SORPTION OF NEPTUNIUM ON CLAYS AND CLAY MINERALS − A REVIEW

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Abstract—During recent decades, the search for possible repositories for high-level nuclear waste has yielded large amounts of sorption data for actinides on different minerals. Clays and clay minerals are of special interest as potential host-rock formations and backfill materials, by virtue of their good retardation properties. Neptunium (Np) is one of the actinides which is considered in long-term scenarios due to its long-lived nuclide ^{237}Np ($t_{1/2} = 2.1 \times 10^6$ y). Because neptunium sorption is heavily dependent on the experimental conditions, comparison of sorption data from different experiments is challenging. Normalizing reported data with respect to the surface area of the sorbent enables conversion of conventional distribution coefficients (K_d) to normalized (K_a) values, which improves comparability among the results of different experiments. The present review gives a detailed summary of sorption data of Np on clays and clay minerals and examines critically the applicability of the K_a approach.

Key Words—Clay, Neptunium, Nuclear Waste Disposal, Sorption.

BACKGROUND

Introduction

During recent decades, much scientific effort has been expended in the investigation of potential host-rock formations and backfill materials for high-level nuclear waste. The different possible geologic formations considered and studied as potential repository host-rocks include salt rock, crystalline formations (*e.g.* granite), and clay rocks. Clay-rich sedimentary rocks are being considered in various European countries (*i.e.* Belgium, France, Germany, and Switzerland). Additionally, clay minerals are a major component of bentonite, a potential backfill material.

The large sorption capacity of clays and clay minerals for heavy metals enables strong retardation and attenuated mobilization of radiogenic nuclides. Radionuclides of interest in high-level nuclear waste include relevant short-lived fission products (*e.g.* ^{90}Sr ($t_{1/2} = 28.9$ y), ^{137}Cs ($t_{1/2} = 30.08$ y)), which will determine the radiotoxicity of the waste during the first centuries after waste emplacement in the repository; uranium, the most abundant radioelement in spent fuel; and the long-lived transuranium elements (Np, Pu, Am) with half-lives in the range of thousands (*e.g.* ^{243}Am ($t_{1/2} = 7370$ y), ^{242}Pu ($t_{1/2} = 3.8 \times 10^5$ y)) to millions of years (*e.g.* ^{237}Np ($t_{1/2} = 2.1 \times 10^6$ y)), which will determine the radiotoxicity >1000 y after waste emplacement. The mobility of these actinides is very important for any long-term forecast and safety assessment. Another concern is the possible release of the stored radionuclides from their pre-emplacement containment. In this case, the actinides may interact with the backfill material, the surrounding

host rock, and the aquifer (*e.g.* the porewater of the clay). The retardation of neptunium and the other actinides will be determined by geochemical processes, including sorption, diffusion, solubility, and complexation reactions with various inorganic and organic ligands present in the aquifer. These processes depend heavily on the geochemical conditions in the repository (*i.e.* pH, Eh, ionic strength, partial pressure of CO_2, inorganic and organic content in the aquifer, *etc.*).

The long-lived nuclide ^{237}Np ($t_{1/2} = 2.1 \times 10^6$ y) is of special interest. Published studies have examined the sorption of neptunium on either 'pure' clay minerals (*e.g.* kaolinite, montmorillonite, *etc.*) containing only traces of other minerals, natural clay rocks containing larger amounts of other (non-clay) mineral phases (*e.g.* Opalinus Clay, Callovo-Oxfordian, Boom Clay *etc.*), or synthetic mixtures. These investigations range from simple batch sorption experiments to sensitive spectroscopic speciation techniques. The batch sorption experiments are more common, mainly investigating the effects of different experimental conditions (pH, ionic strength, aerobic/anaerobic conditions, *etc.*) on the extent of neptunium sorption and determining distribution coefficients. To characterize the sorbed surface species specifically, synchrotron-based techniques have been used, mostly X-ray absorption fine structure spectroscopy (XAFS).

Sorption mechanisms and modeling approaches of actinide sorption on minerals in general have been the topic of a recent review article (Geckeis *et al.*, 2013). The present review focuses on the effects of different system parameters on the sorption of neptunium onto clay minerals; a critical discussion of the different methods to describe and quantify these effects; and speciation studies characterizing the related surface species.

