

# RADIONUCLIDE DISTRIBUTION ON CLAY BARRIER MATERIALS – SPECIFIC ASPECTS ASSOCIATED WITH EXPERIMENTAL EVALUATION OF THE DISTRIBUTION COEFFICIENTS

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Article received on February 13, 2023

*The paper discusses methodological approaches providing experimental evaluation of coefficients presenting radionuclide distribution on clay materials. Based on the implemented approach, sorption properties of samples differing in their composition may be compared under unified conditions (simulating actual conditions at radioactive waste storage facilities, if necessary).*

**Keywords:** sorption, distribution coefficient, radionuclides, clay barrier materials, cesium, uranium, radioactive waste.

## Introduction

In Russia, sorption properties of materials relative to radionuclides are commonly described via the distribution coefficient ( $K_d$ ), which is the ratio between the concentrations found in the solid phase and in the solution:

$$K_d = \frac{[\text{RN}_{\text{solid}}]}{[\text{RN}_{\text{solut.}}]} \cdot \frac{V}{m},$$

where  $[\text{RN}_{\text{solid}}]$  is the radionuclide concentration in the solid phase,  $[\text{RN}_{\text{solut.}}]$  is the radionuclide concentration in the equilibrium solution,  $V$  is the volume of the sample,  $m$  is the mass of the sorbent. Most often,  $K_d$  is expressed in ml/g (or in  $\text{cm}^3/\text{g}$ ), which is also equivalent to l/kg. A unit of  $\text{ml}/\text{m}^2$  is used much less often (in this case,  $K_d$  should be divided by the specific surface area). It is worth noting that in this case,  $K_d$  is only a measurement unit for sorption, which can also be expressed in percentages (%), fractions, mol/g and etc.

Back in the 19<sup>th</sup> century, an isotherm equation was proposed to describe the sorption process empirically, which is a dependence between the amount of a sorbed substance and its content in a solution (or gas) at a constant temperature [1]. The simplest one is the linear sorption Henry's isotherm, when the sorption is considered proportional to the content of a substance in a solution and  $K_d$  is its coefficient. In order to maintain this ratio, the following conditions are required to be met:

- concentration of the substance should be low enough, since its increase would trigger the saturation of the sorption sites, which is reflected in the changing shape of the isotherm;
- all sorption sites on the surface should be energetically homogeneous;
- each sorption site should interact with only one molecule of the substance.

In real systems, these conditions are frequently not met, therefore, it appears impossible to describe the process based on the Henry's isotherm.

More ample knowledge of the sorption processes that have evolved globally has prompted wider application of the surface complexation modeling method providing their thermodynamic description [2], [3]. Based on the experimental data, this method can be used to calculate the equilibrium constants of sorption reactions similar to the complex formation process in solutions. These values can be used to calculate the sorption, which can be expressed in different units, including  $K_d$ , under any conditions, as well as with an account taken of changes in the solid-liquid phase ratio (S:L), pH, etc.

In addition to the S:L ratio, radionuclide sorption on clay minerals is known to be potentially affected by temperature [4], [5], pH [6]–[9] and the solution composition [10]–[12]. Since the latter may considerably affect the binding capacity in case of some radionuclides, it seems preferable to consider the conditions typical for a particular object to gain more accurate results. For example, Milyutin et al. [13], [14] put forward an idea that  $K_d$  for cesium and strontium can be determined in  $\text{NaNO}_3$  and  $\text{Ca}(\text{NO}_3)_2$  solutions simulating main LRW composition. To date, there is quite ample experience in the  $K_d$  identification for most promising materials (mainly natural clays of various compositions) and a few radionuclides [13]–[17]. However, it appears difficult to compare the results obtained given different experimental conditions.

Despite the apparent simplicity of the sorption experiment and its interpretation, there are quite a few reasons that may affect the result. This study shows the importance of external factors in terms of their impact on the sorption behavior under the experiments, its interpretation and the calculated  $K_d$ .

