCP samples with the aim to reduce the number of degrees of freedom, we obtained, using the hand-sawing, only three experimental points. We are aware that HTO might evaporate by sawing. Therefore, we have decided that these data have not be considered in the evaluation. And therefore, HCP total porosity and geometrical factor were fitted. Since the porosity of compacted bentonite was quantified by gravimetry, the last fitted parameter was geometrical factor of bentonite.

It was assumed that both samples have the same diameter  $d_c = 33 \text{ mm}$  (case c) when evaluating data from experiments on

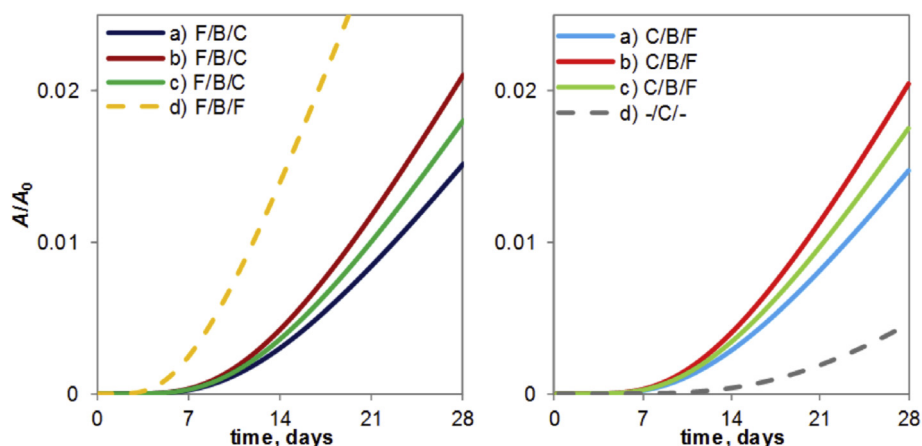


Fig. 2. Modelled break-through curves of HTO relative activity concentrations in the reservoirs (60 mL) for four different cases where the both materials have the same diameter of: a) 30 mm; b) 36 mm; c) 33 mm (as a 1D approximation of the real case); or d) where the individual materials have the same diameter of 33 mm.

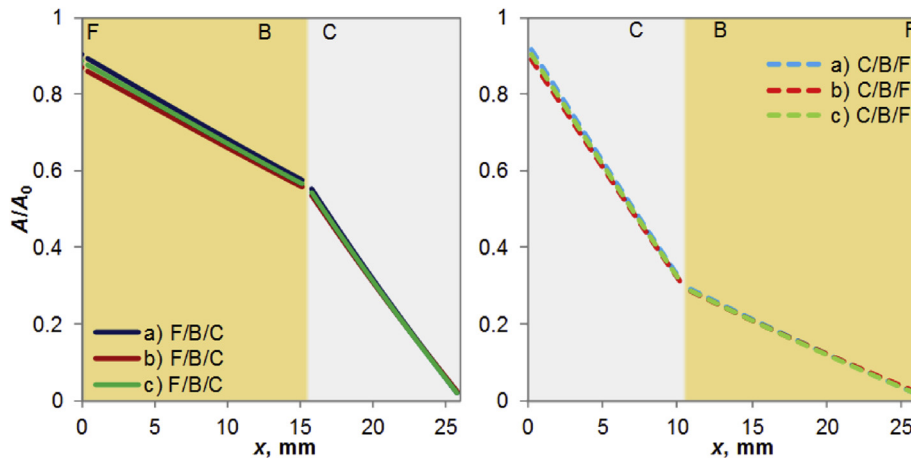


Fig. 3. Modelled concentration profiles of HTO relative activity concentration in the coupled system after 28 days for three different cases where the both materials have the same diameter of: a) 30 mm; b) 36 mm; c) 33 mm (as a 1D approximation of real case).

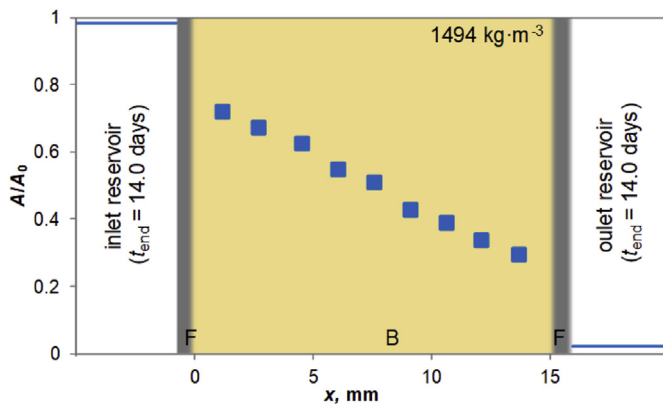


Fig. 4. Filter resistivity: experimental data of HTO in the both reservoirs (180 mL) and in the profile for selected sample BaM in the individual system.

