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Sorption of caesium, strontium and europium ions on clay minerals

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Batch experiments have been performed to study the sorption and transport properties of Cs^+, Sr^{2+} and Eu^{3+} on different clay minerals already established to be predominantly kaolinite and montmorillonite. The uptake of these radionuclides increases in the order $Cs < Sr < Eu$. This trend agrees perfectly with the overall sequence in ion-exchange equilibria.

1. Introduction

Disposal of nuclear wastes in geological media is believed to be an adequate way of providing the necessary protection for humans and the environment. The ultimate disposal of nuclear waste has renewed interest in the adsorption behaviour of various types of repositories that have been proposed. From the view point of radioactive waste isolation, the low permeability, high sorption capacity, and plasticity characteristics of clays make them an effective barrier to radionuclide migration. Other isolation is achieved by the emplacement of waste in clay formations. Placing the wastes encased in iron cannisters in an underground repository is one method considered for permanent disposal in many developed countries. However, the radionuclides may leak out and be transported with moving ground water (in fissures) in the backfill. Information on the mobility behaviour of radionuclides in the environment is essential for assessment of safety hazards arising from potential repositories in which wastes are stored. Of special interest among the many media in which migration of radionuclide can occur, are certain types of clay that may be used as backfill, plugging and sealing cavities, and fractures in other repositories which constitute the geological barrier of nuclear waste disposal [1–8].

Clay minerals exhibit adsorption and/or chemical reaction with radioactive or stable trace elements. Some investigators [9–11] have found montmorillonite clays to be the best natural agents for adsorption of radioisotopes strontium, caesium, cobalt, other fission and actinide products. The use of clay minerals is particularly attractive because they are inexpensive and widely available all over the world. However, the results available in the literature on clays cannot be directly applied to different clay mineral deposits because of well-known variability of characteristic of clays with locality. A hazard analysis is required to establish the suitability of a specific clay site for radioactive waste disposal hence the need for this study.

The objective of this study is to determine the sorptive properties and transport of radionuclides (caesium, strontium, europium) with clay minerals as potential backfill materials. Because the effectiveness of a geological barrier is a key function for the long-term safety of the disposal of nuclear waste, the clay system is modified to study the variation of its mobility in both solution and adsorbed phases. The selection of these radionuclides was based on their relevance to low/intermediate level waste disposal and the considerable hazard posed by radioactive wastes which fall in this range. Additionally, caesium, strontium and europium are suitable models in studying the behaviour of uncomplex monovalent, divalent and trivalent ion, respectively.

2. Experimental procedure

2.1. Sample preparation

Kaolinite and montmorillonite clay minerals used in this study were characterized by X-ray powder diffraction [12] and neutron activation analysis techniques [13]. Malvern instrument (series 2600), which uses a laser dispersion method, was used to measure particle size and specific surface area (Table I)

The raw clay mineral sieved to < 200 mesh size was equilibrated with 1 M each of sodium and calcium perchlorate solutions. The ratio of solid to liquid was 1 g : 10 ml. Equilibration was accomplished by first mixing the clay with standard solution and separating the two phases by high-speed centrifugation after a contact time of 1 week. The clay was then dried in an oven (60–65 °C), and finely ground in an agate mortar. The representative sample used for investigation in each case was obtained by quartering technique from the bulk clay mineral sample [13].

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TABLE I Properties of sample sorbents

Clay mineral	Particle size (μm)	Specific surface area (m^2 cm^{-3})
Kaolinte	28.4–31.1	0.06–0.07
Montmorillonite	8.1–8.8	0.18–0.21

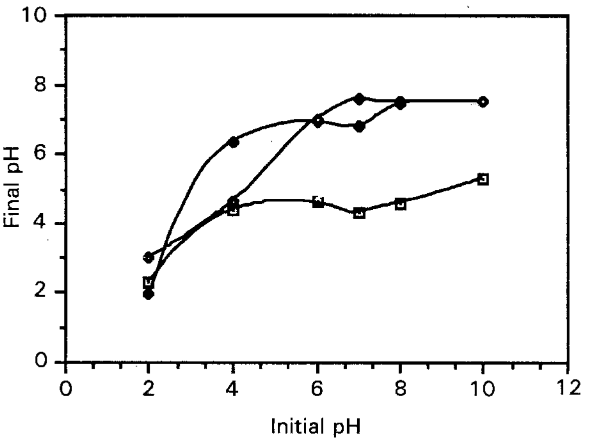

Figure 1 A comparison of pH change in contacting tests for different clay forms (⊡) Unwashed kaolinite, (◆) sodium kaolinite, (◇) sodium montmorillonite.