### The experimental part

A sample of a barrier mechanically activated composite mixture (SBMK) (constituting of kaolinite – 32%, montmorillonite – 32%, illite – 4%, vermiculite – 3% and quartz – 18% by weight) produced by Bentonite Khakassia LLC has been investigated under the study. Distilled water; 0.01 M  $\text{NaClO}_4$  and model water of the following composition: 96.0 mg/l  $\text{NaHCO}_3$ ; 60.0 mg/l  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ; 60.0 mg/l  $\text{MgSO}_4$ , 4.0 mg/l KCl; pH 7.7 were used as sorption solutions.

Cation content in contact solutions was measured using the Agilent 7500C quadrupole ICP-MS.

Sorption dependences were studied both based on the initial sample and after a few washings. Solid

phase concentration was ranging from 0.1 to 40 g/l. An aliquot of the solution with the radionuclide was added to the weighed portion of the sample and the pH level was either set to a required level by adding dilute NaOH and  $\text{HClO}_4$  solutions or simply recorded. The sample was held in an orbital shaker for at least 24 hours under the experiments with  $^{137}\text{Cs}^+$  and for 48 hours under the experiments with  $^{233/232}\text{U}(\text{VI})$ . After the equilibrium was set, the solution was separated by centrifugation at 20,000 g for 20 min (Allegra 64R, Beckman Coulter). The supernatant activity was measured by liquid scintillation spectrometry (Quantulus-1220, Perkin Elmer). The distribution coefficient was calculated based on the difference in the radionuclide activities, i. e., introduced and remaining in the solution at the post-interaction stage, according to the following expression:

$$K_d = \frac{[\text{RN}_{\text{in}}] - [\text{RN}_{\text{solut.}}]}{[\text{RN}_{\text{solut.}}]} \cdot \frac{V}{m},$$

where  $[\text{RN}_{\text{in}}]$  is the introduced concentration of the radionuclide,  $[\text{RN}_{\text{solut.}}]$  is the concentration of the radionuclide in the equilibrium solution,  $V$  is the volume of the sample,  $m$  is the mass of the sorbent. Radionuclide concentrations were calculated according to the specific activity based on the following expression:

$$[\text{RN}] = \frac{A}{\ln 2} \times \frac{T_{1/2}}{\text{Na}},$$

where  $[\text{RN}]$  is the radionuclide concentration (mol/l),  $A$  is the radionuclide activity (Bq/l),  $T_{1/2}$  is the half-life (s).

To evaluate the buffering capacity of the SBMK sample, experiments were carried out at S:L ratio of 40 g/l. 7 vials with a weighed washed and dried sample portion of 0.5 g were taken for the experiment. These were added by 12.5 ml of model water with some preset pH levels (2; 3; 4.2; 5.2; 8.5; 9.3; 10.2). The samples were placed into a shaker, pH was measured after 1, 2, 3 weeks and 3 months. Even though the values remained almost constant after the first week, the data obtained after 3 months were adopted as equilibrium.

### Results and discussion

The S:L ratio appears to be one of the concerns in the analysis of  $K_d$  values obtained experimentally. As mentioned above, if the condition of the Henry's isotherm is satisfied, then any variations in the concentration of the solid phase or radionuclide should not affect the result.

To demonstrate the S:L impact,  $\text{Cs}^+$  sorption on a SBMK sample was evaluated experimentally assuming various solid phase contents (from 0.1 to 5 g/l)

in distilled water (Figure 1A). Some unexpected trend was revealed based on the  $K_d$  values from the experiment:  $K_d$  tended to decrease along with the increasing concentration of the solid phase, while  $K_d$  was supposed to be constant. Similar sorption results in the coordinates of the sorption isotherm (Figure 1B) were also non-systemic and could hardly correspond to the Henry's isotherm. Since an increase in the mass of the sample and, accordingly, in the number of the sorption sites could not explain the observed effect, some additional research was done.