coupled system. The best fitted parameters were found based on simultaneous fitting of three through-diffusion datasets. For these fitted parameters, case a) (both materials have the same diameter of 30 mm) and case b) (both materials have the same diameter of 36 mm) were also calculated. The region defined by case a) and b) can be viewed as an experimental uncertainty of diffusion parameters determination resulting from the simplified conversion of real conditions to the 1D layout. In addition, the uncertainty of the transport properties of the third layer, the separating filter, contributes to combined uncertainty. However, it was not considered in this study. The absence of concentration profile in the HCP samples has here a significant role;

interval of total porosity obtained was in the range of 0.40–0.70.

The effective diffusion coefficients obtained from experiments in the coupled system are in very good agreement with those determined from the results of experiments on individual bentonite samples (Fig. 5). However, slightly lower effective diffusion coefficients for HCP samples were determined for coupled configuration  $(1-2) \cdot 10^{-11} \text{ m}^2 \text{ s}^{-1}$  than for individual configuration. Nevertheless, the obtained data from both configurations are in good agreement with (Bejaoui and Bary, 2007).

Based on the good agreement of the results obtained from experiments on coupled system and on individual materials we can consider the developed experimental methodology and evaluation procedure as verified. It represents an effective tool for modelling and evaluating diffusion experiments of the different tracers (e.g. anionic tracers not retarded in the bentonite but retarded in cementitious materials or cationic tracers being retarded in both materials) and on different types of interface, especially for materials on which the diffusion experiment cannot be performed separately (e.g. such as a layer of corrosion products).

#### 4.5. CEC and cation population on the exchangeable sites

Three samples of bentonite, the raw BaM (obtained from different production lots), BaM after 8 weeks of interaction with SGW, and BaM from the layer adjacent to fresh HCP sample after 30 days of contact in the coupled system were examined. The results of CEC and cation population on the exchangeable sites are displayed in Fig. 8. No significant change in CEC or cation population in three sample types was found showing no significant impact of SGW water nor the fresh HCP sample on bentonite characteristics.

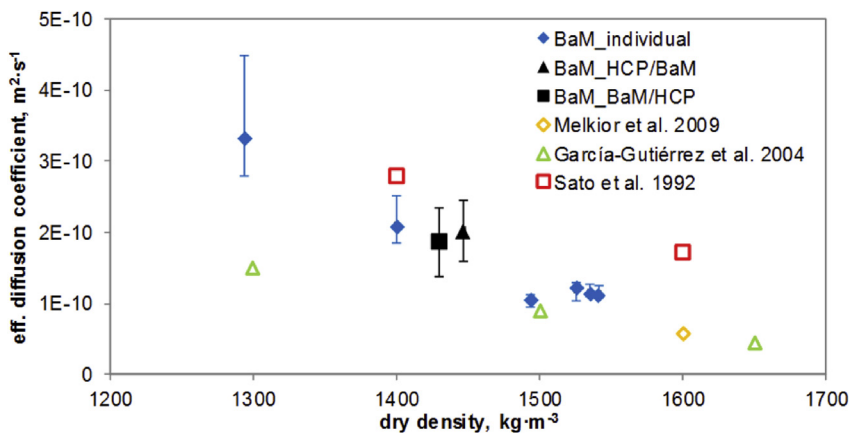


Fig. 5. Determined HTO effective diffusion coefficients on compacted bentonite BaM from through-diffusion experiments on individual and coupled system. Data for MX-80 (Melkior et al., 2009), FEBEX (García-Gutiérrez et al., 2004), and Kunigel-V1 (Sato et al., 1992) are displayed for comparison of bentonite transport properties.

