



Neptunium sorption and redox speciation at the illite surface under highly saline conditions

Nidhu Lal Banik¹, Rémi Marsac^{*}, Johannes Lützenkirchen, Christian Michael Marquardt, Kathy Dardenne, Joerg Rothe, Kerstin Bender, Horst Geckeis

Institut für Nukleare Entsorgung, Karlsruhe Institute of Technology, P.O. Box 3640, D-76021 Karlsruhe, Germany

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Abstract

Neptunium (Np) uptake on illite is investigated in 1 and 3.2 molal (m) NaCl solutions under inert (Ar) atmosphere for $4 < \text{pH}_m < 10$ ($\text{pH}_m = -\log m_{H^+}$) and $5 \times 10^{-8} < [\text{Np(V)}]_{\text{tot}} < 3 \times 10^{-4}$ M. In agreement with a previous study in 0.1 m NaCl solutions (Marsac et al., 2015a), Np(V) is the prevailing oxidation state in the aqueous solution, but Np uptake by illite is affected by surface induced reduction. The extent of Np(V) reduction to Np(IV) follows the measured redox potential (or the $\text{pe} = -\log a_{e^-}$), which is influenced by the introduced Np(V) amount, because of the low redox capacity of the illite. The presence of Np(IV) on the solid phase is verified by X-ray Absorption Near Edge Spectroscopy (XANES). We can conclude that Np uptake by illite is not significantly affected by the variation of m_{NaCl} from 0.1 to 3.2 m and thus is in agreement with reports on tetravalent actinide and Np(V) sorption to clays at high ionic strength. The combination of (i) the two site protolysis non-electrostatic surface complexation and cation exchange model, (ii) the specific ion interaction theory to calculate activity coefficients for dissolved species and (iii) by accounting for redox equilibria and the stability of surface Np species, the overall Np uptake by illite can be simulated as a function of pH_m , pe and m_{NaCl} using a single set of parameters. The present experimental and modeling results are particularly important in the context of deep geological nuclear waste disposal since many sedimentary rocks or clay formations that are deemed suitable for this purpose exhibit highly saline porewaters. © 2017 Elsevier Ltd. All rights reserved.

Keywords: Neptunium; Illite; Redox; Saline; High ionic strength; Surface complexation; Spectroscopy; Geochemical modeling

1. INTRODUCTION

The final disposal in deep geologic formations is considered the most appropriate strategy to isolate high level nuclear waste (HLW) from the biosphere (e.g. OECD/

NEA, 2008). Sedimentary clay rock formations are potential host rocks for HLW in several European countries encompassing Opalinus Clay (OPA) in Switzerland (Nagra, 2002), Boom and Ypresian clays in Belgium (Ondraf, 2001), Callovo-Oxfordian (COx) clays in France (Andra, 2005) or Boda Claystone in Hungary (Lázár and Máthé, 2012). Indeed, clays exhibit low permeability, large surface areas and pronounced sorption capacity for many relevant radionuclides via ion exchange reactions as well as surface complexation to silanol and/or aluminol groups at the edges of clay particles. Illite and smectite are the most important components of the proposed claystone host rocks and may amount to about 50 wt.% of the material

^{*} Corresponding author at: Géosciences Rennes UMR 6118, Université Rennes 1, CNRS, 35042 Rennes cedex, France. Fax: +33 2 23 23 60 90.

E-mail address: remi.marsac@univ-rennes1.fr (R. Marsac).

¹ JRC-KARLSRUHE, G.II.6 – Nuclear Safeguards and Forensics, European Commission, P.O. Box 2340, D-76125 Karlsruhe, Germany.

(Lauber et al., 2000; Gaucher et al., 2004; Bradbury and Baeyens, 2011; Pearson et al., 2011; Chen et al., 2014). Although actinide sorption to clays has been extensively studied (e.g. Bradbury and Baeyens, 2005; Bradbury and Baeyens, 2009a,b; and references therein), the underlying mechanisms were rarely investigated for ionic strengths above 0.1 M. While OPA and COx porewaters exhibit ionic strengths of 0.3–0.4 M, clay rock pore waters as e.g. in the Jurassic and lower Cretaceous clay rock in Northern Germany, which are also discussed as potentially appropriate host rock formations, may contain salt contents as high as about 5 M (Brewitz, 1980). Sedimentary rocks currently investigated in Canada are even in contact with brine solutions up to 6.5 M (Fritz and Frape, 1982). Therefore, detailed sorption investigations and the development of geochemical models that can predict actinide sorption and speciation in concentrated brine solutions are required (Vilks, 2011).