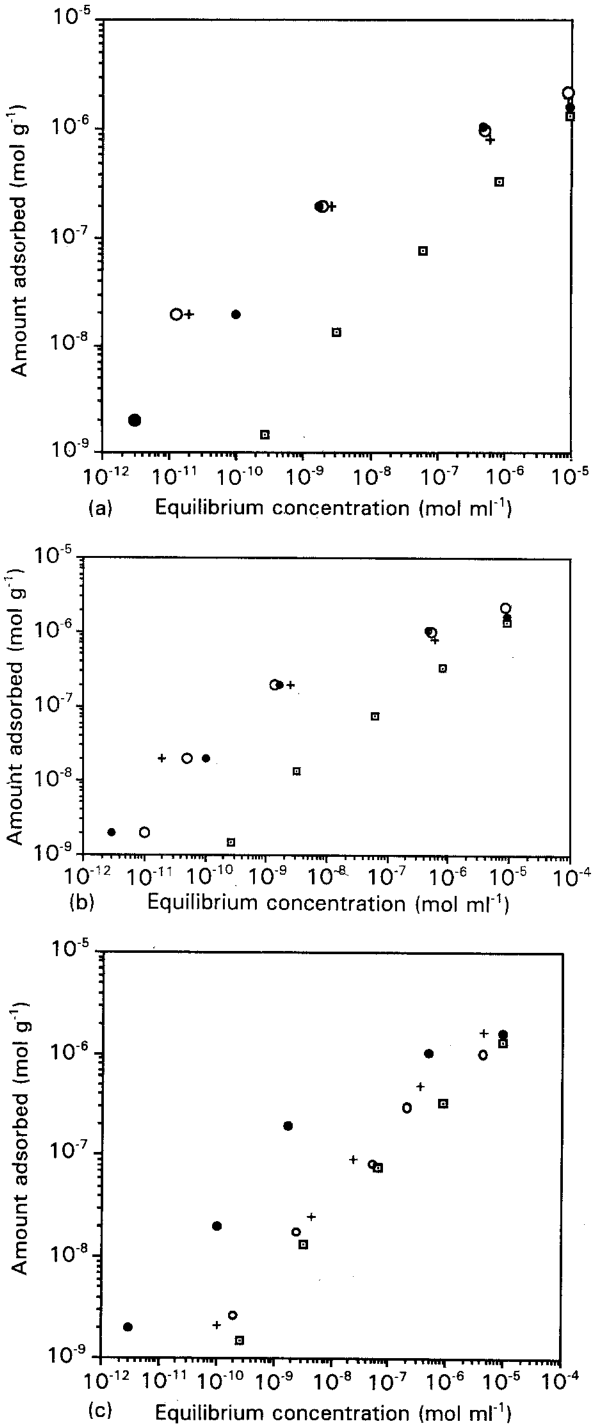

Figure 2 Adsorption isotherm plots of strontium on (a) unwashed kaolinite, (b) sodium kaolinite and (c) calcium montmorillonite at different initial pHs: (⊡) pH 2, (+) pH 4, (○) pH 7, (●) pH 10.

2.2. Procedure

The sorption of caesium, strontium and europium ions in distilled water on kaolinite and montmorillonite were measured using the batch technique [4, 14]. These contacting tests were carried out in stoppered polypropylene centrifuge flasks, each containing 20 ml of the desired nitrates of each of the cation solution at a predetermined initial pH and at concentrations ranging from 10^{-6}–10^{-2} M. The solution was contacted with 0.5 g of the desired clay mineral and equilibrated for 24 h. All the flasks were placed in the shaking bath, and the shaker speed was fixed at 140 strokes per minute in all the experiments performed at room temperature (20 ± 2 °C).

