Regular Article

Sorption and redox speciation of plutonium at the illite surface under highly saline conditions

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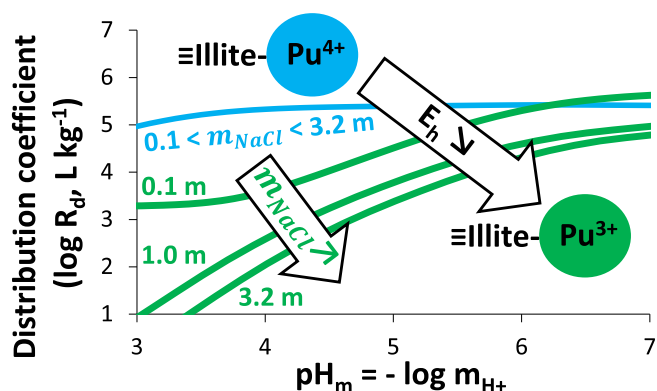
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Natural groundwater may contain high salt concentrations, such as those occurring at several potential deep geological nuclear waste repository sites. Actinide sorption to clays (e.g. illite) under saline conditions has, however, been rarely studied. Furthermore, both illite surface and ionic strength may affect redox speciation of actinides like plutonium. In the present study, Pu sorption to illite is investigated under anaerobic conditions for $3 < pH_m$ ($= -\log m_{H^+}$) < 10 and $m_{NaCl} = 1.0$ and 3.2 molal (m). Results are compared with previous data for $m_{NaCl} = 0.1$ m. According to redox potential measurements and based on Eu(III)-illite sorption data (taken as analogue of Pu(III)), the strong effect of m_{NaCl} on overall Pu uptake observed for $pH_m < 6$ is mainly attributed to the presence of Pu(III) and its competition with Na^+ for ion exchange sites. For $pH_m > 6$, overall Pu uptake is largely insensitive to m_{NaCl} due to the prevalence of strongly adsorbed Pu(IV). By applying appropriate corrections to the activity coefficients of dissolved ions and using the 2-site protolysis non-electrostatic surface complexation and cation exchange (2 SPNE SC/CE) model, experimental data on Pu sorption to illite as a function of pH, Eh and m_{NaCl} can be very well reproduced.

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1. Introduction

Only few investigations of actinide uptake on clay minerals have been carried out at elevated ionic strength (I) [1–3]. The majority of investigations pertains to I = 0.1 molal (m) and rarely up to 1.0 m (e.g. [4–6]; and references therein). However, clay rock pore waters as e.g. in the Jurassic and lower Cretaceous clay rock in Northern Germany, discussed as potentially appropriate host rock formations for a final nuclear waste repository, may contain salt contents as high as about 5 m [7]. Sedimentary rocks currently investigated in Canada are in contact with brine solutions up to 6.5 m [8]. Therefore, detailed sorption investigations of radionuclide onto clay materials under saline conditions become necessary. At high salt concentrations, activity coefficients of aqueous species change dramatically and actinide cations may form aqueous complexes with background anions, which can affect actinide speciation (including redox equilibria). But this can in principle be predicted. By contrast, the effect of high ionic strength on mineral (i.e. including clay minerals) surface properties is elusive. Previous studies performed at high ionic strength show that non-electrostatic sorption models are quite suitable to simulate proton and metal ion sorption to naturally occurring surfaces, e.g. marine microalgae or bacteria [9–11]. Recently, Eu(III) sorption to illite and smectite was investigated in $0.1 < m_{NaCl} < 3.9$ m [3]. The experimental results could be described by the 2 site protolysis non-electrostatic surface complexation and cation exchange (2 SPNE SC/CE) model [5,6] coupled to the specific ion interaction theory (SIT [12]) or the Pitzer formalism [13], to account for activity coefficients of solutes in concentrated media.

Compared to Eu(III), the complex redox chemistry of Pu adds another dimension to sorption studies. Pu occurs in the oxidation states +III, +IV, +V or +VI and its geochemical behavior, such as solubility and mobility, strongly depends on its redox state [14,15]. Under reducing conditions, Pu(IV) and Pu(III) prevail [16–20]. However, Pu(III) sorption to minerals has rarely been studied separately as it is usually accompanied by Pu(IV). It has been shown, that the overall uptake of redox sensitive actinides and their redox speciation at mineral surfaces can be estimated by taking into account the uptake of the individual redox states and the measured redox potentials, i.e. the (apparent) electron activity, or pe [21,22]. Using the 2 SPNE SC/CE model, previous work demonstrated the applicability of the approach to describe Pu uptake on illite under anaerobic conditions in 0.1 m NaCl, where the Pu(IV)/Pu(III) redox couple was involved [23]. Here, the approach is extended to Pu sorption and redox speciation in contact with illite under saline conditions (up to 3.2 m NaCl). While there is no study dedicated to tetravalent actinide sorption to illite at such high ionic strength, Eu(III) sorption to illite (often studied as chemical analogue of Pu (III)) is affected by NaCl concentration [3]. Therefore, Pu sorption and Pu(IV)/Pu(III) redox equilibria at the illite surface are expected to be affected by the ionic strength.

