# Migration Behaviour of Strontium in Czech Bentonite Clay

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## ABSTRACT

The study deals with sorption and diffusion behaviour of strontium in Czech bentonite B75. The study is a part of a research on reactive transport of radioactive contaminants in barrier materials of a deep geological repository of radioactive waste in the Czech Republic. Series of sorption and diffusion experiments with Sr and non-activated Ca bentonite B75 produced in the Czech Republic were performed in two background solutions ($CaCl_2$ and NaCl). On the basis of sorption batch experiments the kinetics of strontium sorption on bentonite was assessed and the sorption isotherms for various experimental conditions were obtained. As a result of performed diffusion experiments the parameters of diffusion (i.e. effective diffusion coefficient $D_e$ and apparent diffusion coefficient $D_a$) were determined. The observed discrepancies between sorption characteristics obtained from the sorption and diffusion experiments are discussed.

## KEYWORDS

*Bentonite, Strontium, Radionuclide migration, Reactive transport, Diffusion experiments, Batch method.*

## INTRODUCTION

The aim of the study is sorption and diffusion behaviour of strontium on Czech bentonite clay. Many studies were carried out worldwide to evaluate suitability of bentonite as a backfill and barrier material. Numerous studies performed in last 20 years with the natural Wyoming bentonite (MX-80) brought not only knowledge about the qualities of this type of bentonite but also established a set of laboratory procedures and methods of their evaluation that is being used for the study of clay materials. Batch experiments with Sr on MX-80 under various conditions accompanied by PHREEQC modelling were carried out by Garrido *et al*. [1]. Sorption behaviour of Sr and Cs on MX-80 was described by Liang *et al*. [2] with the use of two-stage Freundlich isotherm. Principles of ion diffusion in compacted bentonite were studied and summarized by

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Eriksen [3] as early as 1982. Diffusion and mobilities of various radionuclides under various redox conditions were under scope of Torstenfelt *et al*. [4]. Later, Eriksen and Jansson [5] and Eriksen *et al*. [6] combined sorption batch experiments and diffusion experiments to shed some light on the phenomenon of surface diffusion. Another thorough study of sorption and diffusion properties of bentonite was done by Yu and Neretnieks [7] and this work was updated by Ochs [8]. Comparison of $K_d$'s obtained from sorption and diffusion experiments was provided by Brandberg and Skagius [9].

The standardized procedures of sorption and diffusion experiments were also performed for example on Spanish (FEBEX) [10], Slovakian [11], Pakistani [12] or Japanese (Kunipia and Kunigel) [13] bentonites. These studies provided information regarding physical characteristics and sorption behaviour of bentonite and clay minerals of the smectite group, mostly under repository conditions. However, materials from different localities may behave differently due to the variations in their composition. Therefore, each material requires specific studies. Data obtained by sorption and diffusion laboratory and in situ experiments contribute to the understanding of contaminant migration in the environment and also can serve as input data for the predictive models. In some cases [14], data from sorption batch experiments are used in the base documentation for predictive modelling and performance or safety assessment. This simplified approach certainly reduces the time required for the safety data acquisition; however, the accuracy of such data may be questionable. Physico-chemical properties of bentonite material may be altered in compacted state (as in the diffusion experiment) compared to loose state (as in the batch experiment). Therefore, this study shows and compares data obtained for these two types of experiments under various conditions.

### *Sorption and diffusion properties of Sr*

Together with caesium isotopes, isotope $^{90}$Sr belongs to the most abundant fission products and its relatively long half-life ($T_{1/2}$ = 28.8 years) ranks it to the group of radionuclides that occur in the spent nuclear fuel after its disposal [15]. Under repository conditions it exists mainly in the form of $Sr^{2+}$. Owing to it's relatively simple chemistry and chemical similarity with other elements from the group of alkali earth metals, Sr serves in various studies as an analogue of other critical radionuclides, particularly Ra.