QUANTIFICATION OF SORPTION

The sorption of transuranium elements and heavy metals in general is commonly quantified by using distribution coefficients. Sorption is determined mainly in batch experiments; the radionuclide concentration sorbed on the mineral is divided by concentration remaining in solution, resulting in the K_d value:

$$K_d = C_{solid}/C_{liquid} \qquad (1)$$

where C_{solid} (mol/kg sorbent) is the radionuclide concentration sorbed to the mineral and C_{liquid} (mol/L) is the concentration remaining in the liquid phase. Note that the resulting distribution coefficient (L/kg) is a bulk parameter meaning that it represents an average value not taking into account differences in sorption sites, uptake mechanisms, or mineral phases (in the case of soils or other mixtures of different sorbents). Furthermore, the physical characteristics (*e.g.* particle size) of the solid influence the K_d value significantly. As a consequence, comparison of K_d values of different minerals having different surface properties is difficult. Normalizing distribution coefficients with respect to the specific surface area (SSA) of the sorbent (*e.g.* Payne *et al.*, 2011) allows us to take into account the fact that sorption reactions are surface processes. The resulting K_a value (L/m^2) is calculated following equation 2:

$$K_a = K_d/SSA \qquad (2)$$

This approach has not attracted much attention, however, and most sorption studies continue to report K_d values. Normalized distribution coefficients (K_a) for the uptake of U(VI) by various sorbents under the same experimental conditions were shown (Payne *et al.*, 2011) to agree more closely than the related K_d values. This approach might also enable the estimation of distribution coefficients for complicated sorbents (*e.g.* soils or natural clays consisting of mixed minerals) using the SSA. The approach will only work, however, if the heavy metal studied does not have a strong affinity for particular sorption sites or mineral constituents, which might be the case at low metal concentrations.

The fact that numerous sorption studies do not provide information regarding the specific surface area of the sorbent used precludes the application of the K_a concept in many cases. At worst, not even K_d values are determined, with sorption values reported only in percentage terms. In these cases, only estimates of K_d can be made using the reported solid-to-liquid ratio and the sorption given in % (often only given graphically). The estimation of the SSA of a poorly characterized mineral is even more difficult. The RES^{3}T database (Brendler *et al.*, 2003) provides a large number of SSA values of various minerals reported in the literature. The best comparisons, however, can be made for data obtained using well characterized reference materials (*e.g.* the Clay Minerals Society Source Clays). The SSA values of the different Source Clays were reported by Van Olphen and Fripiat (1979) and Dogan *et al.* (2006). A selection of SSA values for various clay minerals (kaolinite, illite, and montmorillonite) which have been used in several sorption studies with transuranium elements is given in Table 1.

Clearly, the SSA values of the same mineral can vary significantly depending on the individual physical properties of the different batches. For example, values for illites of different origin differ by about a factor of ten ranging between 16 and 138 m^2/g. Values determined for the same batch of clay appear to agree very well throughout the literature. Data obtained for Source Clays such as the montmorillonite SWy-1 are, thus, easy to compare with each other even without normalizing with respect to the SSA. In contrast, the SSAs of different clays can differ by orders of magnitude which can complicate the comparison of radionuclide sorption. In the case of natural clay rocks (*e.g.* Opalinus Clay, Callovo-Oxfordian, Boom Clay, *etc.*) which include varying amounts of non-clay minerals (*e.g.* calcite, quartz, iron-containing minerals, *etc.*), the challenge is even greater, clearly underlining the need for a critical analysis of reported sorption data.

Geochemistry of neptunium

In the event of water intrusion into the primary storage location of high-level nuclear waste material, the stored radionuclides may be dissolved and released from their containment, as noted above. Before discussing the uptake of these radionuclides by clay minerals, the aqueous geochemistry of neptunium under environmentally relevant conditions must be considered. Depending on the individual characteristics of the potential host-rock formation, multiple oxidation states or different complexation reactions with (in)organic ligands in the pore waters may be relevant. The following brief summary of the most relevant geochemical processes is based on the work of Kim (1986) (if not stated otherwise).

