



Neptunium redox speciation at the illite surface

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Abstract

Neptunium (Np(V)) sorption onto a purified illite is investigated as a function of pH (3–10) and $[\text{Np}^{\text{V}}\text{O}_2^+]_{\text{tot}}$ (3×10^{-8} – 3×10^{-4} M) in 0.1 M NaCl under Ar atmosphere. After about one week reaction time, only insignificant variation of Np sorption is observed and the establishment of reaction equilibrium can be assumed. Surprisingly, solid–liquid distribution ratios (R_d) are clearly higher than those measured for Np(V) sorption onto illite under aerobic conditions. The observation that R_d increases with decreasing pe ($\text{pe} = -\log a_{e^-}$) suggests partial reduction to Np(IV), although measured redox potentials (pe values) at a first glance suggest the predominance of Np(V). Reduction to Np(IV) at the illite surface could indeed be confirmed by X-ray absorption near-edge spectroscopy (XANES). Np speciation in presence of the purified Na-illite under given conditions is consistently described by applying the 2 sites protolysis non-electrostatic surface complexation and cation exchange model. Measured pe data are taken to calculate Np redox state and surface complexation constants for Np(IV) are derived by applying a data fitting procedure. Constants are very consistent with results obtained by applying an existing linear free energy relationship (LFER). Taking Np(IV) surface complexation constants into account shifts the calculated Np(V)/Np(IV) redox borderline in presence of illite surfaces by 3–5 pe units (0.2–0.3 V) towards redox neutral conditions. Our study suggests that Np(V) reduction in presence of a sorbing mineral phase is thermodynamically favored.
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1. INTRODUCTION

Neptunium (Np) is only a minor constituent of high level radioactive waste. Its environmental chemistry is still of considerable interest due to the long half-life of its main isotope ^{237}Np ($t_{1/2} = 2 \times 10^6$ a) and its high solubility and mobility as pentavalent $\text{Np(V)}\text{O}_2^+$ under oxidizing conditions. In general, Np can exist in oxidation states between +III and +VII in aqueous solution, but penta- and tetravalent Np are the most relevant oxidation states in

the geosphere (Kim, 1986). NpO_2^+ only weakly sorbs to mineral surfaces and is therefore regarded as rather mobile (Geckeis et al., 2013). Under reducing conditions, Np(IV) prevails and is considered as rather immobile because of its strong sorption to minerals and due to 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).

Clay minerals are main components in sedimentary rocks, which are considered as potential host rocks for radioactive waste disposal (e.g. Callovo-Oxfordian mudstone, France; Opalinus Clay) (Claret et al., 2005; Latrille et al., 2006; Wu et al., 2009). Their high sorption capacity for cations via ion exchange reactions as well as surface

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complexation to silanol or aluminol groups at the edge of clay particles have a major impact on radionuclide and metal ion retention. Np sorption onto purified clay minerals has mostly been studied under aerobic conditions, where the +V oxidation state is dominant or under inert atmosphere but without monitoring or controlling the redox potential (Gorgeon, 1994; Turner et al., 1998; Amayri et al., 2011). As slightly reducing conditions are frequently found in soil or natural clay rocks, it is mandatory to assess the impact of redox conditions on the behavior of redox active metal ions such as Np. 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 evidenced by applying synchrotron based spectroscopic techniques (Fröhlich et al., 2012). Np(IV) was found associated with pyrite as the main reductant in the natural clay rock.

