Journal of Colloid and Interface Science 334 (2009) 132–138

Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

www.elsevier.com/locate/jcis

Experimental study and modelling of selenite sorption onto illite and smectite clays

T. Missana *, U. Alonso, M. García-Gutiérrez

CIEMAT, Departamento de Medioambiente Avenida Complutense 22, 28040 Madrid, Spain

ARTICLE INFO

Article history:
Received 2 November 2008
Accepted 22 February 2009
Available online 8 April 2009

Keywords:
Adsorption
Selenium
Clays
Radioactive waste

ABSTRACT

This study provides a large set of experimental selenite sorption data for pure smectite and illite. Similar sorption behavior existed in both clays: linear within a large range of the Se concentrations investigated (from 1×10^{-10} to 1×10^{-3} M); and independent of ionic strength. Selenite sorption was also analysed in the illite/smectite system with the clays mixed in two different proportions, as follows: (a) 30% illite–70% smectite and (b) 43% illite–57% smectite.

The objective of the study was to provide the simplest model possible to fit the experimental data, a model also capable of describing selenite sorption in binary illite/smectite clay systems.

Selenite sorption data, separately obtained in the single mineral systems, were modeled using both a one- and a two-site non-electrostatic model that took into account the formation of two complexes at the edge sites of the clay. Although the use of a two-site model slightly improved the fit of data at a pH below 4, the simpler one-site model reproduced satisfactorily all the sorption data from pH 3 to 8.

The complexation constants obtained by fitting sorption data of the individual minerals were incorporated into a model to predict the adsorption of selenium in the illite/smectite mixtures; the model's predictions were consistent with the experimental adsorption data.

1. Introduction

Argillaceous rock is considered by many waste management programmes as an adequate host formation or engineered barrier for deep geological repositories (DGR) of high-level radioactive waste, because it presents adequate thermo-hydro-mechanical properties, required by these repositories, and it is expected to adsorb radionuclides and retard their migration to the geosphere [1,2].

The determination of the radionuclide retention onto both host rock and the engineered barriers of nuclear waste repositories is an essential component of performance assessment (PA) analyses. PA calculation aims to predict the impact of radionuclides that might accidentally escape from a repository.

In PA, sorption is treated by the semi-empiric "Kd-approach" as a reversible attachment of dissolved species to surfaces. However, a mechanistic approach to sorption processes—based on a thermodynamic description of radionuclide/solid interactions—better predicts sorption behaviour under variable conditions; and its implementation in PA could be of great utility as an alternative to the "Kd-approach" currently in use.

The implementation of a mechanistic approach requires both a detailed analysis of radionuclide sorption processes and the development of mathematical models capable of precisely describing them under the widest possible range of experimental conditions. Simple, yet effective models for describing sorption could be easily incorporated into PA.

The application of a mechanistic description of sorption—to systems composed of two different clay materials—represents the first step in understanding natural clay systems [3].

Among the most common and relevant components of clay rock are smectite and illite. These 2:1 layer type clays are characterised by an octahedral sheet between two tetrahedral sheets. In smectite, isomorphic substitutions occur in the tetrahedral and octahedral sheets. These substitutions impart a permanent negative charge that is compensated by cation adsorption onto the basal surfaces; with the amount of these adsorbed cations corresponding to the cation exchange capacity (CEC) of the clay. In illite, these substitutions take place mainly in the external tetrahedral sheets, so that potassium ions existing in the interlayer cannot be exchanged with other ions in solution [4,5]. Illite, therefore, generally presents a lower CEC than smectite.

Apart from this permanent charge, 2:1 layer clays present amphoteric edge sites, SOH. The SOH sites, similar to those present on the oxides surface—can be protonated or de-protonated [5]—and provide an additional pH-dependent contribution to the surface charge. In clays, surface complexation at SOH sites is expected to be the most relevant sorption process for anions.

Anions are of concern in the context of radioactive waste repositories, because their negative charge limits adsorption onto geological materials [6]. ^{79}Se, present in spent nuclear fuel and high-level radioactive waste, is an element of interest because of its long half-life (650,000 y).

---

* Corresponding author. Fax: +34 91 346 6542.
E-mail address: tiziana.missana@ciemat.es (T. Missana).

0021-9797/$ - see front matter © 2009 Elsevier Inc. All rights reserved.
doi:10.1016/j.jcis.2009.02.059

Selenium chemistry is quite complicated because it depends not only on the redox state of the system but on all factors influencing its speciation (e.g pH, presence of organics, kinetics, etc.). Selenium's mobility is also affected by the chemistry of the system [7]. Depending on geochemical conditions, mainly redox and pH, selenium can be found in various oxidation states: selenide (-II); elemental selenium (0); selenite (IV); and selenate (VI) [8]. Several studies have shown various oxidation states of selenium coexistent within in the same system. Selenides and metallic selenium form highly insoluble precipitates—and selenate shows very weak sorption onto geological materials—therefore, the most interesting oxidation state for analysing selenium sorption behaviour is selenite.

A great number of papers have been published on selenium sorption by (iron) oxides [9–19], or various soils [20–25] but, surprisingly, significantly fewer on selenite sorption onto clay minerals [26–28], and yet even fewer treat the sorption problem with a mechanistic approach. No previous studies exist about selenite sorption onto illite/smectite mixtures.

Montavon et al. [28] proposed an "operational" model to describe the sorption onto MX-80 bentonite, the reference material chosen for the French nuclear waste repository concept, both in its dispersed and compacted state. Boult et al. [29] presented the modelling of selenite sorption edges on a purified Na-bentonite, with data obtained at a unique ionic strength and at a single selenium concentration.

