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Research Paper

Cs^+ sorption onto Kutch clays: Influence of competing ions

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ABSTRACT

The sorption of Cs^+ onto raw Kutch clay (India) over a wide range of concentrations and pH levels was studied and compared with its sorption onto the well-studied FEBEX clay (Spain). The principal clay mineral in both samples is montmorillonite. Non-linear sorption isotherms were measured for both clays. The shapes of the isotherms prompted the use of a two-site exchange thermodynamic model to describe the experimental data. However, differences in the highly selective sorption sites (Type 1) were observed for the two studied clays. It was found that the presence of different cations (H^+, Ca^{2+}, Mg^{2+}, etc.) in solution affected the sorption of Cs^+. A model accounting for the competition process was developed for predicting the behavior of the raw clay in complex solutions.

1. Introduction

The development of the nuclear industry in the twentieth century resulted in the local contamination of several territories by manmade radionuclides. The radioactive fallout from the incidents at the Mayak site (Kryshev et al., 1998; Romanchuk et al., 2016; Shutov et al., 2002), Chernobyl nuclear power plant (NPP) (Lux et al., 1995; Malek et al., 2002), and Fukushima NPP (Buesseler et al., 2011; Chino et al., 2011; Mukai et al., 2016), as well as that developed during nuclear weapon testing (Aoyama et al., 2006), led to the release of significant amounts of radionuclides, including radioactive Cs^+, in the environment. Additionally, large volumes of radioactive waste have accumulated in many countries, and mankind is faced with the problem of safely disposing of such waste. Despite the creation of multilayered defense systems (vitrification, containers, and engineering barriers), leaks could occur with time, releasing radionuclides into the environment. The migration behavior of radionuclides is affected by their interaction with different minerals, including clays. Clay minerals are widespread in the environment and are some of the most accepted materials as engineering barriers. The characteristics of the clay minerals (composition, particle size, admixtures, etc.) and the composition of solutions significantly influence sorption. Therefore, information on the exact mechanisms of the interaction between clays and radioactive waste is necessary to generate a reliable model for predicting the migration behavior of radionuclides. Understanding the migration of radionuclides is also required for designing remediation strategies for their clean-up from the environment.

^{137}Cs has a half-life of approximately 30 years, and it is one of the most radiotoxic nuclear fission products (Lehto and Hou, 2010). In solutions, Cs exists as a monovalent cation, Cs^+, with almost infinite solubility (Coughtrey and Thorne, 1983; Kerpen, 1986). Montmorillonite is a mineral belonging to the smectite group, and its structure consists of 2:1 layers, i.e., two tetrahedral sheets sandwiched on both sides of an octahedral sheet, linked by shared O^{2-} anions. Isomorphous cation substitutions in montmorillonites mostly occur in the octahedral sheets, leading to a negative charge (~0.2–0.6 per formula unit) that is neutralized by the interlayer exchangeable cations (Na^+, Ca^{2+}, Mg^{2+}, etc.), usually in hydrated form (Brindley and B, 1980; Drits and C, 1990; Guggenheim et al., 2006; Wilson, 2013). Because of this property, Cs^+ is strongly adsorbed onto clay minerals through an ion exchange mechanism.

The sorption of Cs^+ onto montmorillonite has been widely studied (Adeleye et al., 1994; Durrant et al., 2018; Dyer et al., 2000; Erten et al., 1988; Iijima et al., 2010; Kasar et al., 2014; Missana et al., 2014a;

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Tertre et al., 2005; Wu et al., 2009). However, only a few studies have included numerical modeling of the sorption data. Creating a sorption model capable of comprehensively interpreting the uptake of Cs^+ is still a work in progress, as evidenced by several published papers (Cherif et al., 2017; Durrant et al., 2018; Gutierrez and Fuentes, 1996; Kasar et al., 2017; Missana et al., 2014b, 2014a; Montavon et al., 2006; Siroux et al., 2017; Tachi et al., 2011; Wissocq et al., 2018). Furthermore, observations on the sorption of Cs^+ using natural raw bentonite clays (without treatment) are still lacking.

Raw clay with high montmorillonite content from a commercial source located in the Kutch region of Gujarat, India, was selected for the study. This particular bentonite is a barrier material candidate and has the high structural Fe content (Anastácio et al., 2008). The sorption of Np(V) onto raw Kutch clays has already been investigated (Semenkova et al., 2018; Verma et al., 2017). The atypical sorption behavior of Np (V) by this clay was explained by the influence of impurities (such as goethite). Studies of Cs^+ sorption, however, have not yet been reported for this material.

In this investigation, the sorption behavior of Cs^+ onto Kutch clay (India) was studied and compared with that of Cs^+ onto the relatively well-studied FEBEX clay (Spain). In particular, the objective of the present study was to develop a thermodynamic model for describing the interactions of Cs^+ with raw clay samples capable of accounting for the competition involving different cations in complex solutions.

2. Materials and methods

2.1. Clay sources and treatment

In this work, the raw bentonite obtained from the Kutch deposit (India) was studied. The Kutch clay was crushed in a ball mill and sieved to size fractions < 75 μm. This sample will be referred to as the "Original Kutch clay", hereafter. Part of the sample was subjected to a purification procedure that dissolved the iron oxide/hydroxide phases and converted the clay into a Na-form. The procedure was previously described in detail (Semenkova et al., 2018). Briefly, the Kutch clay sample was treated using a mixture of citrate buffer and sodium dithionite ($Na_2S_2O_4$) as reducing agent. This sample will be referred to as the "Purified Kutch clay".