Neptunium (Np) is a minor constituent of high level radioactive waste. Yet, its environmental chemistry is of considerable interest due to the long half-life of its main isotope ^{237}Np ($t_{1/2} = 2 \times 10^6$ a) and the high solubility and mobility of its pentavalent state (NpO_2^+) under oxidizing conditions. Np is redox sensitive and its most relevant oxidation states in the geosphere are the penta- and tetravalent states (Kim, 1986). Both redox states show drastically different geochemical behavior concerning, for instance, complexation by organic and inorganic ligands, solubility, as well as sorption to minerals (e.g. Altmaier et al., 2013). Under reducing conditions, Np(IV) prevails and is considered rather immobile because of its strong sorption to minerals and its low solubility, as other tetravalent actinides (An; e.g. Th(IV)) or other tetravalent elements (e.g. Sn(IV)) (Bradbury and Baeyens, 2009a,b). Under oxidizing conditions, Np(V) prevails, which weakly sorbs to minerals and is regarded as rather mobile (e.g. Geckeis et al., 2013). However, partial reduction of Np(V) to Np(IV) when in contact with Opalinus Clay was suggested by comparing sorption data obtained under aerobic and anaerobic conditions: stronger Np sorption (Fröhlich et al., 2011) was found under anaerobic conditions and significant reduction to Np(IV) was observed using synchrotron based spectroscopic techniques (Fröhlich et al., 2012). A more recent Np-illite batch sorption study under oxygen-free argon atmosphere in 0.1 M NaCl showed that the strongly adsorbing Np(IV) is thermodynamically favored at a mineral surface compared to Np(V) (Marsac et al., 2015a). Although Np(V) prevailed in aqueous solution at $\text{pH} \approx 7$, as evidenced by liquid-liquid extraction method and by capillary electrophoresis hyphenated to inductively coupled plasma mass spectrometry (Graser et al., 2015), Np(IV) was observed at the illite surface by X-ray absorption near edge structure spectroscopy (XANES). When accounting for the uptake of both Np(V) and Np(IV) on illite and the redox potential of the illite suspension, Marsac et al. (2015a) were able to describe the overall Np uptake on illite for various redox conditions. The modeling approach was subsequently extended to the sorption behavior of plutonium, which exhibits an even more complex redox chemistry than Np. Pu can be found in the redox states +III

to +VI under environmental conditions. The experimentally determined overall Pu uptake on kaolinite (Marsac et al., 2015b) and illite (Banik et al., 2016) in 0.1 M NaCl/ ClO_4 was successfully reproduced.

The above cited studies focused on aqueous solutions of low ionic strength. At high salt concentrations, activity coefficients of aqueous species change dramatically, whereas the effect of high ionic strengths on the surface properties of adsorbents and surface species is elusive. Previous work showed that non-electrostatic models are quite suitable to predict proton and metal ion sorption at high ionic strength to naturally occurring matrices that bear surface functional groups that are affected by pH and can be treated by the same formalism and with similar numerical models. This includes marine microalgae (Schijf and Ebling, 2010; Zoll and Schijf, 2012) or bacteria (Ams et al., 2013). Eu(III) sorption to illite and smectite was investigated experimentally in $0.1 < m_{\text{NaCl}} < 3.9$ molal (m) (Schnurr et al., 2015). The results obtained in the latter study showed that the 2 site protolysis non-electrostatic surface complexation and cation exchange (2 SPNE SC/CE) model coupled to either the specific ion interaction theory (SIT; Ciavatta, 1980) or the Pitzer formalism (Pitzer, 1991) to account for activity coefficients in concentrated media was able to reproduce sorption data also at elevated ionic strength. By using the modeling approach of Schnurr et al. (2015), the Pu-illite study in 0.1 M NaCl of Banik et al. (2016) was extended to high ionic strength ($0.1 < m_{\text{NaCl}} < 3.2$ m; Marsac et al., 2017). In the latter studies, the Pu(IV)/Pu(III) is involved. The present study is a similar extension of the work of Marsac et al. (2015a) on Np uptake on illite in 0.1 M NaCl to highly saline conditions (up to $m_{\text{NaCl}} = 3.2$ m), but here a An(V)/An(IV) couple is involved. Together, the work of Marsac et al. (2017) and the present one should elucidate the actinide (III, IV, V) sorption and redox speciation at the illite surface under highly saline conditions. Classical batch experiments at various pH, total Np concentrations and $m_{\text{NaCl}} = 1.0$ and 3.2 m were performed, and the redox potential was monitored. XANES was applied to determine the Np redox state at the illite surface. The coupling of the 2 SPNE SC/CE model with SIT was used to describe Np sorption and redox speciation on illite under saline conditions.

2. MATERIALS AND METHODS

All chemicals were of pro analytical quality or better and were obtained from Merck (Darmstadt, Germany) or Riedel de Haen (Seelze, Germany). Experiments were conducted with de-ionized “MilliQ” water (specific resistivity, 18.2 $\text{M}\Omega\text{ cm}$). 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 ($< 63 \mu\text{m}$) were previously described in detail (Marsac et al., 2015a). Concerning redox processes, it is noted that the iron content is 0.88 mol Fe per kg of illite (Marsac et al., 2015a). The

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