Then centrifugation was applied to separate the liquid phase from the solid phase. An aliquot of the supernatent fluid was removed from the centrifuge tube for pH analysis using a Corning 240 pH meter and for analysis of the cations of interest using a "Philips PW 4800" machine incorporating an NaI detector with a microcomputer-controlled automatic sample changer. Blank experiments showed that no sorption of caesium, strontium or europium on the walls of the centrifuge tube was present. The initial and final solution pHs were noted in all experimentals and typical results are shown in Fig. 1.

3. Results and discussion

It was observed that unwashed montmorillonite clay mineral unlike kaolinite clay mineral did not give a clear supernant after centrifugation was applied. Different sizes of millipore filters were used to correct this, however a favourable result was not obtained. Probably this resistance might be due to some pigment present in the clay having great affinity for water. The anomally was, however, corrected for sodium and calcium clay forms.

The distribution ratio, K_d, were determined at the desired pH for different clay minerals. K_d expressed in terms of the amount of ions sorbed by a unit mass of solid sorbent, q (mol g^{-1}) divided by the equilibrium ion concentration of aqueous phase, C (mol ml^{-1}) was obtained by batch techniques. At constant temperature, q can be represented by the Freundlich or Langmuir type equation

$$K_d = q/c \tag{1}$$

$$q = KC^{1/m} \tag{2a}$$

or

$$q = \frac{ac}{1 + cb} \tag{2b}$$

where k, m, a and b are constants under given conditions. Combining Equations 1 and 2 gives Equation 3

$$K_d = kC^{m-1} \tag{3a}$$

or

$$K_d = \frac{a}{1 + cb} \tag{3b}$$

The amount of ions adsorbed at concentration of ions ranging from 10^{-9}–10^{-5} mol ml^{-1} were measured for each ion except europium in which for unwashed and sodium kaolinites, measurements were carried out at 10^{-9}–10^{-6} mol ml^{-1} range. Representative adsorption isotherm of strontium at different initial pHs are shown in Fig. 2a–c.

The graph was fitted with both Freundlich and Langmuir-type equations (2a and b) and the constants thus obtained are presented in Tables II–IV.

It was observed that the clay forms obeyed the Freundlich isotherm fit with the coefficient of regression ranging from 0.94–0.99. Most of the clay forms had values above 0.93 except for unwashed kaolinite at pH 2, 4 and 8 for caesium; sodium kaolinite at pH 4, 6 and 8, and sodium montmorillonite at pH10 for strontium. However, much deviation was observed for the Langmuir fit for all sodium and calcium clay forms. The unwashed kaolinite gave fairly good correlation at pH 4, 6, 8 and 10 and the constants are shown in Table V. The corresponding constants for each fit are shown (Tables II–IV). The isotherm constants obtained are of the same order of magnitude with Konishi *et al.* [4] who performed a similar study. However, every measured sorption parameter is valid only for a special set of conditions. The strontium uptake was least at pH 2 (Fig. 2a and b) for unwashed

TABLE II Freundlich fit for caesium ions

Clay mineral	Ion	pH	Freundlich constants	
			k	m
Unwashed kaolinite	Cs	2	2.70×10^{-4}	5.46×10^{-1}
		4	5.26×10^{-4}	5.43×10^{-1}
		10	2.04×10^{-3}	5.88×10^{-1}
Sodium kaolinite	Cs	2	2.27×10^{-3}	5.86×10^{-1}
		4	5.04×10^{-2}	7.23×10^{-1}
		7	3.49×10^{-2}	7.03×10^{-1}
		10	2.35×10^{-1}	8.21×10^{-1}
Calcium kaolinite	Cs	2	3.03×10^{-2}	8.04×10^{-1}
		4	1.35×10^{-1}	8.45×10^{-1}
		7	2.47×10^{-1}	8.81×10^{-1}
		10	8.71×10^{-3}	6.94×10^{-1}
Sodium monmorillonite	Cs	2	1.02×10^{-4}	5.03×10^{-1}
		4	1.05×10^{-2}	7.09×10^{-1}
		7	3.17×10^{-2}	7.55×10^{-1}
		10	2.24×10^{-1}	8.15×10^{-1}
Calcium monmorillonite	Cs	2	2.41×10^{-1}	8.39×10^{-1}
		4	4.81×10^{-1}	8.97×10^{-1}
		7	1.84×10^{0}	9.38×10^{-1}
		10	2.74×10^{-1}	8.20×10^{-1}

