Modelling of Cs sorption in natural mixed-clays and the effects of ion competition

CrossMark

Tiziana Missana [a],[*], Miguel García-Gutiérrez [a], Ana Benedicto [a], Carlos Ayora [b], Katrien De-Pourcq [b]

[a] *CIEMAT, Avenida Complutense, 40, 28040 Madrid, Spain*
[b] *IDAEA-CSIC, Jordi Girona, 18-26, 08034 Barcelona, Spain*

ARTICLE INFO

ABSTRACT

Cs migration in the environment is mainly controlled by sorption onto mineral surfaces, in particular on clay minerals. With the objective of designing a geochemical reactive barrier to treat ^{137}Cs accidental pollution in an industrial waste repository, different natural clayrocks were studied to analyse their capacity to retain Cs.

The simple semi-empiric K_d-approach for experimental data analysis, is unsatisfactory to describe the variability of sorption upon chemical changes. Indeed, due to the high salinity of the site, the effects of competitive ions must be evaluated and quantified. Thus, the development of sorption models, capable of reproducing experimental data obtained under conditions representative of the contaminated site, and applicable to reactive transport studies, is needed.

In this study, a model for Cs sorption, which takes into account the main mineralogy of the sorbent, the composition of the natural water (and ion competition) was successfully applied to interpret the non-linear Cs sorption under natural conditions.

The selectivity coefficients of Cs with respect to the most important cations present in the site water (Na, K, NH$_4$, Ca) were derived by means of experiments in single clay minerals and synthetic mono-component solutions. Then, these parameters were tested in systems of increasing complexity.

Considering the mineralogical composition of raw materials, it was shown that the principal contribution to Cs sorption is given by the mineral illite, while smectite starts to be relevant only at very high Cs loadings. Kaolinite, even in concentrations around 10 wt% of the clayey fraction, played only a minor role.

With respect to the solution composition, the model was able to predict Cs sorption in electrolyte concentrations up to twice than that of seawater and up to 500 mg/L NH$_4^+$. The effect of highly competing ions, especially NH$_4^+$ and K$^+$, on Cs retention is more important at low ionic strengths and low Cs loadings, where adsorption is dominated by illite selective frayed edge sites, FES. Divalent cations are not especially relevant as competing cations for Cs.

© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

Cesium-137 is an important fission product from the irradiation of uranium-based fuels and it has been released in the past to soils and waters as a result of nuclear accidents or weapon testing. Radiocesium always exists as the monovalent cation Cs$^+$, which presents very high solubility and mobility, thus being a very relevant element from an environmental point of view.

For preventing radionuclide migration, the use of engineered barriers is often required. In addition, to predict contaminant retention under different chemical conditions, geochemical modelling must be applied, but adequate methodologies are needed to

test models and make realistic predictions (Wang and Staunton, 2010).

Suitable materials for the construction of barriers for contaminant migration must fulfill several properties; they must be *reactive*, i.e. they must interact with the contaminant and retain it and, at the same time, they must be more *permeable* than the surrounding soil, to facilitate the income of the contaminated water and its cleaning. After the selection of reactive materials, the permeability of the barrier is achieved mixing the reactive components with a porous filling, for example wood shavings (Rötting et al., 2008). All the materials must be durable, environmentally suitable, reasonably cheap and accessible, as large quantities are often needed to construct the barriers.

After the accidental contamination by ^{137}Cs of an industrial water repository, located in a marsh zone from Andalusia (Southern Spain), different studies were carried out to design a permeable

---

reactive barrier to ensure that the water outflowing from the repository to the environment is depleted of ^{137}Cs (Ayora et al., 2012). Many solids have been under study for Cs retention (Borai et al., 2009; Park et al., 2012), but the barriers comprised of argillaceous materials, are reported to be the most effective for its retardation (Krumhans et al., 2001). Cs is, in fact, rather strongly sorbed onto clays by ionic exchange. The extent of Cs uptake mainly depends on the cation exchange capacity (CEC) of the sorbents and their content in mica-like minerals, which present highly selective sorption sites for alkali cations (Cornell, 1993).

Several argillaceous rocks, available near the ^{137}Cs contaminated site or commercials, were selected and their retention capacity was studied (García-Gutiérrez et al. (2012)). Amongst the analysed materials, two of them were particularly suitable for sorbing Cs, presenting high illite content: the San Juan (SJ) and the Rojo Carbonero (RC) clays. The sorption behaviour of these two clayey materials had to be studied more in depth, with the objective of understanding and describing in quasi-mechanistic form the retention of Cs in the marsh contaminated environment, because the simple K_d approach is not enough to predict contaminant migration under natural variable conditions.

Furthermore, the porewater from the studied site is industrial and seawater-derived with high amounts of Na (up to 23 g/L), K (up to 1.2 g/L) and NH$_4$ (up to 0.7 g/L). Since these cations are expected to compete with Cs for the exchange sites, the existing models have to be tested for such high concentrations of K$^+$, NH$_4^+$, Ca^{2+} and Na$^+$ and ion competition must be explicitly accounted for.

To accomplish the mentioned objectives, in this study, detailed experiments of Cs sorption on single minerals (illite and kaolinite, as main components of clayey materials) and on these two natural clays was carried out. Previously obtained data on smectite as other main component of natural clayrocks (Missana et al., 2014) were used for the modelling of the natural system.