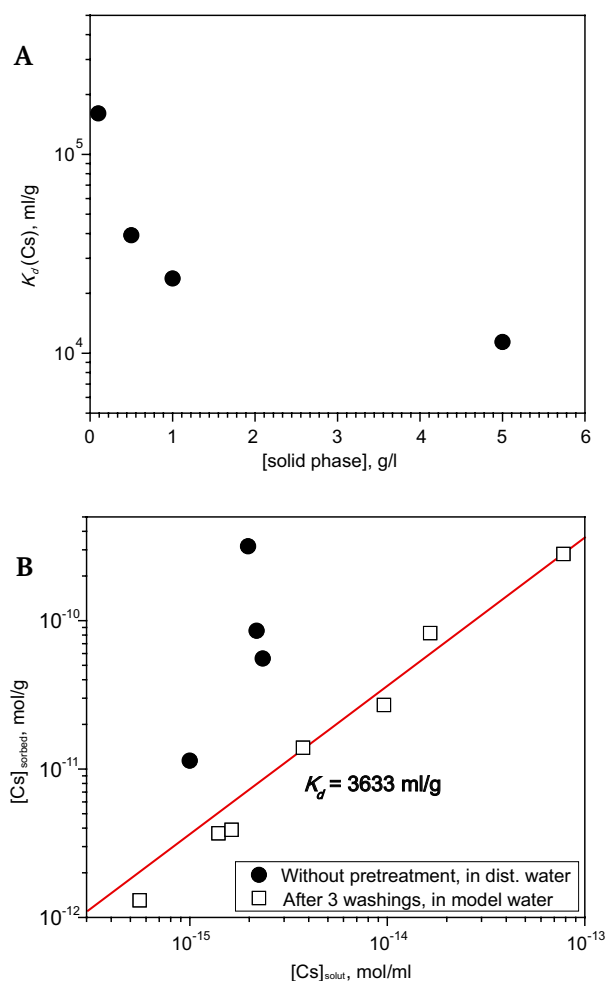
The analysis showed that SBMK sample during its interaction with the aqueous phase prompted quite considerable release of various cations into the solution (Table 1). In this case, as the content of the solid phase was getting higher, the content of leachable elements appeared to get higher as well.

**Table 1. Content of cations in the solution after having interacted with the SBMK sample**

Initial solution	S:L, g/l	Cation contents in the contact solution, mol/l				
		Na	Mg	Al	K	Ca
H <sub>2</sub> O	0.1	$<2 \cdot 10^{-5}$	$2.08 \cdot 10^{-5}$	$1.67 \cdot 10^{-5}$	$2.49 \cdot 10^{-5}$	$1.25 \cdot 10^{-5}$
	0.5	$<2 \cdot 10^{-5}$	$2.08 \cdot 10^{-5}$	$2.31 \cdot 10^{-5}$	$2.64 \cdot 10^{-5}$	$2.78 \cdot 10^{-5}$
	1	$1.04 \cdot 10^{-4}$	$3.17 \cdot 10^{-5}$	$1.93 \cdot 10^{-5}$	$4.87 \cdot 10^{-5}$	$1.10 \cdot 10^{-4}$
	5	$6.09 \cdot 10^{-4}$	$9.17 \cdot 10^{-5}$	$3.15 \cdot 10^{-5}$	$7.69 \cdot 10^{-5}$	$2.35 \cdot 10^{-4}$
0.01 M NaClO <sub>4</sub>	0.1	–	$2.08 \cdot 10^{-5}$	$4.43 \cdot 10^{-5}$	$6.21 \cdot 10^{-5}$	$2.33 \cdot 10^{-5}$
	0.5	–	$2.08 \cdot 10^{-5}$	$3.79 \cdot 10^{-5}$	$4.67 \cdot 10^{-5}$	$5.38 \cdot 10^{-5}$
	1	–	$3.63 \cdot 10^{-5}$	$7.41 \cdot 10^{-5}$	$6.92 \cdot 10^{-5}$	$1.15 \cdot 10^{-4}$
	5	–	$1.08 \cdot 10^{-4}$	$2.93 \cdot 10^{-5}$	$6.92 \cdot 10^{-5}$	$2.88 \cdot 10^{-4}$
Model water	0	$1.20 \cdot 10^{-3}$	$1.70 \cdot 10^{-4}$	$1.39 \cdot 10^{-4}$	$9.96 \cdot 10^{-4}$	$1.59 \cdot 10^{-4}$
	0.5	$1.29 \cdot 10^{-3}$	$2.35 \cdot 10^{-4}$	$4.65 \cdot 10^{-6}$	$1.02 \cdot 10^{-3}$	$2.91 \cdot 10^{-4}$
	1	$1.26 \cdot 10^{-3}$	$2.66 \cdot 10^{-4}$	$6.49 \cdot 10^{-6}$	$9.96 \cdot 10^{-4}$	$2.99 \cdot 10^{-4}$
	5	$1.34 \cdot 10^{-3}$	$2.40 \cdot 10^{-4}$	$2.67 \cdot 10^{-5}$	$9.86 \cdot 10^{-4}$	$3.31 \cdot 10^{-4}$

