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Influence of pH, layer charge location and crystal thickness distribution on U(VI) sorption onto heterogeneous dioctahedral smectite

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HIGHLIGHTS

- The UO_2^{2+} sorption at pH 4 and 6 on heterogeneous smectite structure.
- The cation exchange process is affected by layer charge distribution.
- Surface complexation and cation exchange modelling.
- New binding energy components identified by X-ray photoelectron spectroscopy.

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ABSTRACT

The UO_2^{2+} adsorption on smectite (samples BA1, PS2 and PS3) with a heterogeneous structure was investigated at pH 4 ($I = 0.02$ M) and pH 6 ($I = 0.2$ M) in batch experiments, with the aim to evaluate the influence of pH, layer charge location and crystal thickness distribution. Mean crystal thickness distribution of smectite crystallite used in sorption experiments range from 4.8 nm (sample PS2), to 5.1 nm (sample PS3) and, to 7.4 nm (sample BA1). Smaller crystallites have higher total surface area and sorption capacity. Octahedral charge location favor higher sorption capacity. The sorption isotherms of Freundlich, Langmuir and SIPS were used to model the sorption experiments. The surface complexation and cation exchange reactions were modeled using PHREEQC-code to describe the UO_2^{2+} sorption on smectite. The amount of UO_2^{2+} adsorbed on smectite samples decreased significantly at pH 6 and higher ionic strength, where the sorption mechanism was restricted to the edge sites of smectite. Two binding energy components at 380.8 ± 0.3 and 382.2 ± 0.3 eV, assigned to hydrated UO_2^{2+} adsorbed by cation exchange and by inner-sphere complexation on the external sites at pH 4, were identified after the $U4f_{7/2}$ peak deconvolution by X-photoelectron spectroscopy. Also, two new binding energy components at 380.3 ± 0.3 and 381.8 ± 0.3 eV assigned to $\equiv AlOUO_2^+$ and $\equiv SiOUO_2^+$ surface species were observed at pH 6.

1. Introduction

Smectite clay is widely used as “buffer” barrier in engineered radioactive waste containment systems, owing to their low permeability and high sorption capacity [1]. The performance of the engineering barrier in a high-level waste repository is highly affected by structural changes caused by alteration of the original smectite [2,3]. The effect of temperature is reflected by increase of smectite surface charge, induced by silica for aluminium substitution in the tetrahedral sheet, affecting also the cation exchange capacity (CEC) and their swelling properties [4–8].

Long-term smectite stability after waste emplacement is low because buffer material will be exposed to a maximum temperature of 150 °C at the surface of the waste package, pressure in the range of 100–300 bars and groundwaters of various compositions depending to the geological environment [9]. Detailed studies of the reactivity of dioctahedral smectite have shown that the hydrothermal conditions imply the formation of high- and low-charge layers

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in different proportions on smectite [10] and the progressive formation of illite-montmorillonite mixed layers [11,12].

Uranium (U) occurs as uranyl (UO_2^{2+}) ions under oxidizing geochemical conditions and acidic aqueous solutions, forming monomers, dimers, and trimers at higher pH hydrolyses [13]. The pH dependent adsorption behaviour under these conditions is similar to other metal oxides with a cationic adsorption on edge sites at pH 5–6 and an additional anionic adsorption on edge sites around pH 8 in systems equilibrated with atmospheric CO_2 [14]. Despite the importance of this mechanism, there is a limited knowledge about the interactions between UO_2^{2+} ions and clay mineral surfaces [15]. The interaction of UO_2^{2+} ions with clay minerals as potential adsorbent materials with high surface area were carried out with montmorillonite [14,16–28], tri-smectite [29–31] or bentonite rocks [32].

Uranyl sorption onto smectite involves multiple binding sites, including ion exchange and edge surface sites. Previous works reported that the adsorption of UO_2^{2+} on smectite follows two main mechanisms: ion-exchange through outer-sphere complexation at low pH and low ionic strength, whereas at near-neutral pH and high ionic strength through inner-sphere complexation on the edge sites controls the sorption mechanism [14,18,26,29,31,33,34].

The development of surface complexation models (SCM) predicts the behavior of uranyl sorption on different clay minerals by fitting the thermodynamic data obtained from reference methods under different environmental conditions [35–37]. The use of a "unique model" was developed to defend the standardization of SCM using thermodynamic approaches and parameter optimization in order to achieve the best fit to the experimental sorption data [22,37–39]. In this way, it was possible to reduce the number of adjustable parameters and provide a set of uniform parameters based on common reference values.

The main aim of this study is to understand the degree of interaction between UO_2^{2+} and dioctahedral smectite with a heterogeneous structure as a function of layer charge location and the type of interstratified layers, in order to predict the possible changes on sorption mechanism caused by structural modification of smectite during alteration. The heterogeneous smectite structure used in sorption experiments represents in fact the first alteration stage of smectite exposed to circulation of hydrothermal fluids or as backfilling materials in nuclear waste disposal [2].