TABLE III Freundlich fit for strontium ions

Clay mineral	Ion	pH	Freundlich constants	
			k	m
Unwashed kaolinite	Sr	2	4.88×10^{-2}	9.35×10^{-1}
		4	9.58×10^{-3}	6.35×10^{-1}
		7	1.29×10^{-2}	6.51×10^{-1}
		10	1.17×10^{-2}	6.36×10^{-1}
Sodium kaolinite	Sr	2	2.48×10^{-3}	6.36×10^{-1}
		4	8.39×10^{-4}	4.82×10^{-1}
		7	4.86×10^{-4}	4.29×10^{-1}
		10	5.41×10^{-4}	4.45×10^{-1}
Calcium kaolinite	Sr	2	9.46×10^{-4}	6.11×10^{-1}
		4	3.51×10^{-3}	6.64×10^{-1}
		7	2.76×10^{-3}	6.48×10^{-1}
		10	1.12×10^{-3}	5.77×10^{-1}
Sodium monmorillonite	Sr	2	4.22×10^{-3}	6.41×10^{-1}
		4	3.59×10^{-3}	6.17×10^{-1}
		7	7.55×10^{-4}	5.51×10^{-1}
		10	3.66×10^{-3}	6.12×10^{-1}
Calcium monmorillonite	Sr	2	8.69×10^{-3}	6.97×10^{-1}
		4	2.95×10^{-3}	6.39×10^{-1}
		7	2.20×10^{-3}	6.15×10^{-1}
		10	1.71×10^{-3}	5.57×10^{-1}

TABLE IV Freundlich fit for europium ions

Clay mineral	Ion	pH	Freundlich constants	
			k	m
Unwashed kaolinite	Eu	4	3.39×10^{-2}	6.33×10^{-1}
		6	1.23×10^{1}	8.75×10^{-1}
		8	9.0×10^{2}	1.04×10^{0}
Sodium kaolinite	Eu	4	1.09×10^{2}	9.39×10^{-1}
		6	1.14×10^{2}	9.48×10^{-1}
		8	8.95×10^{2}	1.06×10^{0}
Calcium kaolinite	Eu	4	1.92×10^{-1}	7.49×10^{-1}
		6	3.65×10^{-1}	7.19×10^{-1}
		8	7.17×10^{0}	8.63×10^{-1}
Sodium monmorillonite	Eu	4	7.95×10^{-2}	6.89×10^{-1}
		6	3.18×10^{-2}	6.42×10^{-1}
		8	1.51×10^{-1}	6.92×10^{-1}
Calcium monmorillonite	Eu	4	6.40×10^{-2}	6.36×10^{-1}
		6	3.23×10^{-2}	5.92×10^{-1}
		8	2.15×10^{-1}	6.95×10^{-1}

TABLE V Langmuir fit for unwashed kaolinite

Clay mineral	Ion	pH	Langmuir constants	
			a	b
Unwashed kaolinite	Sr	4	1.27×10^{-3}	4.71×10^{-1}
		6	9.40×10^{-4}	5.11×10^{-1}
		8	1.50×10^{-3}	4.81×10^{-1}
		10	1.33×10^{-3}	5.41×10^{-1}