Low selectivity of clay sorption sites contributes to lower radionuclide sorption in presence of cations with similar charges. Thus, [18] shows that a significant increase in the content of Ca<sup>2+</sup> and Mg<sup>2+</sup> (up to 10<sup>-3</sup> M) in the solution upon its interaction with bentonite greatly reduces Cs<sup>+</sup> sorption in its content ranges from 10<sup>-9</sup> to 10<sup>-6</sup> M. At the same time, modern thermodynamic modeling approaches can predict the effect produced by competing cations on the radionuclide sorption, which requires sufficiently accurate identification of the solution composition [17], [11].

Therefore, changes in Cs<sup>+</sup> sorption with variation of the S:L ratio in distilled water (Figure 1) appear to be triggered by the modified solution composition due to an increasing solid phase concentration.



**Figure 1. Dependences: A –  $K_d(Cs)$  on the concentration of the solid phase in water; B – equilibrium concentration of sorbed Cs versus its content in the solution after triple solid phase washing (squares indicate the experiments involving a sample after its washing in model water, S:L=0.5 g/l; dots indicate the results in water for a sample without pretreatment)**

As noted above, the content of leachable cations evolves along with the changing concentration of the solid phase, which indicates indirectly that they were not equilibrium for these substances. Indeed, upon sample interaction, increased concentrations of Na<sup>+</sup>, Ca<sup>2+</sup> and Mg<sup>2+</sup> in the solution are observed along with an increasing mass of the sample (Table 1). This dependence is observed when the composition of the solution is varied in distilled water, in 0.01 M NaClO<sub>4</sub> and in model water. It should be noted that in the latter case, if the mass is varied, the changes in the cation content are the least notable. Therefore, this water seems to be most suitable for application when one needs to obtain the distribution coefficient not depending on the S:L ratio.

Since the washed-out cations demonstrate a nonequilibrium behavior, it was proposed to do the washings before the experiment, which could contribute to more reproducible conditions. In contrast to the above sorption experiment, after three

## Disposal of Radioactive Waste

washings, Cs<sup>+</sup> sorption began to adhere to the Henry's isotherm equation (Figure 1B). Moreover, this trend is observed when varied are both the concentrations of cesium and the solid phase. The  $K_d$  calculated in this way can be used in a wider range of conditions, and, in the considered case, the S:L ratio in its calculation did not affect the result.

The radioactive waste (RW) final disposal concept suggests that during the first decades the waste is contained inside the containers and does not interact with the clay barrier. During this period, the material of the engineered safety barriers comes into contact with local waters, which is accompanied by cation leaching and dissolution of mineral impurities. Thus, by the time when the radionuclides start interacting with the clay-based barriers, they are expected to be already balanced with the natural waters. Therefore, real conditions can be simulated via the preliminary sample washing with a solution identical in its composition to the waters of a particular facility.