In one of SKB reports, Yu and Neretnieks [7] described basic principles of sorption and diffusion behaviour of various radionuclides in compacted bentonite (MX-80). Sorption experiments with Sr on other types of bentonite were carried out e.g. on Spanish FEBEX bentonite [10], Slovakian [11] or Pakistani bentonite [12]. All of these sources agree that the sorption kinetics of Sr on clay-type material is fast and equilibrium state is reached within few hours. The sorption of Sr is usually described as non-specific and reversible and the sorption mechanism is mostly considered to be ion exchange. This is supported by the fact that Sr sorption is dependent on the ionic strength and the composition of exchangeable complexes. Competitive strength of an ion depends on it's charge and hydrated diameter. Most important competitive ion for Sr is reported to be Ca due to it's similar hydrated diameter and the same charge. This may be also illustrated by the fact that the sorption behaviour of Sr and Ca was found to be very similar from both qualitative and quantitative points of view [10]. Decreasing trend of Sr sorption with the increasing ionic strength is described in studies of Missana *et al*. [10] or Ruminin *et al*. [16]. At higher pH values (>8) mechanism of surface complexation may be also of importance. Both Cole *et al*. [17] and Carrol *et al*. [18] studied thoroughly sorption process of Sr in loose or compacted clay materials with the use of EXAFS method and mathematical modelling and in their works they describe Sr pore water and surface speciation in detail. The results of both authors indicate that adsorption of Sr to clay surfaces occurs as weak outer sphere bonding (single coordination shell of the ion interacts with the mineral surface). Cole *et al*. [17] also showed that minor occurrence of an aquo-carbonate species $SrCO_3$(aq) significantly increases the total adsorption affinity of Sr for the clay surface above pH 8.5. In the study of Eriksen *et al*. [6] sorption of Sr on bentonite was also found to be pH dependent and the highest uptake was observed at pH 8.5. According to Liang *et al*. [2], several reasons may be responsible for this behaviour, e.g. enhanced negative surface charge of bentonite clay minerals; enhanced dissolution of bentonite; precipitation of Sr as $Sr(OH)_2$. It was also found that pH dependence increases with increasing initial concentration of Sr [1]. On the other hand, Spanish researchers [10] showed that sorption of Sr in concentration range from $10^{-9}$ to $10^{-4}$ mol/L is more dependent on ionic strength than on pH. Precipitation or co-precipitation of Sr with carbonates, sulphates or hydroxides may influence Sr removal from the liquid phase, especially at higher pH values (>8) or at higher concentrations of these compounds in the system.

## MATERIALS AND METHODS

Two types of methodologies were performed within the frame of this work with the aim to determine diffusion parameters of Sr in the Czech bentonite B75 and to compare distribution coefficients obtained from sorption batch experiments and diffusion experiments with compacted bentonite.

### *Bentonite*

The material used was commercial non-activated bentonite 75 (B75) which originates from the Rokle deposit (Cenozoic neovolcanic area, NW Bohemia, Czech Republic). This material belongs to the natural bentonite product group and no additives or modifications applications were declared [19]. Detailed mineralogical and chemical characterization of bentonite B75 was performed in the Czech Republic [20]. According to the analyses, B75 contained 75.5% of montmorillonite and CEC was 56.8 meq/100 g. The analyses indicated that originally Ca/Mg bentonite was probably contaminated during the processing with the activation reagent which is being used to transform other types of bentonites into Na-form on the same production line, which is illustrated by distribution of major cations summarized in Table 1.

Table 1. Cation Exchange Capacity (CEC) and distribution of major exchangeable cations in bentonite B75 [meq/100g] determined by Cu-trien method [20]

| | [meq/100g] |
|---|---|
| CEC | 56.8 ± 1 |
| Ca | 2.0 ± 0.7 |
| Mg | 26.4 ± 0.7 |
| Na | 36.9 ± 0.4 |
| K | 3.6 ± 0.1 |

### *Description of reactive diffusive transport*

In materials with low hydraulic conductivity, such as in clay materials, the migration of radionuclides is mainly controlled by diffusion. Diffusive transport in saturated homogenous and isotropic system is described by Fick's diffusion laws, solutions of which for simple initial and boundary conditions are used for the evaluation of diffusion experiments. These approaches, which are based on the solution of the 1D diffusion eq. (1), are collected e.g. in the works of Yu and Neretnieks [7] or Shackelford and Moore [21]. Diffusion of radionuclides through the layer of compacted bentonite is influenced by both physical (porosity $\varepsilon$, geometric factor $G$) and chemical parameters of kinetic and equilibrium models describing the interaction of studied species with the solid phase. The dependences of diffusion parameters, namely effective diffusion coefficient $D_\mathrm{e}$ and apparent diffusion coefficient $D_\mathrm{a}$, on physical and chemical parameters were for the description of sorption by the linear equilibrium model expressed by eq. (2) and (3):

$$\frac{dC}{dt} = D_\mathrm{p}\frac{d^2C}{dx^2} - \frac{\rho_\mathrm{d}}{\varepsilon}\frac{dq}{dt} \tag{1}$$

$$D_\mathrm{e} = \varepsilon \times D_\mathrm{p} = \varepsilon \times G \times D_\mathrm{w} \tag{2}$$

$$D_\mathrm{a} = \frac{D_\mathrm{e}}{\varepsilon + \rho_\mathrm{d} \times K_\mathrm{d}} \tag{3}$$

where: $C$ is concentration in the liquid phase, $q$ is concentration in the solid phase, $D_\mathrm{w}$ is reference diffusivity in water, $D_\mathrm{p}$ is pore diffusion coefficient, $x$ is longitudinal coordinate, $\rho_\mathrm{d}$ is dry density, $\varepsilon$ is porosity, $G$ is geometric factor, $K_\mathrm{d}$ is distribution coefficient.

