



Research paper

From experimental variability to the sorption related retention parameters necessary for performance assessment models for nuclear waste disposal systems: The example of Pb adsorption on clay minerals

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ABSTRACT

Surface complexation models (SCMs) have been developed in the last decades to describe metal ion sorption to clay minerals and especially to montmorillonite. In principle, these models can provide relevant information about sorption of radionuclides to be used in performance assessment (PA) of radioactive waste disposal systems. However, these SCMs have been developed in parallel with the acquisition of distinct adsorption datasets, which are not always consistent with each other. The objective of this study was to compare new experimental adsorption results with literature data to understand these discrepancies and to propose a SCM approach that could be amenable to determine sorption related retention parameters necessary for PA calculations. This study focused on lead (Pb) adsorption on montmorillonite, illite and in a natural clay (Callovo Oxfordian) as case studies of a strongly sorbing radionuclide that undergoes a range of retention processes depending on the chemical conditions. The experiments showed that many experimental artifacts lead to misinterpretations of the processes underlying the measured retention values. These include Pb precipitation in the presence of carbonate in solution. The determination of SCM parameters to provide sorption related information for PA of clay minerals should rely on preliminary building of an adequate adsorption database, where adequate means that all experimental conditions are met to quantify surface complexation only.

1. Introduction

In recent years, the scientific community has seen a remarkable surge of interest in the properties and behavior of clays as they apply to a variety of natural and engineered settings. Clay materials are known as an important part of the multi-barrier system for nuclear waste storage around the world, and their performance must be demonstrated on the time scale of hundreds to millions of years (Altmann, 2008; Busch et al., 2008; Chapman and Hooper, 2012; Armitage et al., 2013; Neuzil, 2013). In these applications, the low hydraulic conductivity of the clay mineral-rich geological formations or of the engineered clay barriers provides at least part of the basis for isolating radionuclide contaminants (RN). Clay minerals have high adsorption capacity for a large range of radionuclides (Bradbury and Bayens, 2005). The strong adsorption and resulting retardation of many contaminants by clay

minerals make them ideal for use in natural or engineered barrier systems, particularly where there is a desire to improve confidence in the safety case beyond the reliance on slower transport rates alone (Altmann et al., 2012; Gaboreau et al., 2012; Borisover and Davis, 2015; Grangeon et al., 2015). Because contaminant mobility in clay materials is mainly driven by diffusion and adsorption processes, a typical (simplified) scheme for estimating radionuclide release relies on knowing three parameters. The first is the effective diffusion coefficient (D_e), which quantifies the transport of each radionuclide across the barriers. The second is the distribution ratio of the radionuclide between the solution and the solid phases/surface (R_D or K_D if the retention is reversible), which quantifies the accumulation on the solid and the retardation of the radionuclide as it migrates from the repository across the barriers. The third is the solubility, which controls the maximum concentration in solution of the radionuclide of interest

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according to the geochemical conditions. These parameters are site specific, so to determine them specific data acquisition programs are needed. However, there is a fundamental difference between solubility and K_D values. Solubility values are usually obtained from the interpretation of experimental data with thermodynamic laws, which can be considered to be always valid, so solubility values can be applied to site-specific conditions, if environmental conditions such as temperature, pressure, and pore water composition are known, and with the assumption of precipitation/dissolution at thermodynamic equilibrium. Conversely, K_D values are directly measured in the presence of experimental conditions that are supposed to be representative of the in situ environmental conditions. As a direct consequence, knowledge about K_D values cannot be easily transferred from one site condition to another. For decades, quasi-thermodynamic models have been developed to predict the adsorption properties of many natural materials including clay minerals, oxides and organic matter. These models, grouped here under the term surface complexation models (SCM), aim to predict adsorption processes in a wide range of environmental conditions (Sposito, 1984; Davis, 1990; Dzombak and Morel, 1990; Hiemstra and Van Riemsdijk, 1996; Davis et al., 1998). If complete enough, they can be transferred from one site condition to another, providing that the dominant mechanisms have been identified and adequately quantified. In principle, these models could be used in performance assessment (PA) with calculations carried out with reactive transport codes. In practice, this is seldom the case, but recently, a hybrid approach, named “Smart K_D ”, which takes advantage of SCM flexibility with regards to changes in environmental conditions together with simplified models more amenable to PA calculations, has been advanced to include more flexibility, predictability and transferability in these PA calculations (Richter et al., 2009; Stockmann et al., 2012; Druteikien et al., 2017). Near-field conditions will change over time following local perturbations induced by the presence of the waste repository. As an example, heat release from a radioactive waste package will temporarily increase the temperature that will itself influence the adsorption properties of clay minerals because of at least two processes. First, the affinity of the clay surfaces for a given RN is dependent on temperature (Tertre et al., 2005). Second, a temperature change influences the geochemical characteristics of the porewater, especially the pH, changing the distribution of species (speciation) in solution for the elements of interest (Gailhanou et al., 2017). So estimating SCM parameters and their associated uncertainties in as wide a range of conditions as possible is a key aspect in developing these PA approaches.