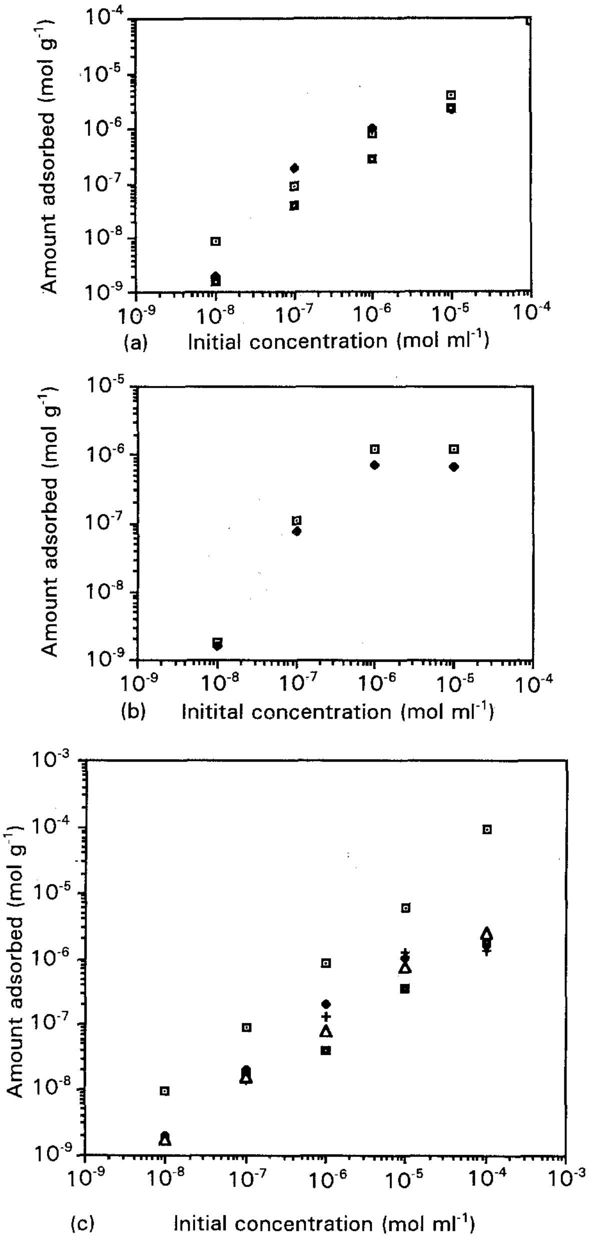

Figure 3 Variation of the amount adsorbed with initial concentration of strontium at pH 2 for (a) kaolinite clay mineral forms and (b) montmorillonite clay mineral forms, and at pH 10 (c) for different clay mineral forms. (a) ⊡ Unwashed kaolinite, (◆) sodium kaolinite, (■) calcium kaolinite. (b) (⊡) Sodium montmorillonite, (◆) Calcium montmorillonite. (c) (⊡) Unwashed kaolinite, (◆) sodium kaolinite, (■) calcium kaolinite, (+) sodium montmorillonite, (△) calcium montmorillonite.

and sodium kaolinite clay minerals, while a change from this general trend was observed for calcium kaolinite (Fig. 2c). The amounts adsorbed were observed in these ranges: 1.49×10^{-9}–2.38×10^{-6} mol g^{-1} (unwashed kaolinite), 1.38×10^{-9}–2.6×10^{-6} mol g^{-1} (sodium kaolinite), 1.4×10^{-10}–9.1×10^{-6} mol g^{-1} (calcium kaolinite), 1.6×10^{-9}–1.24×10^{-6} mol g^{-1} (sodium montmorillonite) and 1.59×10^{-9}–2.54×10^{-6} mol g^{-1} (calcium montmorillonite). In Fig. 4 (see later) the highest uptake of unwashed clay form occurred at pH 10 and pH 8 for sodium and calcium forms whilst highest uptake for sodium and calcium montmorillonite occurred at pH 8 and pH 4, respectively. The changes in the uptake of nuclides on to sodium and calcium clay forms are not remarkably distinct, although unwashed kaolinite is always highest in this study. The amount adsorbed is plotted as a function of initial concentration for different clay forms Fig. 3a–c. The effect of nuclide uptake, elemental concentration and different clay mineral form are shown in the figures.