### *Sorption experiments*

The standard batch method [22] was used for the study of Sr sorption kinetics and equilibrium characteristics. The range of solid-to-liquid ratio (*m/V*) varied from 0.005 to 0.2 g/mL (Figure 1). With the aim to assess the difference between distribution coefficients $K_\mathrm{d}$ obtained from the sorption experiments with equilibrated and non-equilibrated bentonite samples, equilibrated (presaturated) bentonite was prepared. For that purpose, the bentonite samples (weighed with the correction on actual water content) were contacted with background electrolyte for 3 × 24 hours before the start of a batch experiment with Sr.

The experiments were performed with two values of Sr concentration, $10^{-3}$ mol/L and $10^{-5}$ mol/L of $SrCl_2$ spiked with radioactive tracer $^{85}$Sr ($T_{1/2}$ = 64.8 d, produced by LACOMED company). As background solutions were used either 0.033 mol/L $CaCl_2$ or 0.1 mol/L NaCl. The ionic strength of both solutions was 0.1 mol/L. The initial pH was in the neutral range. All experiments were carried out under laboratory temperature. Based on the kinetic experiments, which ranged from 15 minutes up to 19 days, contact time for equilibrium characteristics was set to 3 days.

At the start of the experiment, the bentonite samples were contacted with 6 mL of solution containing background electrolyte and $SrCl_2$ in desired concentration spiked with $^{85}$Sr. Vials were placed into the horizontal shaker (Yellowline RS10 basic, 120 rpm). After the desired contact time they were centrifuged (MPW-350R, 10 min, 966 g), 2 mL of supernatant were extracted into measuring vials and $^{85}$Sr activity was measured in the well-type NaI(Tl) detector (Tesla, $\eta \approx 24\%$) with single-channel analyser (Tema JKA300 RS232). After the termination of experiments, pH was measured to assess the influence of the contact of solution with various amounts of bentonite.

For calculations of $K_\mathrm{d}$ [L/kg] usual eq. (4) was used [23]:

$$K_\mathrm{d} = \frac{q}{C} \tag{4}$$

where: $q$ is concentration of Sr sorbed on the solid phase in equilibrium ($q = \frac{(C_0 - C) \times V}{m}$), $C_0$ is initial concentration in the liquid phase, $C$ is concentration in the liquid phase in equilibrium, $V$ is volume of the liquid phase, $m$ is mass of the solid phase.

Overall distribution coefficient $K_\mathrm{d}$ of each experiment was determined from the slope of the linear regression fitted to the data expressing the relation between $q$ [mol/kg] and $C$ [mol/L].

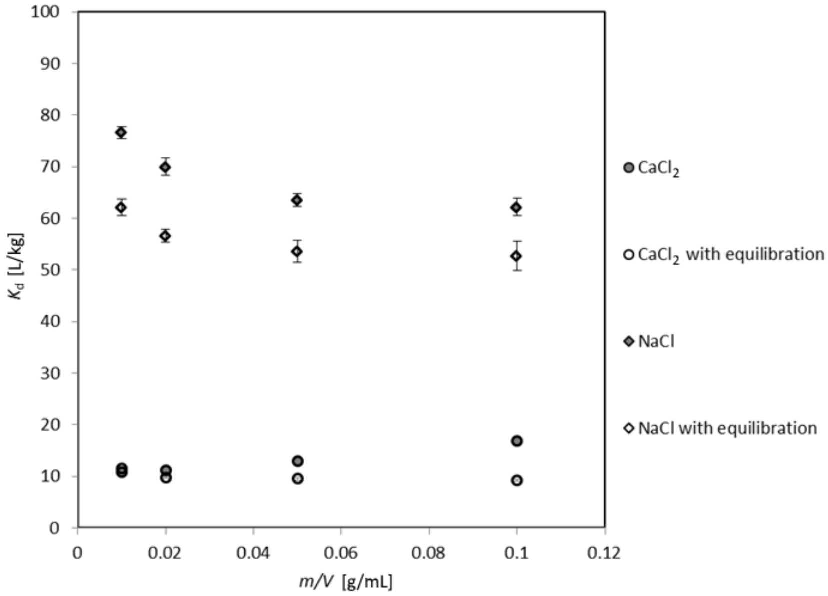

Figure 1. Distribution coefficient $K_\mathrm{d}$ (4) as a function of $m/V$ [g/mL]

### *Diffusion experiments*

Diffusion experiments were carried out in a diffusion cell (the set-up is described in [20]). The amount of bentonite, weighed according to the chosen dry density (1,300 or 1,600 kg/m$^3$) and actual water content, was pressed into the steel sample holder ($d$ = 30 mm) by a simple manual press. Diffusion cells with bentonite plugs of two lengths (15 mm and 5 mm) were prepared and reservoirs of the volume of 190 mL were used. Firstly, the compacted bentonite was saturated with the studied background solution, i.e. 0.033 mol/L $CaCl_2$ or 0.1 mol/L NaCl, in the vacuum chamber for two weeks. The direction of saturation was changed at least once. This step may also partly remove the concentration excess of soluble carbonates, which are present in B75 as a contamination from the activation procedure.