In general, pH values in natural aquatic systems are in the near-neutral range (pH = 5−9). Higher pH values may occur when cement-based backfill materials come into contact with water. The environmentally relevant oxidation states of neptunium are +4 and +5. For nuclear-waste repository conditions +4 will probably be more relevant because of the reducing conditions resulting from corrosion of the steel canisters. For the Opalinus Clay formation (a possible host-rock formation in Switzerland), Bradbury and Baeyens (2003) calculated that +4 will be the dominant oxidation state for Np. Most sorption studies dealing with neptunium, however, concentrate on the pentavalent oxidation state due to the greater mobility compared to Np^{4+} (see below). Although local oxidizing conditions may be possible due to radiolysis of water, the presence of NpO$_2^+$ can be seen as the worst case scenario in most cases (because of its greater mobility).

Table 1. Selection of literature values for SSA values of kaolinite, montmorillonite, and illite of different origins.

Mineral	Origin	SSA (m^2/g)	Reference
Kaolinite	KGa-1 (Georgia, USA)	10.05±0.02	Van Olphen and Fripiat (1979)*
		8.4	Pruett and Webb (1993)
		11.8	Nebelung et al. (2007)
	KGa-1b (Georgia, USA)	11.7	Pruett and Webb (1993)
		13.1	Dogan et al. (2006)
	KGa-2 (Georgia, USA)	23.50±0.06	Van Olphen and Fripiat (1979)*
		21.7	Dogan et al. (2006)
	St. Austell, UK	11.7	Bauer and Berger (1998)
	Iwamoto Mineral Co., Japan	24.5	Niitsu et al. (1997)
		24.5±0.7	Samadfan et al. (2000)
	Nihon Chikagakusha Co. Ltd., Japan	26.4	Ohnuki et al. (2007)
	Nacalai Tesque Inc., Japan	55	Takahashi et al. (2002)
Montmorillonite	STx-1 (Texas, USA)	83.79±0.22	Van Olphen and Fripiat (1979)*
		84	Hartmann et al. (2008a)
	SWy-1 (Wyoming, USA)	31.82±0.22	Van Olphen and Fripiat (1979)*
		30.1	Nebelung et al. (2007)
		31.5±0.17	Begg et al. (2013)
		35	Bruggeman et al. (2012)
		35	Hartmann et al. (2008a)
		32±2	Rabung et al. (2005)
		27.2	Zavarin et al. (2012)
	SWy-2 (Wyoming, USA)	22.7	Dogan et al. (2006)
		32-43	Hartmann et al. (2008b)
		31.5	Benedicto et al. (2014)
	SAz-1 (Arizona, USA)	92±2	Turner et al. (1998)
		97.42±0.58	Van Olphen and Fripiat (1979)*
		65.2	Dogan et al. (2006)
	Milos, Greece	28.4	Hartmann et al. (2008a)
Illite	Silver Hill, Montana, USA	16.4	Bruggeman et al. (2012)
	Du Puy, France	97	Bruggeman et al. (2012)
		138	Hartmann et al. (2011)
		92	Poinssot et al. (1999)
		129	Bradbury and Baeyens (2005)
		132.1	Marsac et al. (2015)
	Rochester, New York, USA	41	Nagasaki et al. (1998)

SSA = specific surface area, *data also available from the website of The Clay Minerals Society (www.clays.org)

The most relevant complexation reactions in aqueous solution over the above-mentioned pH range are hydrolysis and complexation with carbonate. Other inorganic ligands (*e.g.* Cl^-, F^-, HPO_4^{2-}, SO_4^{2-}) play a minor role due to either the lower stability constants of the complexes formed or low ligand concentrations under environmental conditions. Hydrolysis constrains the solubility of the actinides because transuranic oxides/hydroxides are, in general, the least soluble compounds in aquatic systems. Furthermore, the formation of polynuclear and colloidal hydrolysis species must be taken into account. The tendency of the actinides (An) to hydrolyze increases with increasing effective charge of the cation:

$$An^{4+} > AnO_2^{2+} > An^{3+} > AnO_2^+$$
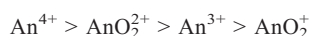
The interaction with carbonate at atmospheric partial pressure of CO_2 dominates at pH > 8. Larger partial pressures are known to occur in deep geological formations, *e.g.* the Opalinus Clay formations in Switzerland (Pearson *et al.*, 2003; Turrero *et al.*, 2006). High carbonate concentrations may lead either to the formation of negatively charged highly mobile actinide species or to precipitation of carbonate or mixed hydroxide-carbonate phases, respectively. A detailed summary of thermodynamic stability constants describing these processes for neptunium can be found in the NEA (Nuclear Energy Agency) thermodynamic database (Lemire *et al.*, 2001; Guillaumont *et al.*, 2003).

