STUDY OF CESIUM SORPTION ON Na AND Ca-Mg BENTONITES USING BATCH AND DIFFUSION EXPERIMENTS

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In this study the cesium sorption on two different bentonites (Ca-Mg bentonite Rokle and Na bentonite Volclay KWK 20-80) has been compared using two different experimental approaches – batch and diffusion methods. The distribution coefficients (K_ds) calculated for variable liquid-to-solid ratio (batch) and dry density (diffusion) were evaluated with respect to the main uncertainties affecting both approaches. It has been concluded that there are significant differences between selected bentonites in mineral composition, cation exchange capacity (CEC) and sorption characteristics. The K_d values calculated from batch sorption and diffusion data were found comparable only for Na bentonite Volclay KWK 20-80. The considerably higher sorption of Cs on Ca-Mg bentonite Rokle was explained by its higher content of cesium-selective sorbents (illite, vermiculite).

1 Introduction

In most deep geological repository concepts sorption of radionuclides on bentonite represents a very important process retarding radionuclide migration into geosphere. The distribution coefficients (K_d) are often used in performance assessment studies, e.g. [1], due to relative simplicity of obtaining their values. These K_d values are usually determined using static (batch) or dynamic (diffusion) methods. A static batch method is used much more frequently than a diffusion method, because of a simple experimental methodology. The major shortage of this method is that the experiments are carried out at very high liquid-to-solid ratios far from the real conditions under which the reverse is the case. On the other hand, the diffusion methodology cannot simply determine the effect of a very slow change of the solution composition by the interaction of bentonite with groundwater in compacted bentonite in a Deep Geological Repository (DGR). K_d values used in performance assessments should be therefore based on both methods.

The problem is that very often not only the K_d values obtained by different methods are not compatible, but even the K_ds obtained using only one method differ due to methodological problems, e.g., sample pre-treatment or liquid-to-solid ratio effect [2,3] in batch methodology or the way of analytical evaluation of data in diffusion methodology.

In this study, the K_d values for cesium were obtained both from batch sorption and in-diffusion methods on two types of bentonite – Ca-Mg bentonite from Rokle deposit, Czech Republic, and Na bentonite Volclay KWK 20-80, produced by SüdChemie, Germany. Cesium has been selected as an element with simple chemistry and geochemistry behavior and relative simple adsorption mechanisms. A great number of publications concerning cesium sorption on various clay minerals and clays are available [4-6]. A number of studies were focused on Na bentonites (e.g. MX-80), which represents a candidate bentonite for Swedish, Finish or Swiss DGR concepts, and special cases of sorption (e.g., adsorption on homoionic form of the clay minerals). Much less studies are dealing with natural, untreated bentonites, especially of the Ca-Mg type, and in many of them closer information describing the clay (detail mineral composition and physical-chemical properties) are missing or incomplete. These data are needed for better understanding their sorption behavior, for sorption results evaluation and also for later comparison with similar samples.

This work aims to answer primarily some methodological questions of the comparison of batch and diffusion methods and to provide closer information for further studies in the Czech DGR concept.

2 Experimental Procedures

Two different bentonite samples were used in this study: natural Czech Ca-Mg bentonite from Rokle deposit (Tertiary neovolcanic area, NW Bohemia) and Na bentonite as industrial sorbent Voclay KWK 20-80 (product of SüdChemie, Germany). Rokle bentonite was provided as fine-grained in amount of approx. 5 kg and Voclay KWK 20-80 as fine grained granulated material in amount of approx. 6 kg. In sorption experiments, both samples were used as they were provided to avoid any unnecessary changes in mineral composition and mineral structure.

The chemical compositions of natural clay samples were determined in the Gematest Laboratories (Černošice, Czech Republic). The bulk samples, the air-dried and ethylene glycol solvated oriented clay samples were analyzed in the Institute of Inorganic Chemistry, Academy of Sciences of the Czech Republic, by powder X-ray diffractometry. The detailed description of mineral composition determination is presented elsewhere [7]. The characteristics of both clays are presented in Tables 1 and 2.

The cation exchange capacity (CEC) was measured by the Cu-trien method [8]. The amount of remaining Cu has been measured by UV-VIS spectrometry.

For Volclay KWK 20-80, the Synthetic Bentonite Pore Water (SBPW) for clay density 1600 $kg.m^{-3}$ with composition given in Tab. 3 has been used [9]. For Rokle bentonite, 0.1 M $CaCl_2$ solution has been used. Carrier-free ^{137}Cs as $^{137}CsCl$ solution in 0.1 M HCl with specific activity of 148 kBq cm^{-3} has been used as a radiotracer. Inactive tracer solution of Cs was prepared from reagent grade CsCl in concentration of 10^{-7} M.

Four liquid-to-solid ratios (V/m) have been chosen for batch experiments, namely 0.1, 0.05, 0.025, and 0.01 $m^3\,kg^{-1}$. The required amount of homogenized bentonite has been contacted with 20 cm^3 of tracer solution in centrifuge tubes and shaken in a programmable orbital shaker for 7 d. Then the samples were centrifuged using high-speed centrifuge for 30 min at 8693 × g. After the phase separation, specified amount of liquid phase has been taken for activity measurement and in the remaining volume the final pH has been measured using a digital pH-meter.