2. Materials and methods

Chemicals (all pro analytical quality or better) were obtained from Merck (Darmstadt, Germany) or Riedel de Haen (Seelze, Germany). Solutions were prepared with de-ionized "MilliQ" water (specific resistivity, 18.2 MΩ cm^{-1}). The purified Na-illite was provided within the EC project CP CatClay. The source material derives from lacustrine continental sediments deposited at the Upper Eocene (∼−35 Ma) in the basin of Le Puy en Velay (Massif Central, France). The purification procedures and the characterization of the purified illite (<63 μm) were previously detailed [21], and will not be repeated here. Note that in the last step of the purification, the clay suspension was freeze dried, to exclude bacterial activity.

2.1. Plutonium and Europium stock solutions

A ^{238}Pu stock solution was prepared from an available Pu solution dissolved in nitric acid, which was fumed three times by 0.1 M HClO$_4$, in order to remove all impurities and organic traces. The concentration of the Pu stock solution was 3.9×10^{-5} M in 0.1 M HClO$_4$. From this, a more dilute solution ([Pu] = 1.9×10^{-6} M) in 0.1 M HClO$_4$ was prepared for experiments at low Pu(IV) concentration. The diluted ^{238}Pu stock solution contained 85% Pu(IV), 11% Pu(V) and 4% Pu(III), as determined by liquid-extraction methods [23]. Aqueous ^{238}Pu concentrations were determined by liquid scintillation counting (LSC) using the scintillation cocktail Ultima Gold XR with a liquid scintillation analyzer (Tri-Carb 3110TR). In addition, the stock solution of ^{238}Pu was checked by ICP-MS and the results were in excellent agreement with LSC measurements.

Eu(III) was used in some experiments as a chemical analogue of Pu(III). A radiotracer solution was purchased from Amersham International (total Eu concentration: 6.0×10^{-4} M) with isotopic composition ^{151}Eu (83%), ^{152}Eu (13%, t$_{1/2}$ = 13.33a) and ^{153}Eu (4%). ^{152}Eu is a β-, γ-emitter and can be conveniently analyzed by γ-counting. In the present study, precise determination of dissolved ^{152}Eu was performed using a Perkin Elmer Wallac gamma counter (Wizard 1480).

2.2. Determination of pH and Eh

The pH in the clay suspensions was measured by an Orion 525A (pH meter) and a Ross electrode calibrated with 4 standard buffers (pH 3, 5, 7, and 9; Merck). The error in pH measurements is ±0.05. For pH measurements in highly saline conditions (I > 0.1 m) a correction term is applied to the measured operational pH-values (pH$_{exp}$). The molal proton concentration, i.e. $-\log m_{H^+}$ (pH$_m$), was obtained involving an empirical correction coefficient (A$_{NaCl}$) according to Eqs. (1) and (2):

$$pH_m = pH_{exp} + A_{NaCl} \tag{1}$$

$$A_{NaCl} = 0.0013 * (m_{NaCl})^2 + 0.1715 * m_{NaCl} - 0.0988 \tag{2}$$

A$_{NaCl}$ depends on background electrolyte composition and concentration and has been accurately determined for NaCl solutions for the electrodes we use [24]. m_{NaCl} is the molality (mol kg^{-1}) of the background electrolyte.

The redox potentials in the clay suspensions were measured using an Orion 525A (E$_h$ meter) and a Pt electrode combined with a Ag/AgCl reference system (Metrohm). Raw data were converted into Eh vs. standard hydrogen electrode (SHE) by correcting for the potential of the reference electrode. Eh was converted to the negative logarithm of the apparent electron activity, pe = $-\log a_{e^-}$ = $16.9 \times$ Eh(V) at 25 °C. A commercial redox-buffer (220 mV, Schott instruments) was used for calibration. An equilibration time of 15 min was allowed for all Eh measurements, after having stirred the suspension. Uncertainties in Eh measurements are ±50 mV (±0.8 for pe-scale) [20,25]. Unlike for the measurement of pH, to our knowledge, there is no ionic strength dependent correction to apply to the experimental Eh with the presently used set-up.

2.3. Batch sorption experiments

All sorption studies were performed as batch type experiments. The procedure is the same as in our previous work dedicated to m_{NaCl} = 0.1 m [23]. The effect of pH$_m$ was investigated at an initial Pu concentration ([Pu]$_{tot}$) of 8×10^{-11} M in 3.2 m NaCl. In addition, the effect of [Pu]$_{tot}$ was investigated for m_{NaCl} = 1.0 and 3.2 m, 8×10^{-11} < [Pu]$_{tot}$ < 10^{-8} M and pH$_m$ ≈ 4.5, 6 and 9.5. Batch experiments were carried out in 40 mL polypropylene centrifuge tubes at room temperature in an argon glove box (<1 ppm O$_2$, absence