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Adsorption of strontium and caesium onto an Na-MX80 bentonite: Experiments and building of a coherent thermodynamic modelling

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ABSTRACT

Multi-site ion exchange modelling permits describing the different adsorption behaviour of cations onto clay minerals. Considering several adsorption sites in the clay minerals' structure allows accurately representing the overall variations of adsorption behaviours. For a wider applicability in soils and sediments, it appears necessary to build a coherent thermodynamic adsorption database for radionuclides. ^{90}Sr and ^{134,137}Cs are major radionuclides to be considered in the case of nuclear accidents, but thermodynamic data on their adsorption on purified smectites are scarce. Therefore, a detailed study to determine Sr^{2+} and Cs^{+} adsorption parameter on smectite seems necessary. To provide this kind of information, this study is proposing multi-site ion exchange modelling of the adsorption of Sr^{2+} and Cs^{+} onto a pure Na-MX80 montmorillonite. The intrinsic parameters—site concentration and corrected selectivity coefficient for the Na^{+}/H^{+} exchange—were first fitted using an already available Na saturation curve of a purified smectite. The adsorption of Sr^{2+} and Cs^{+} on a purified Na-MX80 bentonite was explored, including a kinetic study for Sr, as a function of pH and equilibrium concentration. The isotherms were modelled to determine the corrected selectivity coefficients for the $2Na^{+}/Sr^{2+}$ and Na^{+}/Cs^{+} exchange reactions. This study provides a part of a wider databasis that is currently under construction, which can be used to predict the adsorption of Sr and Cs in soils and sediments.

1. Introduction

With the use and development of nuclear energy, the knowledge of the behaviour of the ^{235}U daughters in the environment is essential and has widely been studied. ^{90}Sr and ^{137}Cs, with half-lives of 29 and 30 years, respectively, are amongst the major by-products from the fission of ^{235}U (England and Rider, 1993). These isotopes were spread in the environment after the fall-out of the different nuclear weapon detonations, and after the nuclear accidents at Chernobyl (IAEA, 2006) and Fukushima-Daiichi (Sahoo et al., 2016). Because of its capacity to substitute with calcium in the food chain, ^{90}Sr can disturb ecological systems (Comar et al., 1957). Concerning ^{137}Cs, it is considered as a dangerous element because its high sol to plant transfer and radioactive decay includes ^{137}Ba and its gamma radiation.

Strontium and caesium are known to be greatly adsorbed onto soils, more specifically by clay minerals as illite (Bilgin et al., 2001) or kaolinite (Erten et al., 1988; Galamboš et al., 2013). If illite and vermiculite are known to be the strongest adsorbents for caesium, particularly due to the presence of the low concentration of high affinity frayed edge sites (Brouwer et al., 1983; Dzene et al., 2015; Sawhney, 1972), montmorillonite could also play an important role in the adsorption of Sr^{2+} and Cs^{+} due to its high cationic exchange capacity (CEC).

The study of the adsorption behaviour of Sr^{2+} onto pure Na-montmorillonite has been mainly led on smectite-rich soils (Galamboš et al., 2010; Kasar et al., 2014) or non-purified bentonite (Wang et al., 2004). Studies on purified smectite remain scarce in the literature. Missana and García-Gutiérrez (2007) have worked on a purified Na-FEBEX bentonite, which contains illite-smectite interstratified layers that provide specific fixation sites for Cs^{+} or K^{+}. Thereby, FEBEX bentonite cannot be considered as a pure smectite. Nevertheless, the similarity of the adsorption behaviour of Sr^{2+} onto illite and smectite (Missana et al., 2008) could permit comparing these results with those obtained on purified smectite.