The first necessary step in the creation of a reliable sorption model is to experimentally analyse sorption behaviour over a wide range of experimental conditions (pH, ionic strength, and radionuclide concentration).

We present a large set of experimental selenite sorption data for pure smectite and illite with the objective of providing the simplest model possible to describe them; a simple model also capable of describing selenite sorption onto binary illite/smectite clay systems.

2. Materials and methods

2.1. Clays

The smectite clay (FEBEX bentonite) mined at the Cortijo de Archidona deposit (Almeria, Spain), has a high smectite content (93 ± 2%). Its accessory minerals are: quartz (2 ± 1%), plagioclase (3 ± 1%), cristobalite (2 ± 1%), potassic feldspar, calcite, and tridymite. A comprehensive characterization of the FEBEX bentonite can be found elsewhere [30]. FEBEX smectite's features of interests are as follows: its cation exchange capacity (CEC) is 102 ± 4 meq/100 g; its N_2-BET surface area is 33 $m^2\ g^{-1}$ and its EGME surface area 725 $m^2\ g^{-1}$.

The "as-received" illite (Illite du Puy) comes from the region of Le Puy-en-Velay (France); it contains 74% illite and kaolinite, 20% calcite and 5% quartz. After the purification and homoionisation process, this clay has a small percentage of kaolinite (7%) but high illite content (93%).

A comprehensive characterization of this illite can be found elsewhere [31]. Illite du Puy's features of interest here are as follows: its cation exchange capacity (CEC) is 22.5 ± 2 meq/100 g [32]; its N_2-BET surface area is 97 $m^2\ g^{-1}$; and its EGME surface area 95 $m^2\ g^{-1}$.

2.2. Radionuclide

The radionuclide used in this study was a carrier-free ^{75}Se (as H_2SeO_3 (selenite) in 0.1 HCl, Isotope Products). Most ^{75}Se radiation is in the form of gamma emissions at 136 and 265 keV. The half-life of ^{75}Se is 119.8 days. The activity of selenium in solution was measured by γ-counting with a NaI detector (Packard Autogamma COBRA 2).

2.3. Preparation of the clay suspensions

Previous to use in sorption experiments, the clays were purified and homoionised in Na. These "natural" clays were washed three times with 1 M $NaClO_4$ to eliminate all the soluble salts and to obtain the homoionic Na-form. The "Na-form" of illite is defined as a form where the exchangeable cations at the external surfaces are substituted by Na (obviously, ions in the interlayer cannot be substituted).

After elimination of the supernatant from the last washing, the Na-clay was placed in centrifuge tubes with deionised water. With centrifuging (600*g*, 10 min.) we separated the clay particles of less than 0.5 μm to be used in sorption tests. For the prevention of extensive dissolution of the clay, this fine fraction was precipitated in a glass container with 1 M $NaClO_4$. The clay washing/centrifuging procedure was repeated approximately 20 times. When enough of this fine fraction was collected, the clay suspension was introduced into dialysis bags that were sealed then placed in 3 L containers filled with the electrolyte ($NaClO_4$)—to bring the suspension to the required ionic strength.

The electrolyte was changed two or three times per day until both the conductivity of the suspension in the bags and the external electrolyte were the same. The homoionisation process did not affect the main properties of the clays (CEC or surface area).

The concentration of the clay material in the suspension—for later utilisation in sorption experiments—was determined by gravimetry. The solid to liquid ratio (S), used in these experiments was 0.5–1 g L^{-1}.

In addition to the pure smectite and pure illite suspensions, two more suspensions were prepared by mixing the two original clays to a known ratio: (a) 30% illite–70% smectite and (b) 43% illite - 57% smectite. The suspensions of the mixed clays were prepared at approximately 0.5 g L^{-1}.

2.4. Sorption experiments

The experiments were carried out under atmospheric conditions. Suspensions of both clays at various ionic strengths were used for the experiments (from 1×10^{-3} to 0.5 M in $NaClO_4$). For the samples with a pH from 5.5 to 10, buffer solutions were used to maintain the pH stable over time. The pH was readjusted, if necessary, after the addition of the radionuclide.

We used the following buffer solutions at a concentration of 2×10^{-3} M: 2-(N-morpholino) ethane-sulphonic acid (MES, pH 5.5–6.5); 3-(N-morpholino) propanesulphonic acid (MPS, pH 6.8–7.7); Tris(hydroxymetil)aminomethane (TRIS, pH 7.5–8.5); and 3-(cyclohexyl amino)ethanesulphonic acid (CHES, pH 9.0–10.0). Prior to the sorption experiments, several tests were carried out at various buffer concentrations. With the buffer concentration ranging from 1×10^{-3} to 1×10^{-2} M, the K_d values remained the same. We concluded that using the buffer—in a concentration below 10^{-2} M—would not affect selenite sorption.

Measurements of pH were made using a combined glass pH electrode (Metrohm) that incorporated an Ag/AgCl reference electrode. The electrode was calibrated using buffer solutions (Scharlau) at pH 4.00, 7.00, and 10.00.

The kinetics of the sorption process was first investigated to determine the time needed to reach the sorption steady-state. Kinetic tests were carried out at pH 5–6 and an ionic strength of 1×10^{-1} M.

Sorption edges were carried out by varying the pH of the suspensions from approximately pH 3 to 11 with NaOH or HCl 0.1 or 1 M.