A sample of the well-known FEBEX bentonite (Spain) was used for comparison. The FEBEX clay was converted into a Na-form by shaking the clay suspension in a 1 M solution of NaCl for 24 h. The above procedure was repeated twice to convert the original FEBEX into its Na-form; afterward the sample was washed with water and dried at 70 °C overnight.

Studies on the thorough characterization of the clays using X-ray diffraction (XRD), X-ray fluorescence (XRF), differential thermal gravimetric (DTG) analysis, Fourier-transform infrared (FTIR) analysis, Brunauer–Emmett-Teller (BET) absorption and Mossbauer spectroscopy have already been published (Semenkova et al., 2018; Verma et al., 2017).

The cation exchange capacities (CECs) of the Na-form of FEBEX and those of the Original and Purified Kutch clays were determined as the sums of the major cations (Na^+, K^+, Mg^{2+}, and Ca^{2+}) as charge equivalents observed in solution after extractions using the ammonium acetate (NH_4Ac) method (Kyllonen et al., 2014). For these measurements, 0.1 g of each clay sample was mixed with 20 mL of a 0.02 M NH_4Ac solution. After one week of agitation, the samples were separated by centrifugation at 40000*g* for 30 mins. The Na^+, K^+, Ca^{2+}, and Mg^{2+} contents were determined using an Agilent 7500C quadrupole mass spectrometer with inductively coupled plasma (Agilent Technologies, Japan). The instrument was controlled using the ICP-MS ChemStation software (version G1834B).

2.2. Sorption experiments

Sorption experiments were performed using Cs^+ concentrations in the 10^{-11} to 10^{-2} M range, which were obtained by adding the required quantity of CsCl solution to the ^{137}Cs tracer. Aliquots of CsCl and ^{137}Cs were added to 1 g/L clay suspensions in 0.01 M $NaClO_4$ solution. The pH values $(2-11)$ were adjusted by adding dilute $HClO_4$ (ultrapure grade) or NaOH (ultrapure grade). The samples were mixed continuously using an end-over-end mixer. After some time, 1 mL of each suspension was centrifuged at 40000*g* (Allegra 64R, Beckman Coulter) for 15 min to remove colloidal clay particles, and the supernatant was collected and used for radioactivity measurements. This procedure was sufficient to remove particles larger than 40 nm. According to the literature, the particle size of clay colloids is usually higher than 50 nm (Mayordomo et al., 2016). Dynamic light scattering measurements confirmed the absence of colloidal clay particles in the supernatant. A control sample, which was subjected to a longer centrifugation time, was also prepared. However, significant differences in the obtained sorption values of the samples produced using different centrifugation times were not observed.

The concentration of ^{137}Cs was measured by liquid scintillation counting using a Quantulus-1220 (Perkin Elmer) device and a scintillation cocktail (Ultima gold). Sorption was calculated based on the difference between the radioactivity of the ^{137}Cs initially added to the suspension and the radioactivity remaining in the supernatant after equilibrium was reached using the following expression:

$$Sorption,\,\% = \frac{A(Cs)_{tot} - A(Cs)_{sol}}{A(Cs)_{tot}} \times 100\%$$

where $A(Cs)_{tot}$ is the total activity of Cs^+ added to the system, in Bq, $A(Cs)_{sol}$ is the equilibrium activity of Cs^+ in the liquid phase, in Bq. The distribution coefficient (K_d) was also calculated:

$$K_d = \frac{A(Cs)_{tot} - A(Cs)_{sol}}{A(Cs)_{tot}} \times \frac{L}{S}$$

where S is mass of the clay, in g, and L is the total volume of the suspension, in mL.

Experiments using conditioned clays in 0.01 M $NaClO_4$ solutions as a function of pH were carried out under conditions similar to those used to obtain the Cs^+ sorption data (1 g/L clay suspension). After one week of equilibration, 5 mL of each suspension was centrifuged at 40000 *g* (Allegra 64R, Beckman Coulter) for 15 min to remove colloidal clay particles. The concentrations of K^+, Ca^{2+}, Mg^{2+}, and Al^{3+} in solutions were measured using an Agilent 7500C quadrupole mass spectrometer with inductively coupled plasma (Agilent Technologies, Japan).

2.3. Sorption modeling

The sorption data were modeled using the geochemical speciation software PHREEQC (Parkhurst and Appelo, 2013) coupled with the UCODE2005 software (Poeter et al., 2005). The two-site ion exchange model was used to describe the sorption of Cs^+. The ion exchange reaction between Cs^+ and the Na-form of clay minerals can be written as follows:

$$Cs^+ + NaX \leftrightarrows CsX + Na^+$$

where X is the ion exchange site. Moreover, the constants of the ion-exchange reactions were calculated.

3. Results and discussions

3.1. Cs^+ sorption experimental results

Table 1 presents the characterization results of the studied clay samples. Summarizing our previous work, where a detailed characterization of these clays was performed (Semenkova et al., 2018; Verma