Only a few papers deal with Cs^{+} adsorption onto pure Na-montmorillonite. As for Sr^{2+}, most of these works deal with smectite-rich soils (Vejsada et al., 2005), non-purified (Galamboš et al., 2010; Montavon et al., 2006; Wang et al., 2010) or not mono-ionic conditioned bentonite (Wu et al., 2009). Gorgeon (1994) reported trace Cs^{+} adsorption onto a pure Na-saturated Wyoming montmorillonite in 1 mol per kg of water ($mol.kg_{w}^{-1}$) NaCl. As the ionic strength is well

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outside the validity domain of the Davies (1962) equation, they will not be included in our discussion. As the specific interaction parameter $\varepsilon(Cs^+,Cl^-)$ is not available, and in view of the specific $\log_{10}\gamma_{\pm,CsCl}$ vs. m_{CsCl} variation (Hamer and Wu, 1972), a complete refitting using the specific interaction theory (Ciavatta, 1980) would be necessary, which is out of the framework of this study. This data can only be used as qualitative comparison. Missana et al. (2014a) studied the adsorption of caesium onto an Na-FEBEX bentonite, which carries a significant part of interstratified illite-smectite (*vide ante*). The illite part from these interstratified is well known to show specific adsorption behaviour towards Cs^+ partly due to the FES. As explained in Ogasawara et al. (2013), even a slight proportion of illite in clay minerals tends to drive the adsorption of Cs^+ at trace level and prevents the direct comparison between the results of Missana et al. (2014a) with results that could be obtained on purified smectite. Even at high concentration of Cs, illite could dominates the adsorption, as shown by Missana et al. (2014b) in San Juan clay (illite, smectite, kaolinite mixture).

The adsorption onto bentonite, as for many clay minerals (Carroll, 1959), is mainly controlled by an ion-exchange mechanism. Semi-empirical approaches of these adsorption mechanisms onto bentonite were used (Dyer et al., 2000; Guimarães et al., 2015; Mahoney and Langmuir, 1991; Rafferty et al., 1981; Shaban and Macášek, 1998), but few works used a mechanistic, or semi-mechanistic, approach. Bradbury and Baeyens (1999) have developed a model based on a mechanistic description of the cation adsorption between a clay minerals and a liquid phase—namely the two-site protolysis non-electrostatic surface complexation and cation exchange model or 2SPNE SC/CE. This model is combining both cation exchange reactions based on the Gaines and Thomas (1953) formalism—with no account for the Na^+/H^+ exchange—, and non-electrostatic surface complexation terms. Missana et al. (2008) applied a model derived from 2SPNE-SC/CE to study the adsorption of Sr^{2+} onto illite, smectite, and illite/smectite mixtures. This approach allows representing the global adsorption behaviour. Within the framework of this model, the pH dependency is given by the adsorption on edge sites $>$ S-OH—either silanol or aluminols sites. Adsorption onto cation exchange sites is not pH dependent. Conversely, adsorption of electrolyte cations only occurs on cation exchange sites. From their basic hypotheses these models do not allow modelling the saturation of a homo-ionic exchanger by a major cation, e.g. the Na^+/H^+ exchange all over the pH range. Conversely, within the multi-site ion exchange modelling framework the Na^+/H^+ exchange is considered intrinsically, as well as the exchange between a metal cation and Na^+ or H^+ exchange (Gaucher, 1998; Gorgeon, 1994; Motellier et al., 2003; Nolin, 1997; Peynet, 2003; Reinoso-Maset and Ly, 2014; Stammose et al., 1992).

In this study, a multi-site ion exchange modelling has been used. This model is based on the ion exchange theory (Tremillon, 1965) and has been developed to represent the adsorption processes on clay minerals (Gaucher, 1998; Gorgeon, 1994; Motellier et al., 2003; Nolin, 1997; Peynet, 2003; Reinoso-Maset and Ly, 2014; Stammose et al., 1992), mixtures of minerals (Peynet, 2003), or soils (Jacquier et al., 2004). The model does not aim to describe clay minerals at the microscopic scale—nature of adsorption sites, particularly affectation of sites defined by the model to the FES sites, surface charge, etc.—but takes into account the adsorption behaviour of major and trace elements in order to represent clay mineral characteristics. The model considers clay minerals as multi-site ion exchangers that bear negative adsorption sites (X_i^-) in contact with the solution. The exchanger(s) and the aqueous solution are considered as non-miscible phases. Each site *i* can potentially adsorb any cation. It is defined by a site concentration (SC_i in mmol per g of exchanger), and a corrected—of adsorbed species activity coefficient—selectivity coefficient for the exchange reaction between cations, e.g. $K^{*i}_{Na^+/H^+}$ for the Na^+/H^+ exchange.