At the start of each experiment, the outlet reservoir was filled with 160 mL of the fresh solution of background electrolyte and in the inlet reservoir was in addition injected solution of $SrCl_2$ in the concentration of $10^{-3}$ mol/L spiked with $^{85}$Sr. The samples of inlet and outlet solutions were withdrawn in regular intervals until the experiment was terminated and measured in the same way as in sorption experiments. After the determination of $^{85}$Sr activity the samples were returned into the reservoirs. At the experiment termination, the bentonite plug was cut into the thin slices of 0.5 or 1 mm. Each slice was placed into the measuring vial, weighed, dried in the air dryer and then weighed again to determine the water content. Before $^{85}$Sr activity measurement, 3 mL of distilled water were added to each sample to maintain homogeneous geometry. As a result, concentration profile of Sr in the bentonite plug was obtained.

Diffusion experiments lasted from 21 to 42 days. With the aim to reduce the duration of the diffusion experiments, they were not led to stationary state. Therefore, no standard evaluation method (e.g. "time-lag" method published e.g. by Shackelford [24]) could be used for the determination of both effective diffusion coefficient $D_e$ and apparent diffusion coefficient $D_a$. An original method was used, in which diffusion coefficients were obtained by simultaneous fitting of the concentration profile curves and the time development of concentrations in both reservoirs with an extension of the code prepared in our laboratory [25], which enables to take into account common conditions of through-diffusion experiments (non-constant concentration in working reservoirs during the experiment and the presence of filters). The code was prepared in the GoldSim environment [26] and uses an implementation of Box's method [27] for the optimization of selected parameters of the model. The values of $K_d$ and geometric factor $G$ were optimized, with fixed values of filter parameters (length $l_f$ = 0.8 mm, bulk density $\rho_f$ = 3,000 kg/m$^3$, porosity $\varepsilon_f$ = 0.33 and geometric factor $G_f$ = 0.045) and with the value of reference diffusivity $D_w = 1.58 \times 10^{-9}$ m$^2$/s [28]. Bentonite B75 specific density $\rho_s$ was 2,772 kg/m$^3$ [20] and porosity $\varepsilon$ was calculated for each sample from the value of weighted dry mass of bentonite.

## RESULTS AND DISCUSSION

### *Sorption experiments*

It was confirmed that $Sr^{2+}$ sorption kinetic on this type of material is very fast, over 90% of the total sorptives was adsorbed within one hour. On the scale of several days some trend in the change of sorption was observed, although the change was below 5% level during 24 hours, which is recommended as a borderline of equilibrium state [22]. Based on this result, contact time for equilibrium sorption experiments was set to 3 days. The sorption kinetics of Sr was faster in the NaCl environment compared to the $CaCl_2$ environment. In this study, initial pH was naturally buffered from the value of about 6.8 up to 7.5 in the case of $CaCl_2$ solution and up to 8.4 in the case of NaCl solution respectively, depending also on $m/V$ ratio. We assume that ion exchange was the dominant sorption mechanism, even though precipitation with carbonates, especially in NaCl background solution, may have contributed to Sr removal from the liquid phase.

Figure 1 shows the difference between distribution coefficients $K_d$ obtained from experiments with equilibrated and non-equilibrated bentonite samples. In the case of $CaCl_2$ solution the decrease in $K_d$ value was of 11.7% and of 18.7% in the case of NaCl solution. Furthermore, after equilibration the dependence of $K_d$ on the $m/V$ ratio decreased, especially in the $CaCl_2$ solution. It supports the hypothesis that bentonite B75 had been contaminated with activation reagent and soluble carbonates contribute to Sr removal from the liquid phase. Many authors report that precipitation or co-precipitation of Sr with carbonates, sulphates or hydroxides may influence Sr removal from the liquid phase, especially at higher pH values (>8) or at higher concentrations of these compounds in the system. Cole *et al*. [17] stated that $K_d$ of $SrCO_3$ for clay material is 60 × higher than $K_d$ for $Sr^{2+}$ and that its sorption is reversible.