Cs sorption dependence on ionic strength and main exchanging ions was evaluated for the selected minerals converted in different homoionic forms. Basic selectivity coefficients were obtained from sorption experiments in simplified (mineral + simple electrolyte) systems; afterwards, Cs sorption onto raw materials and natural waters was experimentally studied and interpreted using the thermodynamic parameters calculated in the simplified systems.

The migration/retention of Cs in clayrocks has been studied by different authors Van Loon et al. (2009), Tachi et al. (2011), Fuller et al. (2014), Poinssot et al. (1999), Bradbury and Baeyens (2000), Zachara et al. (2002) and Liu et al. (2003). In general, illite is very important for cesium sorption, and Bradbury and Baeyens (2000) proposed a generalized cation exchange sorption model for the uptake of Cs by illite, based on the existence of different sorption sites, which cause non-linear Cs sorption.

Micaceous minerals, as illite, in addition to *planar* sites, possess *frayed edge sites*, FES, arising from the weathering of the clay particles edges. Cations like Cs$^+$, Rb$^+$, Li$^+$ or NH$_4^+$, characterised by low hydration energy and small dehydrated radius, can replace K$^+$ at these illite weathered edges and be selectively sorbed. Three exchange sites are usually considered to explain Cs sorption behaviour on illite (Bradbury and Baeyens, 2000; Brouwer et al., 1983; Poinssot et al., 1999).

Even when the presence of illite traces or interstratified with illite can give rise to the existence of selective sites for Cs, similar to illite FES (Missana et al., 2014), the surface of smectite and kaolinite is expected to be uniform and, in these pure minerals, Cs exchange is expected to occur mainly onto planar sites.

In this work, the modelling of Cs sorption on the natural clays will be done by a component additivity (CA) approach considering illite, smectite and kaolinite. A three-site exchange model will be used for the component illite; only exchange in planar sites will be included for smectite and kaolinite (thus, "FES-like" sites are all attributed to illite).

2. Materials and methods

2.1. Clays

Two different natural clays were studied: the Rojo Carbonero (RC) and the San Juan (SJ) clays. The RC clay is a commercial product by Cerámicas Bailén S.L. (Spain). Its mineralogy, provided by the supplier is, in wt%: quartz (27%), phyllosilicates (58%), dolomite (8%), feldspar (2%) and hematite (5%). The clay fraction (<2 μm) is composed by illite (98%) and chlorite. The total cation exchange capacity (CEC) of the RC was determined on the raw material to be 11 meq/100 g (Fernandez, 2012) and its BET surface area, 43.71 ± 0.21 m^2/g.

The SJ clay was sampled near the contaminated site and it contains (in wt%): quartz (15–20%), illite (30–50%), kaolinite (10–15%), smectite (5–20%), calcite (3–10%) and clinochlore (10–20%).

From the RC material, the clay fraction (mostly illite), which has a size <2 μm, was separated by sedimentation (Stokes' law), to perform detailed sorption studies on this individual mineral. The obtained illite has a CEC of approximately 19 meq/100 g, in agreement with previous published CEC data (Bradbury and Baeyens, 2000) and its surface area is 77 m^2/g.

In addition to illite, Cs sorption onto kaolinite (and smectite) and was also analysed, as they are the main clay minerals present in the SJ solid. These sorption studies on the individual minerals allow obtaining basic selectivity coefficients to be tested in more complex systems.

The kaolinite used in the present study was the natural KGa-1-b, obtained from the Clay Mineral Society (CMS, EEUU). The purity of this material is higher than 93%. The main characteristics were provided by the supplier. It has a CEC of 2 meq/100 g and a BET area of 10 m^2/g. The main characteristics of the minerals used in this study are included in Table 1.

As reported in Missana et al. (2014), the smectite was obtained from the Spanish FEBEX bentonite, which has (in wt%) a 93 ± 2% content of smectite, and as main accessory minerals: quartz (2 ± 1%), plagioclase (3 ± 1%), cristobalite (2 ± 1%), calcite (1 ± 0.5%) and potassic feldspar (traces). The BET surface area of this clay is 33 m^2/g and its CEC 102 meq/100 g. More details on its composition and properties can be found in Fernandez et al. (2004) and Huertas et al. (2000). Previous mineralogical studies also showed that the smectite phase is made up by illite–smectite mixed layer with a 10–15% of illite layers (Cuadros and Linares, 1996; Huertas et al., 2000). Sorption of Cs in this smectite has been previously studied in detail by Missana et al. (2014) and, in the present work, we refer to those results.

2.2. Preparation of exchanged clay minerals

The details on the preparation of purified smectite can be found in Missana et al. (2014). In the present work, the clay minerals illite and kaolinite were purified and converted into different exchanged forms (Na, K, NH$_4$ and Ca). To exchange the minerals, they were suspended in 1 M of the respective electrolyte (NaCl, KCl, NH$_4$Cl or CaCl$_2$): the suspensions were stirred overnight and decanted;

Table 1
Main characteristics of clay minerals used in this work.

	Illite	Smectite	Kaolinite
BET (m^2/g)	77	33	10
CEC (meq/100 g)	19	102	2