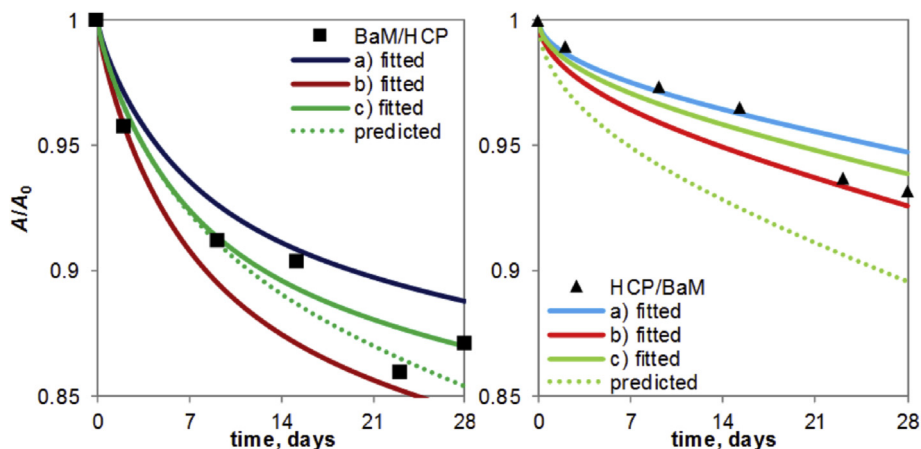


Fig. 6. Experimental, predicted and fitted HTO depletion curves in the inlet reservoir (60 mL).

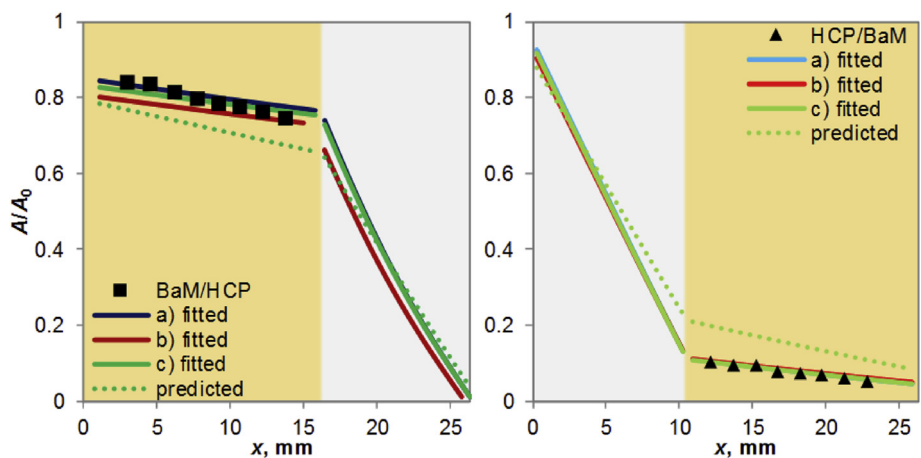


Fig. 7. Experimental, predicted and fitted HTO profiles.

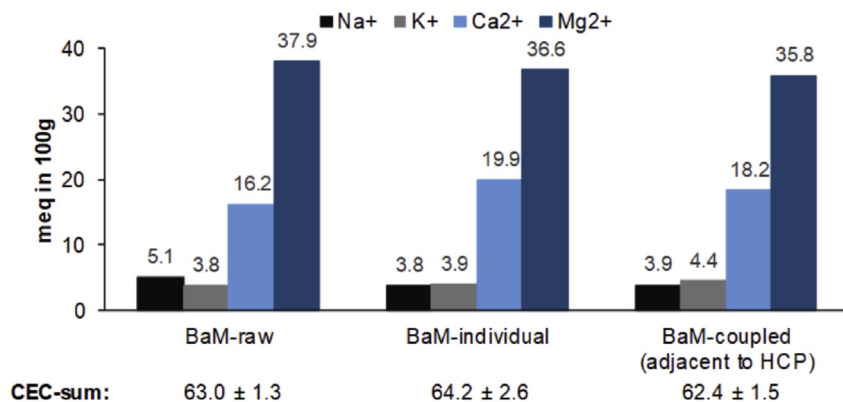


Fig. 8. CEC-sum and cation population on the exchangeable sites of BaM samples.

5. Conclusions

HTO diffusion through two materials, compacted bentonite, and fresh hardened cement paste, was studied. We have particularly focused on the effect of the materials interface on overall diffusion, mainly in bentonite part. This study has shown that if there is no significant interaction of these materials, cementitious materials can contribute to the slowing of the diffusion flux of species. No significant difference in effective diffusion coefficients from the through-diffusion experiments on individual and coupled systems (especially for compacted bentonite) has indicated that the updated diffusion model can be considered as

verified. Thereafter, the validated evaluation procedure will allow evaluating planned diffusion experiments through coupled systems being in contact for longer times. Alteration processes causing changes in the transport properties might be expected and thus also interpreted using this procedure.

The experimental uncertainty of determination of diffusion parameters of coupled system might be reduced. Therefore, in our future research, we intend to concentrate the research on developing an improved tracer profile analysis in cementitious samples.

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