In addition to complexation reactions with inorganic ligands in the aquifer, interactions with organic compounds including small carboxylic ligands (*i.e.* formate,

acetate, propionate, lactate, *etc*.) and complex macro-molecules (*e.g.* fulvic and humic acids) may also affect the speciation of the actinides.

Clays and clay minerals

In general, clay minerals can be divided into three groups: 1:1 (*e.g.* kaolinite), 2:1 (*e.g.* smectite, illite) and 2:1:1 (*e.g.* chlorite) minerals. In the first case, one tetrahedral [SiO_4] sheet and one octahedral [$Al(O,OH)_6$] sheet form one (TO) layer. These uncharged TO layers are held together by hydrogen bonds, dipole-dipole interaction, and Van der Waals interaction. In the case of 2:1 clay minerals, two tetrahedral and one octahedral sheets are combined forming a TOT layer. Among the common 2:1 clay minerals, TOT layers are negatively charged due to substitution of tetrahedral or octahedral cations by cations of lower charge. This negative layer charge is neutralized by incorporation of cations between the tetrahedral sheets of adjacent layers. The identity and charge of these cations can strongly affect the uptake of the actinides depending on the experimental conditions. 2:1:1 minerals with layers consisting of two tetrahedral and two octahedral sheets are of lesser importance in the context of nuclear waste disposal, partly because they lack layer charge and partly because they are only present in minor amounts in most clay rocks considered as potential host-rock formations (which consist predominantly of kaolinite and mixed-layer smectite-illite and 'non-clay' components, *e.g.* calcite, quartz, pyrite, siderite, *etc.*). More details on the structure of clays and clay minerals are found elsewhere (*e.g.* Sposito *et al.*, 1999; Brigatti *et al.*, 2006).

REVIEW OF EXISTING LITERATURE

A large number of sorption studies treating the uptake of neptunium by various clays and clay minerals can be found in the literature. The clay minerals investigated range from pure clays (*e.g.* kaolinite, montmorillonite) to highly heterogeneous sorbents consisting of various mineral phases (*e.g.* Opalinus Clay, Boom Clay, *etc.*). In the following, the literature data will be divided into three sections summarizing sorption data of neptunium on: (1) kaolinite; (2) smectite, bentonite, and illite; and (3) natural clays and heterogeneous sorbents based on naturally occurring clays (Opalinus Clay, Boom Clay, *etc.*). Distribution coefficients for the interaction of Np with various clay minerals are summarized (Table 2). For minerals with known SSA values, the related K_a values are calculated also. Unless stated otherwise, the K_a values in Table 2 were calculated using the SSA values reported or cited in the study in which the related experimental data were reported. Many publications present the K_d values graphically only; in these cases, ranges of K_d and K_a are estimated from the related figures.

Kaolinite

Kaolinite is a major component of many natural clays and therefore has been the subject of a number of sorption studies, mostly investigating the sorption characteristics of well defined reference clays as a function of various experimental parameters. The effects of pH, CO_2, ionic strength, NpO_2^+ concentration, solid-to-liquid (s-l) ratio and contact time on the sorption of NpO_2^+ on kaolinite (KGa-1b) have been investigated by Amayri *et al.* (2011). Under ambient air conditions, the sorption of 8×10^{-6} M NpO_2^+ increased with increasing pH reaching a maximum at pH $\approx$ 9, and sorption decreased to almost 0 at pH = 10. The decrease at high pH is related to the formation of negatively charged NpO_2^+-carbonate species ($NpO_2(CO_3)_n^{2n-1}$) which sorb less strongly to a clay surface which is negatively charged at these experimental conditions. In the absence of CO_2, sorption increased continuously. Furthermore, sorption at pH $\geqslant$ 7 on 4 g/L kaolinite increased when decreasing the initial NpO_2^+ concentration from 8×10^{-6} to 7×10^{-12} M. The effect of ionic strength was investigated by using either 0.01 or 0.1 M $NaClO_4$ solution as the background electrolyte. In the absence of atmospheric CO_2, no visible effect of ionic strength was observed; in the presence of ambient CO_2, sorption increased with increasing ionic strength. The K_d values were determined at pH = 9 by varying either the initial NpO_2^+ concentration or the s-l ratio. Sorption and desorption experiments as a function of time revealed that NpO_2^+ sorption on kaolinite is fast and reversible.