The oxidation state of the early actinides (Pa, U, Np, Pu) is determined by the redox potential in solution, which in turn is controlled by the balance of redox pairs (see e.g. Altmaier et al., 2013). Establishment of redox equilibria in homogeneous solution may however be slow. For instance, Nakata et al. (2002) observed almost no Np(V) reduction by dissolved Fe(II) after one week. By contrast, reactions with redox active solid phases are usually found to proceed fast (Stumm, 1992; Buerge and Hug, 1999; Liger et al., 1999; Nakata et al., 2002; Charlet et al., 2007; Bach et al., 2014). Notably for reactions with Pu(V) with mineral surfaces rapid reduction to Pu(IV) is stated (Powell et al., 2004, 2005; Hixon et al., 2010; Kirsch et al., 2011; Zaravin et al., 2012). The time necessary for a complete Pu(V) reduction varies from few hours to few days depending on the mineral. Spectroscopic and microscopic examination very often reveal that reduced Pu(IV) species are predominantly found at the mineral surface, thus implying surface mediated reduction being the relevant reaction mechanism. Reduction is, however, also found at mineral surfaces where a specific reducing partner is absent (Hixon et al., 2013), suggesting that Pu(IV) under given conditions simply is the thermodynamically favored species. Zaravin et al. (2012) studied Np(V) sorption onto montmorillonite under the same conditions as for Pu(V), but did not observe Np(V) reduction. This observation can be explained by the fact that the standard redox potential of the Np(V)/Np(IV) couple ($E_{\text{NpO}_2^+/ \text{Np}^{4+}}^0 = 0.604 \text{ V}$) is lower than that of the Pu(V)/Pu(IV) pair $E_{\text{PuO}_2^+/ \text{Pu}^{4+}} = 1.031 \text{ V}$ (Guillaumont et al., 2003). Therefore, reduction of Np(V) to Np(IV) in presence of montmorillonite surfaces under given conditions apparently is not thermodynamically favorable.

Only a few attempts are reported in the literature to describe actinide redox reactions in presence of minerals quantitatively by applying mechanistic surface complexation models. Such thermodynamic models are particularly relevant and required for a comprehensive prediction of actinide behavior in natural systems. Degueldre and Bolek (2009) discussed Pu sorption to Al_2O_3 , FeOOH and SiO_2 colloids based on a simple R_d approach. Their

calculations included the effect of the redox potential, which was shown to have a major impact on calculated Pu uptake data. Schwantes and Santschi (2010) proposed a surface complexation model involving all Pu redox states (from +III to +VI) to minerals and a reversible surface mediated Pu(V)–Pu(IV) reaction to explain the observed kinetics of Pu uptake. Experimentally determined redox potential (pe; Eh) or $\text{O}_{2(\text{g})}$ partial pressures are essential for the application of surface complexation models to describe sorption behavior of redox sensitive elements. However, in most studies mentioned above, such data are not provided, very often due to difficulties associated with their experimental determination (Schüring et al., 2000; Altmaier et al., 2010).

The present study is dedicated to NpO_2^+ sorption to a purified clay mineral (illite) under inert gas atmosphere (Argon) in order to exclude the influence of atmospheric CO_2 . Classical batch experiments at various pH, total Np concentrations and reaction times are performed and compared with literature data for the uptake of various metal ions onto illite. Different to many other similar studies a special focus is dedicated to monitor redox conditions. X-ray absorption near edge structure spectroscopy (XANES) is applied to determine the Np redox state at the illite surface. Finally, an attempt is made to consistently describe Np sorption and redox speciation using surface complexation modeling.

2. MATERIALS AND METHODS

All chemicals are of pro analytical quality or better and were obtained from Merck (Darmstadt, Germany) or Riedel de Haen (Seelze, Germany). All experiments were conducted with de-ionized “MilliQ” water (specific resistivity, $18.2 \text{ M}\Omega \text{ cm}^{-1}$). The aqueous concentration of ^{237}Np was analyzed using LSC with a TriCarb 3100 (Beckman/PerkinElmer) and the scintillation cocktail Ultima Gold XR (Packard Instruments Co., USA). To differentiate between the alpha decay of the ^{237}Np and the beta decay of its daughter ^{233}Pa , the measurements have been performed in an alpha–beta discrimination mode applying a Pulse Decay Analysis (PDA), a form of pulse shape analysis, to perform differentiation of alpha and beta events. PDA uses a time based Pulse Decay Discriminator (PDD) to evaluate the pulse duration of scintillation events and categorize the events as either alpha or beta. A discriminator (146) setting was used to reduce the beta spillover to 1.50%. ^{237}Np counting efficiencies for each sample were determined using a ^{237}Np quenching curve. Each sample was counted for a total of 0.5 h. Since we used a constant background electrolyte (0.1 M NaCl), the Quench Indicating Parameter (QIP) tSIE – fixed to 470 – does not change significantly (± 10) during the LSC measurements. Details about the LSC measurement are given in the [supplementary information](#). In addition, the stock solution of ^{237}Np and aqueous concentration of ^{237}Np in the batch sorption experiment after phase separation were also checked at random by ICP-MS measurements and the results are in good agreement with LSC measurements.

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