Clay minerals may impact not only the solution composition, but also the pH values. The buffering clay capacity is associated with the protonation/deprotonation of amphoteric edge sorption sites (silanol and aluminol groups), dissolution/precipitation of carbonates, etc. [18]. Based on the data on the mineral composition of the original sample and information on the acid-base properties of sorption sites, an approach was proposed to predict the composition and the pH values of pore water in highly compacted bentonite systems [19], [20]. Calculations showed that compacted bentonites were expected to get stabilized at a pH level ranging from 7 to 9. At the post-washing stage, the solid phase mass appears to be an essential factor influencing solution acidity level and its composition.

The method proposed by the authors was used to calculate the buffer capacity of the studied SBMK

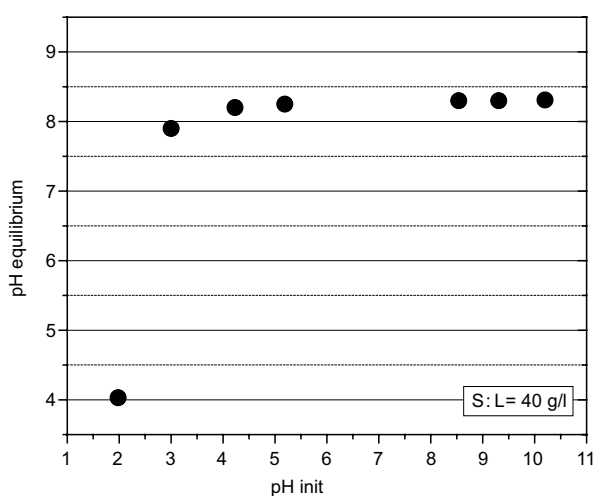


Figure 2. Buffer capacity of SBMK: dependence between the equilibrium pH and the initial value (in distilled water; S:L=40 g/l)

sample. At a solid phase concentration of 40 g/l and assuming a wide range of initial pH levels of the solution (3–10), its equilibrium value accounted for  $8.30 \pm 0.05$  (Figure 2).