SCM parameters must be calibrated with experimental data in well-defined and well-controlled conditions. This is necessary in order to extrapolate the results in a wide range of conditions and to apply them to natural materials using a component additivity (CA) approach (Davis et al., 2004; Chen et al., 2014a, 2014b). The choice of the SCM is also important. A range of SCM that is applied to clay minerals and especially to montmorillonite have been developed and described in the literature (Zachara and Smith, 1994; Bradbury and Baeyens, 1997; Ikhsan et al., 2005; Gu and Evans, 2007; Marcussen et al., 2009; Tertre et al., 2009; Gu et al., 2010; Akafia et al., 2011). These SCMs were developed in parallel with the acquisition of distinct adsorption datasets, which are not always consistent with each other (Tournassat et al., 2013). Several sources of discrepancies explain these inconsistencies, including differences in the properties of the clay materials (for example, natural variability in chemistry and size distribution, and preparation prior to experiments including sedimentation techniques and chemical treatments to remove mineral and organic impurities), differences in experimental procedures (order of reagent addition), and experimental artifacts. So the objective of this study was to compare new experimental adsorption results with literature data in order to understand these discrepancies and to propose a SCM approach that could be amenable to the determine sorption related retention parameters necessary for PA calculations. This study was focused on Pb adsorption as a case study of a strongly sorbing radionuclide on

Table 1
Summary of experimental conditions used with three different reference clays (purified MX-80, Kunipia and illite and one clay fraction of COx claystone).

Initial Pb concentration (μM)	R_{SL} ($\text{g}\cdot\text{L}^{-1}$)	NaCl concentration (M)	pH range	T ($^{\circ}\text{C}$)
1	1	0.1	3–9	20 ^a
10	1	0.1	3–9	20 ^a
50	1	0.1	3–9	20 ^a
1	0.5	0.025	3–9	20 ^a
1	1	0.1	3–7	67

^a Room temperature.

montmorillonite, illite and a natural clay mineral (Callovian-Oxfordian) (COx) that undergoes a range of retention processes as a function of chemical conditions.

2. Material and methods

2.1. Overview of experiments

Batch adsorption experiments were conducted with three different reference clay minerals, namely two montmorillonites (MX-80 and Kunipia-P) and one illite, and with a natural clay mineral assemblage present in COx claystone, in order to quantify the main adsorption mechanisms of Pb on clays. To clarify the effect of each of these mechanisms, various adsorption experiments were designed spanning a range of different solid/liquid ratio (R_{SL} , in $\text{g}\cdot\text{L}^{-1}$), ionic strength (NaCl as a background electrolyte), pH, temperature, and initial Pb concentrations (Table 1).

2.2. Chemicals

All chemicals used in the experiments were analytical grade: Pb ($\text{NO}_3)_2$ (Prolab R.P. Normapur, > 99.5%), NaCl (Merck, 99.6%), 30% HCl (Merck, Suprapur), NaOH pellets (Merck, > 99%), 65% HNO_3 (VWR Prolabo, 69.4% for cleaning, and Merck, Suprapur for AAS measurements), acetic acid ($\text{C}_2\text{H}_4\text{O}_2$, VWR Prolab, 96%), citric acid ($\text{C}_6\text{H}_8\text{O}_7\cdot\text{H}_2\text{O}$, Carlo Erbar, > 99.8%), sodium bicarbonate (NaHCO_3 , ACS Amresco), 30% H_2O_2 (Merck), sodium dithionite ($\text{Na}_2\text{S}_2\text{O}_4$), MES ($\text{C}_6\text{H}_{13}\text{NO}_4\text{S}$, Sigma Aldrich, > 99%), MOPS ($\text{C}_7\text{H}_{15}\text{NO}_4\text{S}$, Sigma Aldrich, > 99.5%), tri sodium citrate dihydrate ($\text{C}_6\text{H}_5\text{Na}_3\text{O}_7\cdot 2\text{H}_2\text{O}$, Fluka, 99.99%). Milli-Q 18 M Ω water was used in all solution preparation, clay suspension and clay purification processes.

2.3. Solution preparation

NaCl stock solutions (0.1 M and 0.025 M) were prepared from crystalline NaCl. HCl stock solution (1 mM) and NaOH stock solution (1 mM) were prepared from 30% HCl acid solution and NaOH pellets, respectively. Two 1 mM Pb stock solutions at two different ionic strength were prepared by dissolving crystalline $\text{Pb}(\text{NO}_3)_2$ in a 1 mM HCl/0.1 M NaCl solution and in a 1 mM HCl solution. For experiments conducted with low Pb concentrations, 10 and 100 μM stock solutions were prepared by diluting these solutions in a 1 mM HCl/0.1 M NaCl solution and in a 1 mM HCl solution. All solutions were prepared in an air atmosphere.

2.4. Clay material

Clay stock dispersions with a solid/liquid ratio of $2\text{ g}\cdot\text{L}^{-1}$ were prepared in a 0.1 M NaCl solution background for two montmorillonites (MX-80, and Kunipia-P), one purified illite (Illite du Puy, IdP), and the clay fraction of COx claystone. MX-80 montmorillonite was extracted from a stock of MX-80 bentonite and the clay fraction of COx claystone was obtained from the core EST 51779 (borehole OHZ6126 – depth:

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