This approach requires a careful and thorough characterisation of adsorption. First, the ion exchange properties (SC_i and corrected selectivity coefficients) have to be measured in a wide parametric domain of pH, ionic strength, and metal concentration (Jacquier et al., 2004; Motellier et al., 2003; Reinoso-Maset and Ly, 2014; Robin et al., 2015; Stammose et al., 1992), forming a coherent thermodynamic database for adsorption. All the exchange properties are experimentally measurable with adsorption isotherms. Afterwards, these properties can be used to study the metal adsorption (Tertre et al., 2009), or diffusion (Lu et al., 2014; Savoye et al., 2012), in different mineral contexts.

In order to continue building a coherent database, including Sr and Cs, and in light of the few amount of data on the adsorption of these cations onto pure smectite, the aim of this paper is first to ascertain the exchange properties of smectite—SC_i and corrected selectivity coefficient for the Na^+/H^+ exchange—, and second to acquire experimental data on the adsorption of Sr^{2+} and Cs^+ on a homo-ionic pure smectite—here the MX80 bentonite—as a function of pH, ionic strength, and initial concentration of cations. Then, the isotherms will be fitted using multi-site ion exchange modelling to determine the corrected selectivity coefficients for the $2Na^+/Sr^{2+}$ and Na^+/Cs^+ exchange reactions. The overall objective is to propose a coherent set of data for describing the adsorption behaviour of Na^+, H^+, Sr^{2+}, and Cs^+ on a pure smectite. This set of data could then be used to predict the adsorption of Sr and Cs in Na-rich soils.

2. Materials and methods

2.1. Materials

Wyoming MX80 bentonite was used as the adsorbent. It was purified to keep only the montmorillonite part, and conditioned under Na-saturated form following protocols in Gaucher (1998) and Peynet (2003). The organic matter potentially present in the material was removed using H_2O_2 at 80 °C, and calcite was dissolved using 0.1 M HCl solution. The montmorillonite was Na-conditioned by several washings using a 1 M NaCl solution. The reported CEC for the MX80 varies from 0.71 to 1.03 $mmol.g^{-1}$ (Alonso and Ledesma, 2005; Karnland, 2010; Meier, 1999). This value depends upon the measurement protocol or the sample purity. A CEC of 1.03 $mmol.g^{-1}$ was measured for this MX80, extracting all exchangeable cations with a KCl solution at pH ca. 10 (KOH). Supernatant was removed and the MX80 was washed with milli-Q water, then with ethanol. The adsorbed K^+ cations were extracted with a CsCl solution, and analysed by inductively coupled plasma atomic emission spectroscopy (ICP-AES). This high CEC value tends to confirm the high purity of the montmorillonite extracted from the MX80 bentonite. The purity was also confirmed by X-ray crystallography (XRG 3000, Inel)—see Fig. A1 of the Appendices. Moreover, the material only presents traces of exchangeable K and Mg (less than 1%) and is Na-saturated.

The chemicals used were at least of analytical grade. Stable Sr solutions were prepared from a $SrCl_2{\cdot}6H_2O$ salt (99.995% trace metals basis, Sigma Aldrich). Stable Cs solutions were from CsCl (99.999% trace metals basis, Sigma Aldrich). ^{85}Sr and ^{137}Cs solutions were obtained from Cerca LEA. Ionic strength was fixed using NaCl (Analar Normapur, VWR).

2.2. Adsorption experiments

2.2.1. Experimental protocols

All experiments were performed by batch method at room temperature (22 ± 2 °C) with the same 3.8 $g.L^{-1}$ solid/solution ratio. Polycarbonate Nalgene centrifuge tube (10 mL, 3138–0010, Thermo Scientific) were used. All the solutions and suspensions were made by weighing.

In all experiments the MX80 bentonite was first equilibrated under agitation with the NaCl electrolyte for 24 h. The pH values were adjusted with 1, 0.1 or 0.01 $mol.kg_w^{-1}$ solutions of HCl or NaOH, and suspension were left under agitation for 24 h. A total concentration of stable strontium—1.5 10^{-5} $mol.kg_w^{-1}$ of $SrCl_2$ for the kinetic