



# A robust and parsimonious model for caesium sorption on clay minerals and natural clay materials



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## ABSTRACT

Caesium (Cs) is one of the most studied radionuclides in the fields of nuclear waste disposal and environmental sciences. The overall objective of this work is to improve the tools designed to describe and predict migration, retention, and bioaccumulation processes in the geosphere and the biosphere, particularly in the soil/solution soil/plant roots systems. Cs sorption on clay minerals has been extensively measured and modeled because these minerals control Cs mobility and (bio)availability in the environment.

A critical analysis of published experimental data on Cs sorption by clay minerals and natural clay materials along with the different models was performed in an attempt to elaborate and evaluate a generic model for Cs sorption. This work enabled us to propose a robust and parsimonious model for Cs sorption, which combines the surface complexation and cation exchange approaches invoking only two types of surface sites: frayed edge and exchange sites. Our model, referred to as the “1-pK DL/IE model”, takes into account the competition between Cs and other cations as well as the influence of the ionic strength and pH of the solution.

This model was successfully calibrated for Cs sorption on three reference clay minerals (illite, montmorillonite and kaolinite), in a wide range of Cs concentrations and physicochemical conditions. Using the same parameters, we tested our model on several natural clayey materials containing a single to several clay minerals. The goodness-of-fit obtained with natural materials containing a single clay mineral demonstrates the robustness of the model. The results obtained with natural mixed clay materials confirm the predictive capability of the model and also allowed us to test the sensitivity to the mineral composition of these materials (uncertainties). We found that illite is usually the most reactive clay mineral with respect to Cs sorption and that component additivity is applicable when the contribution of other clay minerals becomes non negligible. The whole set of model-measurement comparisons performed in this study provides a high level of confidence in the capabilities of the 1-pK DL/IE model as an interesting predictive tool.

## 1. Introduction

Since decades the pollution of natural ecosystems by radionuclides has become a major concern for society. In particular, caesium (Cs) is widely studied by environmental scientists using different analytic and experimental techniques (Benedicto et al., 2014; Bostick et al., 2002; Chorover et al., 2003; Missana et al., 2014a; Savoye et al., 2012; Wendling et al., 2005). One of the Cs radio-isotopes, <sup>137</sup>Cs, is an important fission product from the irradiation of uranium-based fuels, has a relatively long life ( $t_{1/2} = 30$  years), and constitutes a significant radioecological hazard due to its hard gamma emission. After release of radioactivity into the environment, this radioelement is considered as the main source of contamination of soils (Avery, 1996; Strebl et al.,

1999) and the principal source of radioactivity of nuclear waste in the timeframe of the first one hundred years. Moreover, radiocaesium always exists as the monovalent cation Cs<sup>+</sup>, with chemical properties similar to potassium (K<sup>+</sup>) (Kamei-Ishikawa et al., 2011; Roca and Vallejo, 1995), having very high solubility (Benedicto et al., 2014; Fuller et al., 2014; Missana et al., 2014b; NDA, 2010). Cs mobility in soils environment is also known to be significantly influenced by retention capacity for Cs<sup>+</sup> (Avery, 1996; Strebl et al., 1999).

Understanding the processes that control the bioavailability and mobility of Cs in the biosphere and geosphere constitutes a major challenge that has to be tackled in order to provide a good estimate of its health and ecological hazard. Geochemical reactions, particularly those occurring at mineral/water interfaces, closely control the fate and

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behavior of the major elements or trace in these systems (Koretsky, 2000). The adsorption/desorption process (i.e. sorption) generally dominates the interactions between Cs and soil as this element hardly forms solid species in natural environments (Dzene et al., 2015).

Clay minerals are often invoked as the most important minerals that control the bioavailability and mobility (migration-retention) of Cs in subsurface (e.g. soils and sediments) and groundwater environments (Bostick et al., 2002; Chorover et al., 2003; Missana et al., 2014a; Savoye et al., 2012; Shenber and Eriksson, 1993; Wendling et al., 2005). In soils, the most efficient carrier phases of Cs<sup>+</sup> are clay minerals, especially 2:1 layer clays, with a permanent charge arising from isomorphous substitution (Bostick et al., 2002; Comans et al., 1991; Comans and Hockley, 1992; Cornell, 1993; Maes and Cremers, 1986; Nakano et al., 2003; Sawhney, 1972; Watanabe et al., 2012); firstly because of their ubiquity and secondly because they have large specific surface areas with a high density of (negatively and positively) charged surface sites (Kraepiel et al., 1999; Langmuir, 1997).

Among the different properties of Cs/clay mineral interactions, the non-linear Cs sorption isotherms on phyllosilicate clays, such as illite (Bradbury and Baeyens, 2000; Cornell, 1993; Eliason, 1966; Missana et al., 2004; Poinssot et al., 1999; Staunton and Roubaud, 1997; Wahlberg and Fishman, 1962), is considered to be the result of the heterogeneity of the surface adsorption sites. (i) High affinity sites, which adsorb strongly and specifically Cs, are located on the edges of clay minerals and are therefore usually termed as « Frayed Edge Sites » (FES) (Brouwer et al., 1983; Eberl, 1980; Francis and Brinkley, 1976; Jackson, 1963; Maes and Cremers, 1986; Poinssot et al., 1999; Rich and Black, 1964; Sawhney, 1972; Zachara et al., 2002). (ii.) The remaining sites, which have a lower, non-specific, affinity for Cs, are present in large quantities and located on planar surface and mainly constitute the cation exchange capacity (CEC). On these sites, the adsorption of Cs strongly depends on the composition of the cationic exchangeable population, since the adsorption reaction partly proceeds as cation exchange (Cornell, 1993; Rigol et al., 2002; Staunton and Roubaud, 1997; Zachara et al., 2002). Cs can also be selectively fixed on interlayer sites of phyllosilicate clays (Rigol et al., 2002; Salles et al., 2013). Adsorption therefore depends on the relative affinities of Cs, the nature of the competitive exchanging cations, pH and the ionic strength.