As showed in Figure 2, for sorption of Sr in the NaCl environment the linear isotherm (4) is applicable. The slope of the linear regression represents the overall $K_d$ of the experiment. Values of $K_d$ were generally higher for the experiment where NaCl background solution was used (see Figure 1). This could be accounted to the effect of weaker competitive strength of Na relative to Ca [1]. Some data, especially from $CaCl_2$ solution, show a rather non-linear trend. This may be caused by relatively high concentration of Sr combined with competition with Ca ion. According to Liang *et al*. [2], Sr concentration of $10^{-3}$ mol/L may be high enough to result in the curved shape of the isotherm.

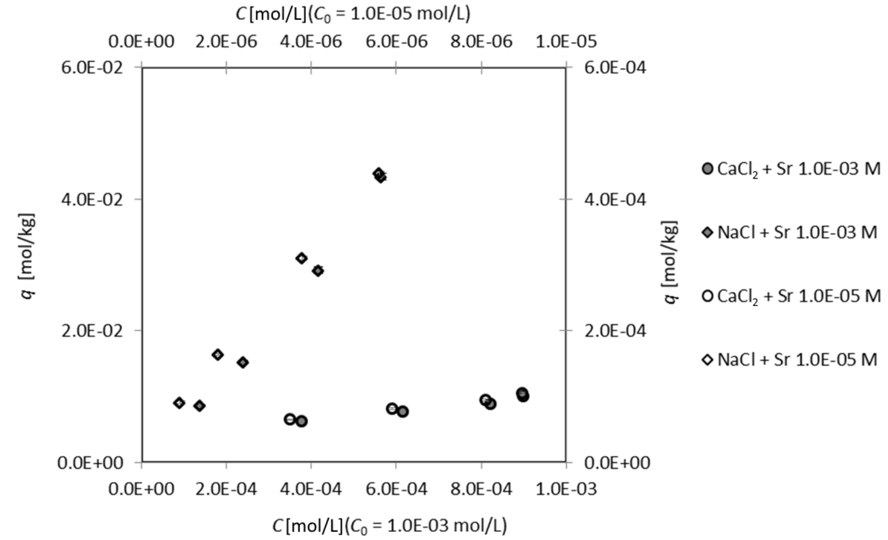

Figure 2. Sorption isotherms of Sr on bentonite B75 for four types of initial solution

Regarding the linearity of Sr sorption, sources are not absolutely unambiguous. Some authors, e.g. [10], consider the use of $K_d$ for Sr sorption on bentonite and similar materials to be sufficient. Freundlich isotherm for Sr sorption on bentonite was used by Liang *et al*. [2] and Tsai *et al*. [29]. Galambos *et al*. [11] used Langmuir isotherm for the evaluation of Sr sorption on Slovak bentonite. The main advantage of the use of $K_d$ is that it may be relatively easily determined and compared. On the other hand, the disadvantage is it's exclusive relevance for given conditions, resulting in problematic transfer to real conditions. $K_d$ dependence on experimental conditions causes relatively wide variability of values found in literature. For example, sorption and diffusion behaviour of various radionuclides including Sr in the granitic environment is summarized in the SKB report [30] and the authors recommend $K_d$ value to be 10 L/kg with the uncertainty interval from 5 to 50 L/kg.

### *Diffusion experiments*

The graphs in Figure 3 show the relative change of concentration in the inlet reservoirs in time of the experiment duration and concentration profiles in the bentonite plugs after the experiment termination. From the qualitative evaluation of these experiments it is possible to draw following conclusions.

The linear course of concentration profiles in the bentonite layer suggests that the experiments performed in diffusion cells of 5 mm in length approached stationary state. However, the comparison of in-flow to and out-flow from the bentonite layer showed that these are not equivalent and therefore the assumption that the stationary state is reached is not true. In the cells with length of 15 mm reaching stationary state would last several more weeks or months [31].