The diffusion in bentonite samples of the dry density in the range 600 – 1750 $kg.m^{-3}$ was studied using in-diffusion method. The cylindrical sample of compacted bentonite with a diameter of 3.0 cm and height of 1.5 cm was placed in the diffusion cell and separated from solutions on both sides by 0.3 cm thick metal filters. The diffusion cells were made from stainless steel (both the cell body and filters) and the construction enabled to connect it directly to the input and/or output reservoirs without any tubing. The plastic vessels (volume 190 cm^3) were used as inlet and outlet reservoir, distilled water served as a standard liquid medium in diffusion experiments with carrier-free ^{137}Cs tracer (starting Cs concentration 10^{-7} M). At the end of the experiment (100 d), the bentonite was sliced and the cesium concentration profile within the sample measured.

The value of apparent diffusion coefficient D_a for the each experiment was determined using numerical solution of diffusion equation that accounted for filter resistance, analogously to [12]. The primary data obtained by the evaluation of diffusion experiments were apparent diffusivities D_a from which the corresponding K_ds were derived taking into account values of porosity ε and dry density ρ corresponding to the given compaction of bentonite (1).

$$D_a = \frac{\varepsilon D_p}{\varepsilon + \rho K_d} \tag{1}$$

Values of diffusion coefficient in bentonite pores were evaluated using relation $D_p = G.D_w$, where geometric factor G [13] was measured in the preceding through-diffusion experiment using HTO on the same bentonite plug, and the literature value 2.06×10^{-9} $m^2.s^{-1}$ [14] was used for diffusion coefficient D_w of Cs^+ in an unconfined solution. The V/m ratio in the bentonite plug was evaluated using known values of porosity ε and dry density ρ.

The activity measurements were carried out with the Perkin Elmer 1480 Wizard 3“ Gamma counter. All experiments and measurements were carried out at temperature 22 ± 2 °C, atmospheric pressure (101.3 kPa) and normal oxic atmosphere ($CO_2 \approx 0.038$ vol%).

3 Results and Discussion

The mineralogical and chemical analyses of the samples indicated significant differences in their composition. Bentonite Volclay KWK 20-80 represents bentonite with high content of smectite and low amount of other mineral phases that might have been removed during industrial processing. Rokle bentonite, on the other hand, represents natural material taken from an operating deposit. In comparison with Volclay KWK 20-80 it is a more complicated mixture of various minerals, including vermiculite and illite as a part of weathering sequence biotite → smectite. The content of expandable clay minerals is significantly lower (cf. Tab. 2) and represents the sum of all expandable structures - smectite (prevails) and vermiculite. Vermiculite quantification cannot be obtained

Table 1. Bulk chemical composition of bentonites (contents in wt. %)

	Rokle bentonite	Volclay KWK 20-80
SiO_2	43.21	61.75
Al_2O_3	12.01	20.50
Fe_2O_3	12.43	3.87
FeO	0.07	1.02
TiO_2	4.51	0.22
CaO	9.62	0.94
MgO	2.87	2.58
Na_2O	0.18	2.08
K_2O	1.01	0.59
MnO	0.27	0.01
P_2O_5	0.87	0.22
CO_2	5.77	0.33

Table 2. Mineralogical composition of bentonites (estimations in wt.%) and CEC

	Rokle bentonite	Volclay KWK 20-80
Smectite	59[a]	90
Micas	10[b]	2
Kaolinite	1	-
SiO_2 phases	4	3
Calcite	14	1
Anatase	4	-
Feldspars	-	4[c]
Free Fe-oxides	7	-
Hematite	1	-
CEC (meq/100g)	*56*	*81*

[a] all expandable structures, including vermiculite

[b] biotite prevails, illite presumably present

[c] K-Na feldspars

because of its expandability and main peak interference with Ca-smectite peak, but its presence was proven. The same problem consists in illite identification and quantification, because of biotite presence in significant amount. The lower amount of smectite in Rokle bentonite is also reflected in a lower CEC value.

Table 3. Composition of Synthetic Bentonite PoreWater (SBPW) for clay density 1600 kg.m^{-3}

	Concentration (mol.dm^{-3})
Na^+	2.00×10^{-1}
K^+	3.58×10^{-3}
Mg^{2+}	1.19×10^{-2}
Ca^{2+}	8.73×10^{-3}
Cl^-	6.49×10^{-2}
SO_4^{2-}	9.99×10^{-2}
F^-	2.90×10^{-4}
HCO_3^-	7.50×10^{-4}
pH	7.49
Conductivity (mS.m^{-1})	2100
Ionic Strength (mol.dm^{-3})	0.29