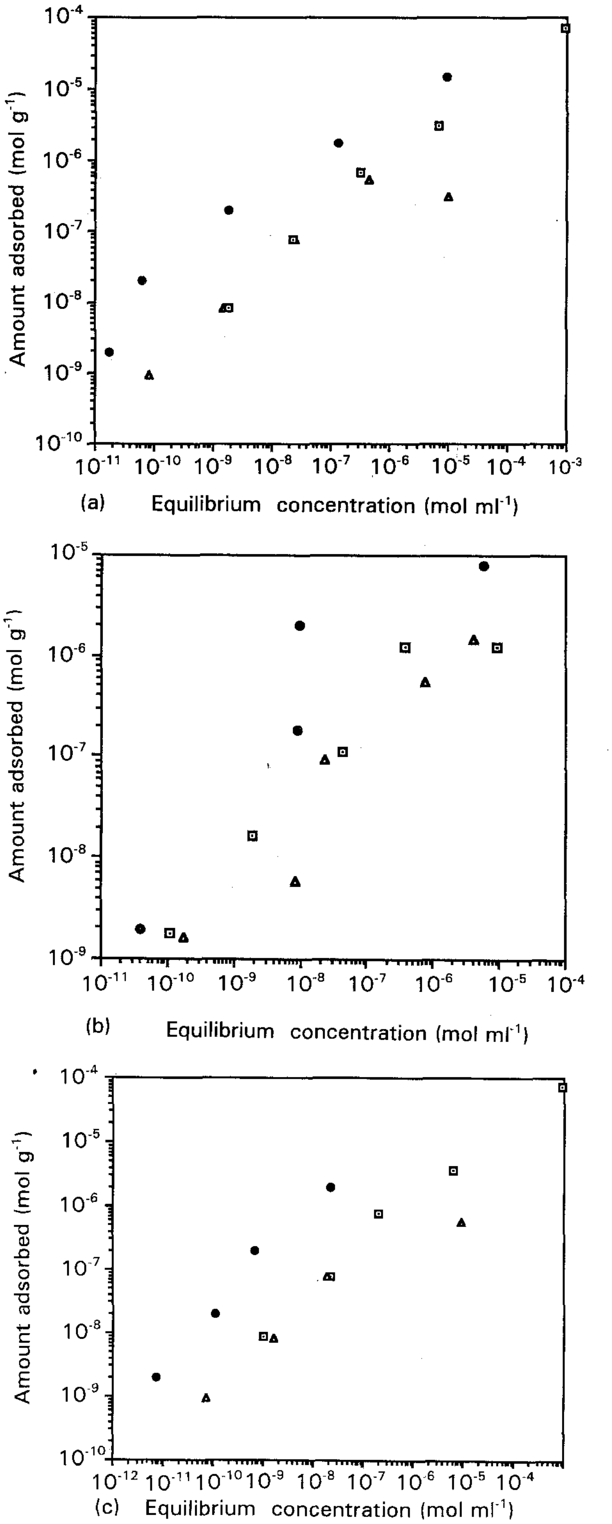

Figure 4 (△) caesium, (□) strontium and (●) europium uptake on (a) unwashed kaolinite at pH 4, (b) sodium montmorillonite at pH4, and (c) sodium kaolinite at pH 6.

In the calcium clay forms uptake was highest for caesium, unwashed kaolinite for strontium and sodium kaolinite for europium as shown in Figs 2 and 3. These characteristics are probably due to the presence of impurities in unwashed kaolinite and the presence of the sheet of hydroxyl on one side of the basal cleavage plane in its structure [10]. For sodium and calcium clay forms, the amount adsorbed decreases within the pH ranges studied except for pH 8. The change is likely due to an interplay of factors. This decrease in amount adsorbed by other clay mineral forms could also be due to the fact that caesium, strontium and europium ions are more easily exchanged with hydrogen ion than with sodium and calcium. The low uptake of ions by sodium and calcium clay forms may also be explained by the findings of Mistry *et al.* [15] where the cation loading corresponds to 70%–75% of total cation loading capacity for UAR clays. Because the unwashed clay forms were first treated with sodium and calcium available exchanged sites thus explaining the reason for the reduction in the number of such sites available for subsequent "reactions" hence the results obtained. Generally, sodium and calcium montmorillonite clay forms had slightly higher sorption than their kaolinite form. Although the changes in uptake of both sodium and calcium clay forms of kaolinite and montmorillonite were minimal. The typical isotherms showing the effect of nuclide, ionic charge, solution pH and different clay form are presented in Fig. 4a–c.

The uptake of radionuclides by the clays studied in this work increases in the order caesium < strontium < europium. The trend obtained agrees with overall sequence normally observed for ion exchange equilibra, namely increasing affinity with increasing ionic charge (for a given ionic radius) and decreasing radius of hydrated cation [16, 17].

4. Conclusion

The general agreement of results obtained in this work with those in the literature lend some confidence to the use of these data in computation for sorption ratios. However, it must always be remembered that the sorption parameter is valid only for a special set of conditions such as pH, concentration of nuclide, temperature, etc. The behaviour of caesium, strontium and europium in batch experiments is best characterized through adsorption isotherms of the Freundlich-type under the conditions studied.

Relative physiochemical properties of clay minerals and the migration of nuclides are matching the hopes initially based on clay options for geological backfill. However, much work is needed in diffusion studies to substantiate the results obtained for proper modelling.

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