It is showed that the course of the diffusion experiments (especially of those which lasted 21 days) differs significantly for different background solutions but it does not differ much in dependence of dry density. This can be noted even for the diffusion parameters summarized in Table 2, even though diffusion parameters exhibit relatively large variance. $D_e$ and $D_a$ values should, according to Yu and Neretnieks [7], decrease with increasing dry density. Others [3], however, did not observe significant influence of dry density and homogeneity of material on diffusion parameters. Here, the difference is expressed mainly in the amount of Sr sorbed in the solid phase. When the compaction is higher, the more sorbent is available to take up higher amount of Sr which is in agreement with theoretical assumption. The ratio of the sorbed amount in the two environments is, however, in contrast to the results of sorption experiments, where higher sorption of Sr was observed in the NaCl environment (compare Table 2 and Table 3). Explanation of differences between values of $K_d$ determined from diffusion and sorption experiments as well as explanation of differences in migration behaviour of Ca and Na bentonite are discussed by many authors. In studies of Eriksen *et al*. [6] and Eriksen and Jansson [5], distribution coefficients $K_d$ found in sorption and diffusion experiments were similar and the assumption that $K_d$ would be lower for diffusion experiment was not proved. The difference between $K_d$ obtained from sorption and diffusion experiments was reported by Missana *et al*. [10] and Van Loon *et al*. [32] but, according to these authors, the uncertainty was within the range and was accounted to the difference in methodology of experiments. Another authors, e.g. Yu and Neretnieks [7] and Brandberg and Skagius [9], observed the differences between $K_d$ values obtained from sorption and diffusion experiments. These differences may be accounted to different preference of ion exchange in loose and compacted bentonite. While in the case of loose bentonite, divalent ions and ions with larger diameter are competitively stronger, it is just opposite in the case of compacted bentonite. It may be due to two reasons:

- The interlayer spaces are not completely opened in compacted bentonite and therefore not all of the sorption places are available;
- Ions in the compacted bentonite move without (or partly without) their hydration shell.

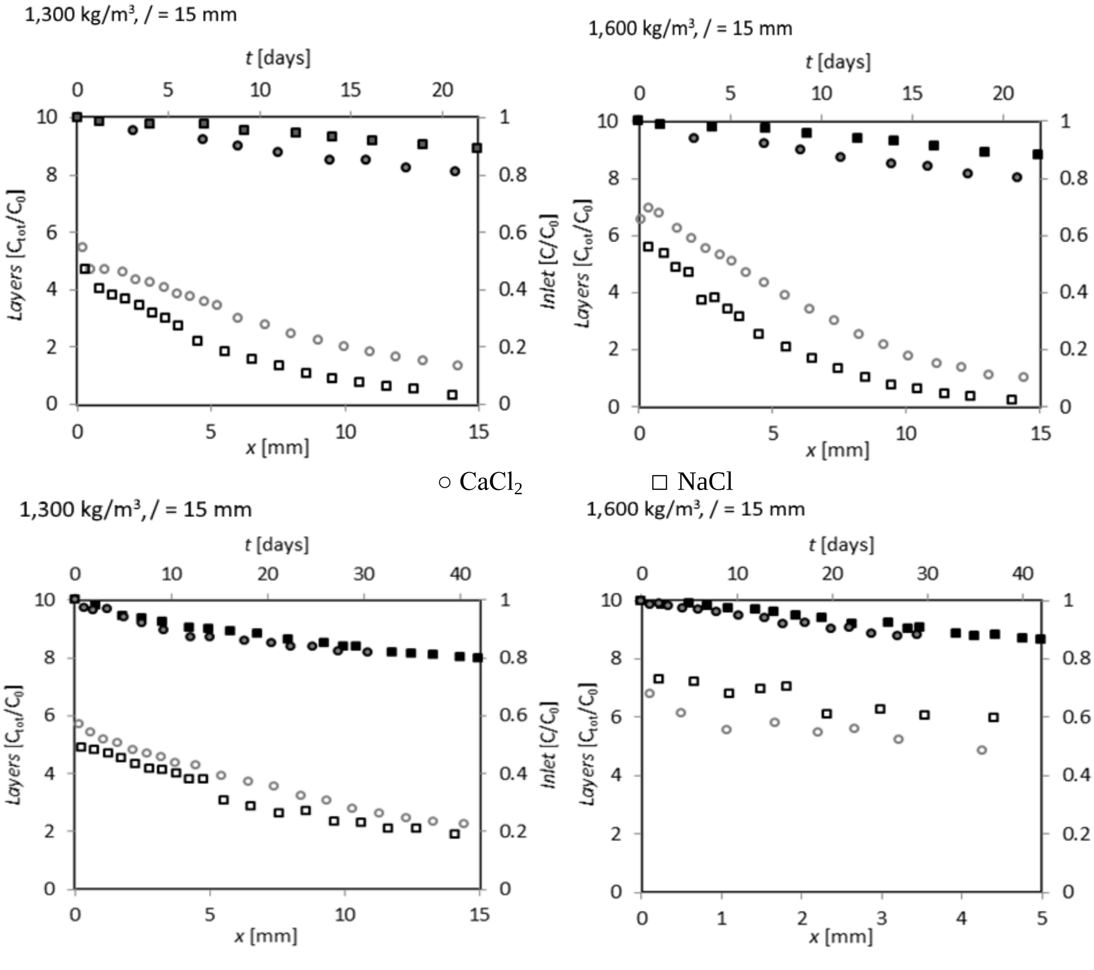

Figure 3. Data obtained from diffusion experiments with Sr and bentonite B75 compacted to 1,300 kg/m$^3$ (left) and 1,600 kg/m$^3$ (right) for two types of background solution ($CaCl_2$ and NaCl)

Some studies [14], where the use of data from sorption experiments is applied, are defended, e.g. in previous study [33] or by Ochs *et al*. [34], who claim that distribution coefficients are applicable for the conditions of compacted material, when appropriate *m/V* ratio and pore water chemistry is considered and the data are extrapolated for these conditions.