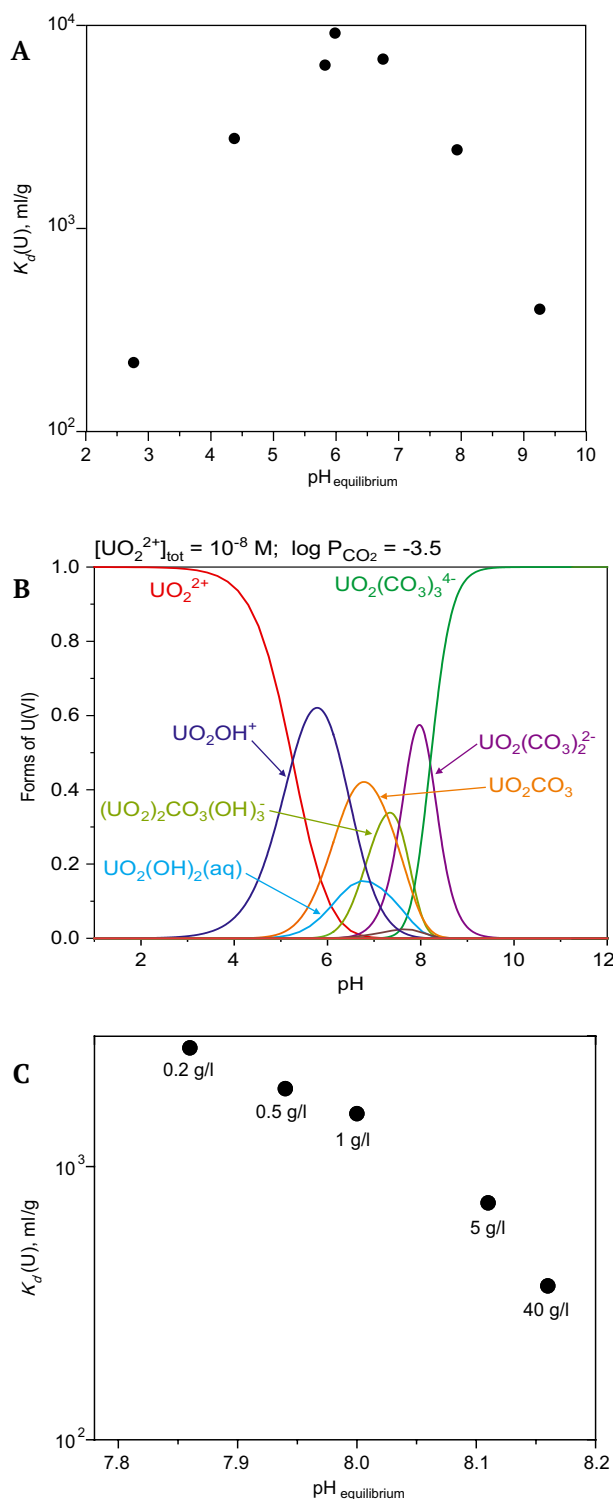


Figure 3. A – Relationships between  $K_d(U(VI))$  in the model solution and the equilibrium pH at  $[SBMA] = 0.5$  g/l; B – physicochemical forms of U(VI) in the solution being in equilibrium with air ( $[U(VI)] = 2 \cdot 10^{-8} M$ ,  $\lg P_{CO_2} = -3.5$ , calculation was done in the HYDRA MEDUSA software); C – relationship between  $K_d(U(VI))$  in the model solution and different content of the washed sorbent

In case of U(VI), the buffering clay capacity has some major effect on the sorption process. It is a common fact that in case of clay minerals this dependence has a characteristic dome shape with a maximum pH level of about 6 (Figure 3A) [21], [22]. Its further increase goes in parallel with a significant decrease in the proportion of bound radionuclide due to the stable carbonate complexes formed in the solution (Figure 3B). Clay minerals constituting to the SBMK sample, stabilize the pH indicators in the alkaline region, whereas the increased S:L ratio contributes to increased pH, which, in turn, may result in a  $K_d(\text{U})$  decrease. This effect has been demonstrated experimentally. Figure 3C shows  $K_d$  with the corresponding pH calculated at different concentrations of the solid phase. A regular increase in the pH values along with the increasing S:L ratio yielded natural decrease in the sorption capacity. These effects can be predicted through thermodynamic description of a clay mineral according to its sorption and buffering capacities.

Considerable effect of the pH on sorption capacity can be observed in case of other actinides and fission products as well, for example, Np(V), Pu(V, VI), Sr(II) and others.

## Conclusions

The paper describes the methodological problems faced in the experimental determination of radionuclide distribution coefficients on clay minerals. It shows the relevance of competing cations (including those leached from the substance under study), the buffering capacity of the clay material and their consideration in the studies.

To minimize changes in the solution composition, it was suggested to wash the sample three times with a model natural water, which is further used as a solution for sorption experiments. It appears important to record the change in the pH upon solution interaction with the aqueous phase and to consider its effect on the sorption process. These measures are thought to provide the implementation of the experiments under conditions as far as possible similar to the actual disposal ones and to compare the sorption properties for clays with different compositions in a somewhat unified environment. All technical details were documented in a certified provision, namely, Radionuclide Distribution Coefficient Measurement Methodology for Barrier Clay Material Characterization FR.1.31.2022.44412.

It is important to note that modern thermodynamic approaches to the description of sorption processes may take into account the effects of the solution composition and the S:L ratio on sorption.

The study was supported by the University named after M.V. Lomonosov under the state contract Addressing Challenges in Nuclear Power and Environmental Safety, as well as Material Diagnostics Based on Ionizing Radiation (project ID 122030200324-1). The methodology was certified under the Scientific and Technical Support Program for the Feasibility Study of Clay Barrier Materials Used in the Designs Developed for the Final Stage of Nuclear Facilities' Life Cycle.

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### Bibliographic description

Semenkova A. S., Romanchuk A. Yu., Mikheev I. V., Kalmykov S. N. Radionuclide Distribution on Clay Barrier Materials — Specific Aspects Associated with Experimental Evaluation of the Distribution Coefficients. *Radioactive Waste*, 2023, no. 2 (23), pp. 90–97. DOI: 10.25283/2587-9707-2023-2-90-97. (In Russian).