In batch sorption experiments, the solutions with high ionic strength simulating pore waters were used to approximate the conditions in compacted bentonite [9]. For Rokle bentonite, pore water was simulated by the 0.1 M $CaCl_2$ solution with respect to the high content of calcite in bentonite and our preliminary results of determination of Rokle bentonite pore water. The sorption of cesium has been described using K_d dependence on V/m ratio. It has been found that there is no change of K_d with V/m for Volclay KWK 20-80 (see Fig. 1). The different trend was observed for Rokle bentonite where significantly higher K_d values were attained, especially at high V/m ratios, and also K_d was found to be dependant on V/m (Fig. 1). The presence of the above mentioned cesium-selective sorbents (illite, vermiculite) in this bentonite causing entrapment of trace cesium from solution that could result in partially irreversible sorption and K_d dependence on V/m is a possible explanation, as suggested by Wauters and Cremers [10]. In such a case, the K_d approach that assumes fully reversible sorption cannot describe the data adequately.

Results of diffusion experiments confirmed differences between used bentonites concerning sorption of Cs at the given concentration (10^{-7} M). A slight increase of K_d values can be even seen with the increase of V/m for Volclay KWK 20-80 bentonite, but for Rokle bentonite this increase is more evident (see Fig. 1), in agreement with batch sorption experiments.

As can be seen in Fig. 2 the measured dependence of D_a on compaction of Na bentonite Volclay KWK 20-80 was in good relation with the data reported for a similar Na bentonite, Kunipia F [11]; on the contrary, the D_a values of Cs in Ca-Mg bentonite Rokle were lower, in agreement with the higher Cs-sorption at given concentration on this type of bentonite.

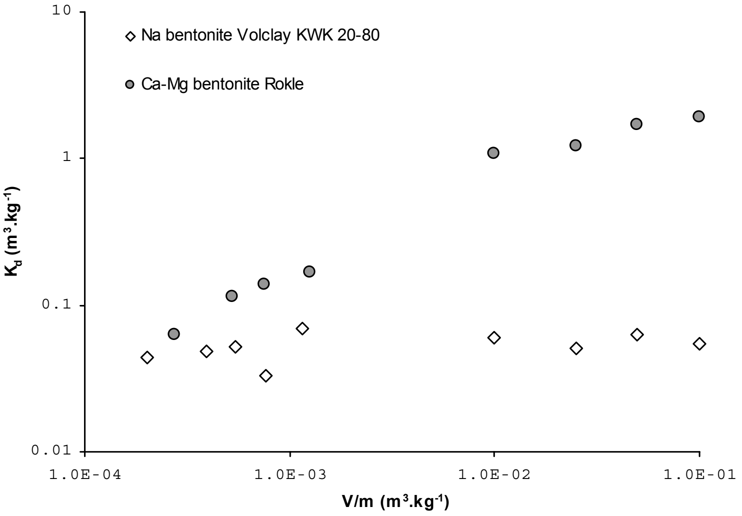

Fig. 1. Dependence of measured distribution coefficient K_d on liquid-to-solid ratio V/m for two studied bentonites and two method of measurement – batch (rhs) and diffusion (lhs)

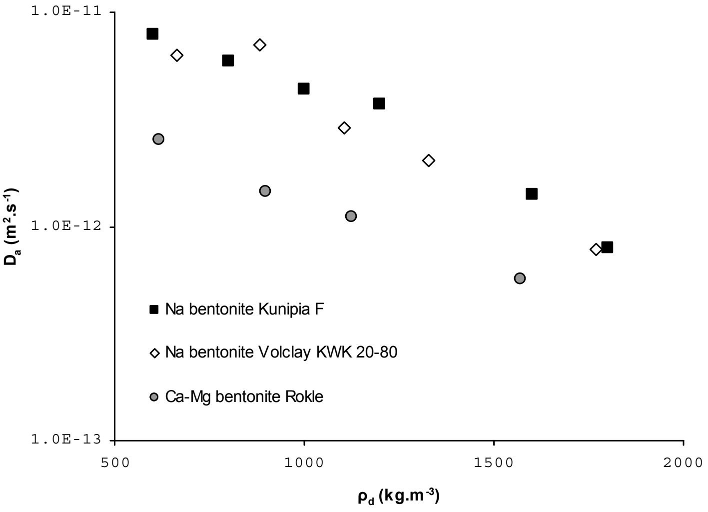

Fig. 2. Comparison of apparent diffusivity D_a as function of dry density ρ_d of studied bentonites (Volclay KWK 20-80 of Na type and Rokle of Ca-Mg type) with data reported for Na bentonite Kunipia F [10]

4 Conclusions

The interchangeability of diffusion and static batch sorption methods as sources of experimental K_d data for performance assessment studies has been evaluated. It was shown that the methods are interchangeable for bentonite with a very high content of smectite, as Volclay KWK 20-80, where diffusion and batch sorption methods provided comparable results that are also in agreement with published data for Na bentonites. In the case of Rokle bentonite, both methods yielded significantly different results and confirmed the K_d dependence on V/m ratio. Such dependence can be explained by the presence of Cs-selective sorbents (illite, vermiculite) in this bentonite. Its presence has to be taken into account in further experiments with Rokle bentonite and in performance assessment studies.

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