Table 2. Summary of diffusion parameters of Sr on bentonite B75

| Background solution | Length of cell [mm] | Contact time [days] | $\rho_d$ [kg/m$^3$] | $\varepsilon$ [-] | $K_d$ [L/kg] | $G$ [-] | $D_a \times 10^{11}$ [m$^2$/s] | $D_e \times 10^{10}$ [m$^2$/s] |
|---|---|---|---|---|---|---|---|---|
| 0.033 M $CaCl_2$ | 15 | 29 | 1,604 | 0.422 | 8.3 | 0.410 | 2.25 | 2.74 |
| | 5 | 29 | 1,637 | 0.410 | 7.3 | 0.840 | 4.15 | 5.45 |
| | 15 | 30 | 1,604 | 0.421 | 6.9 | 0.466 | 3.04 | 3.11 |
| | 15 | 30 | 1,314 | 0.526 | 7.5 | 0.679 | 5.77 | 5.65 |
| | 15 | 21 | 1,296 | 0.523 | 6.7 | 0.501 | 4.97 | 4.14 |
| | 15 | 21 | 1,596 | 0.414 | 8.2 | 0.542 | 3.74 | 3.55 |
| 0.1 M NaCl | 15 | 42 | 1,300 | 0.531 | 5.8 | 0.362 | 3.63 | 3.04 |
| | 5 | 42 | 1,596 | 0.424 | 9.3 | 0.800 | 8.82 | 5.37 |
| | 15 | 21 | 1,300 | 0.531 | 4.1 | 0.104 | 1.44 | 0.877 |
| | 15 | 21 | 1,600 | 0.423 | 4.6 | 0.126 | 1.27 | 0.845 |

Table 3. Summary of experimental conditions and distribution coefficients of Sr on bentonite B75

| Sr initial concentration [mol/L] | Background solution | $K_d$ [L/kg] |
|---|---|---|
| 1.0E-03 | 0.033 M $CaCl_2$ | 11.6 ± 0.8 |
| 1.0E-03 | 0.033 M $CaCl_2$ with equilibration | 10.3 ± 0.6 |
| 1.0E-05 | 0.033 M $CaCl_2$ | 12.5 ± 1.0 |
| 1.0E-03 | 0.1 M NaCl | 72.8 ± 2.8 |
| 1.0E-03 | 0.1 M NaCl with equilibration | 59.2 ± 2.0 |
| 1.0E-05 | 0.1 M NaCl | 80.3 ± 2.4 |

Contact time was 21 days (top) and 30 or 42 days (bottom). Solid points represent Sr concentration decrease in inlet reservoirs during the experiment duration. Open points represent Sr concentration profile in the bentonite plug after the experiment termination.

From the different speed of concentration decrease in the inlet reservoirs of the experiments it can be seen that for both values of compaction the diffusive transport was slower in the NaCl environment compared to $CaCl_2$ environment (see Figure 3). It may be caused by higher sorption in the $CaCl_2$ environment under the conditions of compacted bentonite and/or higher diffusive resistance of the bentonite in the NaCl environment. The first conclusion is supported by the higher Sr concentration in the bentonite layer in the $CaCl_2$ environment. Sorption generally enhances diffusive transport because it lowers the concentration in the liquid phase and thus enhances concentration gradient. The second conclusion is also in agreement with the recent state of knowledge. Different behaviour of Ca and Na bentonite lies above all in their different physical behaviour, which is quite well described in literature, e.g. by Katsumi *et al*. [35] or Montes-H. *et al*. [36]. In Na bentonites are observed higher swelling pressures, which is accompanied by the decrease in the volume of wider (intergranular) pores in ratio to smaller (intragranular/interlayer) pores. The first effect should lead to decrease in the value of $K_d$ in Na compared to Ca environment, which may be confirmed by the data presented here. The second effect should lead to decrease in the value of $D_e$ in Na bentonite. This is confirmed by Choi and Oscarsson [37] who observed 2-6× lower $D_e$ in Na bentonite compared to Ca bentonite. They also compared porosities of these two types of bentonite by Hg porosimetry measurement. Although the values of diffusion coefficients presented here show rather large variance, the observed breakthrough times of Sr through bentonite plug were generally longer in NaCl environment compared to $CaCl_2$ environment.