Caesium adsorption mechanisms on illite has received a lot of attention for several decades and different studies were produced that inferred the prevailing mechanism (Sawhney, 1972) and, more recently, gave spectroscopic evidence that Cs initially sorbs on illite FES and can eventually enter into the interlayer and be incorporated into the mineral structure (Fuller et al., 2015; Lee et al., 2017). Caesium adsorption on vermiculite and montmorillonite was described by Bostick et al. (2002) as a function of surface coverage using EXAFS. These authors also found that inner-sphere surface complexes may form within the interlayer or at frayed edge sites and were less accessible than outer-sphere complexes. None of these studies exclude the possibility of having Cs adsorbed onto amphoteric sites, at least in the early stage of sorption which would account for the pH-dependency of Cs sorption as opposed to ion exchange in the interlayer. This aspect has received much less attention and experimental data is still lacking, especially for illite. Furthermore, the partial reversibility of Cs is difficult to reconcile with the “collapsed” interlayer resulting from Cs incorporation into the structure of illite (Comans et al., 1991; Comans and Hockley, 1992; De Koning and Comans, 2004; Durant et al., 2018).

Several models have been developed in the last two decades in order to interpret and model non-linear Cs sorption onto mineral phases under specific conditions (homoionized mineral phases, many fixed experimental parameters such as pH and ionic strength) (Baeyens and Bradbury, 1997; Benedicto et al., 2014; Bradbury and Baeyens, 2000; Brouwer et al., 1983; Chen et al., 2014; Gutierrez and Fuentes, 1996; Liu et al., 2004; Marques Fernandes et al., 2015; Missana et al., 2014a, 2014b; Montavon et al., 2006; Poinssot et al., 1999; Savoye et al., 2012; Silva et al., 1979; Zachara et al., 2002). However, no compilation or

comparison study of these models has ever been proposed. Moreover, these models, whose parameters are obtained in a semi-empirical manner, do not take into account the effect of pH on the mineral surface charge: this implies that their transferability to heterogeneous environments is limited (Koretsky, 2000; Missana et al., 2008). Another important point is that these models were calibrated for specific physicochemical conditions proper to each study without considering the transferability to other conditions. This constitutes the major limitation of cation exchange models found in literature, which appear to be unsatisfactory to predict Cs sorption a wide range of conditions in natural systems without any modification of the thermodynamic parameters.

The objective of this work was (i) to establish a compilation of the current models describing Cs sorption on natural clayey materials and (ii) to perform a cross-comparison of all these models with all the data available in the literature for pure clay minerals and for clay materials. (iii) An alternative model was finally developed in order to improve the performance, the robustness and the predictability of the existing models, based on the combining approach (i.e. cation exchange and surface complexation models) described above, and requiring fewer parameters (i.e. parsimonious) than most of the others modelling approaches. It is designed to be capable of modelling Cs adsorption without any parameter changes over a larger range of chemical conditions (i.e. robustness). We calibrated this model with all the data available in the literature for pure clay minerals (illite, montmorillonite, and kaolinite) and we assessed its validity for clay materials of increasing complexity, ranging for relatively simple materials containing only a single clay mineral to materials such as bentonite and claystones containing several types of clay minerals.

## 2. Material and methods

### 2.1. Available data on clay minerals and clay materials

A compilation of existing experimental and modeled data found in the literature was performed in order to evaluate the existing models for Cs sorption on clay minerals and the one developed here. These data are mostly constituted by Cs sorption isotherms on the most common clay minerals, i.e. illite, montmorillonite, and kaolinite (243 observations), and on a variety of clay materials (378 observations) (Tables 2 and 4). The adsorption data usually presented in the form of a distribution coefficient ( $K_d$ ) for the adsorbed Cs as a function of Cs concentration in solution at equilibrium or as a function of pH. The distribution coefficient between the solid and the liquid phase,  $K_d$  (L kg<sup>-1</sup>), is calculated using the following relationship:

$$K_d = \frac{[Cs]_{tot} - [Cs]_{eq}}{[Cs]_{eq}} \frac{V}{m} \quad (1)$$

where  $[Cs]_{tot}$  is the total Cs concentration of the suspension (mol L<sup>-1</sup>),  $[Cs]_{eq}$  is the Cs concentration in solution at equilibrium (mol L<sup>-1</sup>),  $m/V$  is the solid: liquid ratio with  $m$  the mass of the clay (kg), and  $V$  is the volume of the liquid (L).

Table 1 shows the different clay minerals considered in the present investigation, together with their mineralogical properties and the experimental conditions used in the studies. The most abundant set of experimental data concerns illite with a total 191 observations. Fewer experimental data were found for montmorillonite (51 observations) and kaolinite (67 observations). All the clay minerals had been purified and homoionized in Na, K, Ca or NH<sub>4</sub> before performing Cs sorption. The different types of illite considered in this investigation have different origins (Le Puy, Rojo Carbonero and Morris), but exhibit consistent values for the cationic exchange capacities (CEC) and Specific Surface Area (SSA) (Table 1). Note that the illite from Le Puy-en-Velay is usually considered as the “reference” illite and its parameters are preferentially used in several studies (Bradbury and Baeyens, 2000; Chen et al., 2014; Maes et al., 2008; Marques Fernandes et al., 2015).

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