The kinetic of sorption-desorption experiments of the UO_2^{2+} retardation onto heterogeneous smectite samples using a continuous stirred tank reactor was previously interpreted by the reaction-controlled model (pseudo-first order and pseudo-second order) and diffusion-controlled model (intra-particle diffusion and liquid-film diffusion) [40]. The adsorption experiments in this work were carried out to evaluate the role of pH, charge location and the crystal thickness distribution of smectite on the UO_2^{2+} sorption mechanism. The pH variation influences the UO_2^{2+} aqueous speciation defining the species involved during the sorption mechanism. Also, it may play an important role in the surface sites distribution, controlling the adsorption capacity and the binding strength of surface complexes. The adsorption process on different smectite samples was simulated using the cation exchange and surface complexation model based on diffuse double layer (DDL) [41]. The UO_2^{2+} surface species adsorbed on smectite at pH 4 and pH 6 were also identified by X-ray photoelectron spectroscopy (XPS) experiments.

2. Experimental

2.1. Batch experiments

Batch experiments were carried out to investigate the UO_2^{2+} adsorption on three different heterogeneous smectites (<2 μm fractions), with a different distribution of charge deficit. The adsorption experiments were carried out at pH 4 and 6, using low (I = 0.02 M) and high ionic strength (I = 0.2 M), in order to promote the study of both sorption mechanisms on smectite surface: ion exchange and inner-sphere complexation on the surface edge sites. Batch experiments performed at pH = 4 were carried out by adding 0.025 g of the respective clay mineral with 14.00 mL (S: L = 1.79 g/L) of different stock solutions at different UO_2^{2+} concentrations, ranged between 1.00×10^{-5} M and 6.50×10^{-4} M, with NaCl (0.02 M). At pH = 6, 0.050 g (S: L = 3.60 g/L) of each smectite was added, and the UO_2^{2+} concentration of stock solutions ranged between 1.00×10^{-6} M and 1.00×10^{-4}M, with NaCl (0.2 M). Suspensions were shaken for 48 h, and then centrifuged, separated and the resulted (supernatant) solutions were preserved by adding HCl and stored at 4 °C for subsequent chemical analysis. Uranyl stock solutions were prepared from a primary standard solution (1.0×10^{-3} M), obtained by dissolving of $UO_2(CH_3COO)_2 \times 2H_2O$ in deionized water. The pH was adjusted to the required value and monitored with NaOH (0.05 M) or HCl (0.05 M) (Merck, Germany), using a pH meter (Corning 240) calibrated with buffer solutions (pH 4, 7 and 10, Merck).

2.2. Isothermal models

The Langmuir model assumes that the sorption sites are identical and energetically equivalent due to its homogeneous structure [42]. The equilibrium is obtained when the monolayer formation on the sorbent occurs. Langmuir isotherm is described according to the following Eq. (1):

$$q_e = \frac{q_m K_L C_e}{(1 + K_L C_e)} \quad (1)$$

where q_e (mol/kg) and C_e (mol/L) are the equilibrium concentrations of UO_2^{2+} in the solid and the liquid phase, respectively, q_m (mol/kg) is the maximum sorption capacity, and K_L (L/kg) is the Langmuir constant related to the energy of adsorption. The q_e is obtained according to Eq. (2):

$$q_e = (C_i - C_f)\frac{V}{m} \quad (2)$$

where C_i and C_f are the concentrations of UO_2^{2+} in the beginning and the end of the adsorption process, V is the solution volume used during batch experiments (14.00 mL) and m is the mass of smectite used.

Freundlich model was used to describe the adsorption of contaminants on heterogeneous surface consisting of sites with different exponential distribution and energies [43,44]. The equation of the Freundlich sorption isotherm is expressed by Eq. (3):

$$q_e = K_F C_e^{\,n} \quad (3)$$

where, K_F and n are the Freundlich adsorption isotherm constants, being indicative of the adsorption extension and the degree of the surface heterogeneity. The Sips isotherm combines both Freundlich and Langmuir isotherms where at low adsorbate concentration behaves as Freundlich isotherm, whereas at high concentration predicts a monolayer adsorption capacity characteristic to Langmuir model [45,46]. The mathematical representation of this model is given by Eq. (4):

$$q_e = \frac{q_m (K_S C_e)^n}{1 + (K_S C_e)^n} \quad (4)$$

where, q_m (mol/kg) is the maximum sorption capacity, which can also be expressed as Nt, a measure of the total number of binding sites available per g of sorbent, K_S is the affinity constant for adsorption (L/kg) and n is the Freundlich parameter that takes into account the system heterogeneity. The Sips isotherm is reduced to