Values of $D_e$ for Sr on compacted bentonite usually range in the order of $10^{-10}$ $m^2/s$ and $D_a$ in the order of $10^{-11}$ $m^2/s$, as reviewed in many reports and articles. All of the values summarized in the Table 3 are within this range. In general, it can be concluded that diffusion parameters ($K_d$, $G$, $D_a$, $D_e$) are higher in the $CaCl_2$ environment compared to NaCl environment. This is related to the above described differences between Ca and Na bentonite. This is also supported by the difference in the relative change in concentration decrease in inlet reservoirs. The values of diffusion coefficients, however, exhibit relatively large variance and their uncertainty may be relatively large (>10%). It is given by heterogeneity of bentonite material, uncertainties of experimental character and uncertainties related to newly established optimization program. Experimental set up may also influence values of diffusion parameters and their associated uncertainties. Aldaba *et al*. [38] for example compared diffusion coefficients obtained from evaluation of various types of diffusion experiments of Sr and Spanish soil samples, e.g. using half-cell or planar source method, and it was found out that the planar source method underestimates the resulting values of diffusion coefficients.

## CONCLUSION

Sorption and diffusion experiments were performed to investigate sorption and diffusion of Sr on Czech bentonite B75 under various conditions. Sorption kinetics, sorption isotherms and diffusion parameters were assessed and compared for two types of background solutions. It was confirmed that the sorption of Sr on bentonite is fast which indicates that the main mechanism of sorption is ion exchange. Diffusion of cationic species through the porous material is influenced by their interaction with the charged surface of the material and by the physical properties of the material. $K_d$ values obtained from sorption and diffusion experiments were compared and it was shown that there may occur significant discrepancies between $K_d$ values obtained from these two types of experiments. Whereas $K_d$ values of Sr obtained from sorption experiments in NaCl environment were approximately 7 times higher compared to $CaCl_2$ environment, this ratio was opposite in diffusion experiments. This was accounted to different physical conditions of bentonite during these two types of experiments. Moreover, the diffusion of Sr was slower in NaCl environment than in $CaCl_2$ environment, which may be explained by higher tortuosity of bentonite with dominating Na ion. Prepared original method of evaluation of diffusion experiments which are not led to the stationary state does not require long duration of experiments, which is very valuable in terms of minimization of time necessary for migration data acquisition. Development of experimental and modelling methodologies is an important part of scientific support for the future repository. This work contributes to the understanding of transport processes in bentonite barrier of geological repository with respect to the conditions of Czech concept and helps to evaluate local materials. Development of experimental and modelling methodologies is also an important part of scientific support for future geological repository. Further work is needed to investigate the influence of other factors, such as bentonite and related pore water composition and their alterations and combinations under real conditions, on the sorption and diffusion processes.

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## NOMENCLATURE

| | | |
|---|---|---|
| B75 | Czech bentonite 75 produced by Keramost company | |
| $C$ | solute concentration in the liquid phase | [mol/L] |
| $C_0$ | solute initial concentration in the liquid phase | [mol/L] |
| $C_{\text{tot}}$ | solute concentration in the layer of bentonite plug (in both liquid and solid phase) after the experiment termination | [mol/L] |
| CEC | cation exchange capacity | [meq/100 g] |
| $D_a$ | apparent diffusion coefficient | [m$^2$/s] |
| $D_e$ | effective diffusion coefficient | [m$^2$/s] |
| $D_p$ | pore diffusion coefficient | [m$^2$/s] |
| $D_w$ | reference diffusivity in water | [m$^2$/s] |
| $G$ | geometric factor | [-] |
| $G_f$ | filter geometric factor | [-] |
| $K_d$ | distribution coefficient | [L/kg] |
| $l$ | length of bentonite plug | [mm] |
| $l_f$ | length of filter | [mm] |
| $m$ | mass | [g, kg] |
| $m/V$ | solid-to-liquid ratio | [g/mL, kg/L] |
| MX-80 | natural Wyoming bentonite | |
| $q$ | solute concentration in the solid phase | [mol/kg] |
| $t$ | contact time | [days] |
| $T_{1/2}$ | half-life of radioactive decay | [days, years] |
| $V$ | volume | [mL, L] |
| $x$ | longitudinal coordinate | [m] |

### *Greek letters*

| | | |
|---|---|---|
| $\varepsilon$ | bentonite porosity | [-] |
| $\varepsilon_f$ | filter porosity | [-] |
| $\eta$ | efficiency of gama activity measurement | [%] |
| $\rho_d$ | bentonite bulk density | [kg/m$^3$] |
| $\rho_f$ | filter bulk density | [kg/m$^3$] |
| $\rho_s$ | bentonite specific density | [kg/m$^3$] |

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