The same trend for pH dependence and influence of CO_2 was observed by Reich *et al.* (2007), Dierking *et al.* (2008), and Schmeide and Bernhard (2010), using the same batch of clay. As in the work of Amayri *et al.* (2011), Schmeide and Bernhard (2010) observed an increase in NpO_2^+ sorption with increasing ionic strength (0.01 and 0.1 M $NaClO_4$ solution) and decreasing NpO_2^+ concentration (1×10^{-5} and 1×10^{-6} M). Furthermore, the effect of humic acid (HA) was investigated. In the presence of HA, NpO_2^+ sorption increased at pH 6−9 and decreased at pH > 9 in the absence of ambient CO_2. Under ambient air conditions, the reduction of NpO_2^+ sorption was pronounced more strongly and over a wider pH range (7.7−10.5). Lower sorption was attributed to the formation of soluble NpO_2^+-humate and NpO_2^+-humate-carbonate species. Schmeide and Bernhard (2010) also investigated the sorption of 1×10^{-6} M Np^{4+} on kaolinite in the presence of 50 mg/L HA (CO_2-free conditions). Although tetravalent actinides are known to sorb very strongly on clays, HA was shown to mobilize Np^{4+} (maximum sorption: 35%), probably because of binding of Np^{4+} to HA colloids.

The effect of HA on NpO_2^+ taken up by kaolinite (Iwamoto Mineral Co., Japan) was also studied by Niitsu *et al.* (1997) as a function of the pH value (6−11) in the absence of CO_2 in 0.1 M $NaClO_4$ solution. Sorption of

NpO_2^+ in the absence of HA was found to increase continuously with increasing pH, in agreement with the studies mentioned above (Dierking *et al.*, 2008; Schmeide and Bernhard, 2010; Amayri *et al.*, 2011). With increasing HA concentration, NpO_2^+ sorption increased at pH < 8 and decreased at higher pH. Increased sorption at pH < 8 was attributed to the sorption of NpO_2^+-bound humic acid to the clay surface, whereas the formation of NpO_2^+-humate complexes at high pH reduced the extent of sorption.

The effect of divalent cations on the sorption of NpO_2^+ on kaolinite (Glukhovets, Ukraine) was investigated by Mironenko *et al.* (2006a) at pH = 6.5 as a function of ionic strength using $CaCl_2$ and $MgCl_2$ as a background electrolyte. In general, sorption decreased with increasing ionic strength (0.005−0.1875 M) and increasing initial NpO_2^+ concentration. The ionic strength dependence can be explained by increasing competition between NpO_2^+ and divalent cations for the sorption sites. At lower initial Np concentration this effect is less pronounced due to a greater excess of potential sorption sites for Np.

Keeney-Kennicutt and Morse (1984) investigated the interaction of NpO_2^+ with various minerals, reporting sorption data for ~1×10^{-13} M NpO_2^+ on kaolinite (KGa-1) as function of the contact time (5 min−6 h) using either deionized water or seawater equilibrated with calcite as the electrolyte solution (pH = 7.8−8.2, ambient air conditions). That study focused more on the sorbents calcite and aragonite, however. Aksoyoglu *et al.* (1991) investigated NpO_2^+ sorption on a kaolinite from Zettlitz (in the former Czechoslovakia) in Säckingen (Germany) groundwater at pH 1.5 and 7.6. The resulting distribution coefficients were 23 and 1100 L/kg, respectively.

Structural data for NpO_2^+ sorbed on kaolinite (KGa-1b) were determined by Reich *et al.* (2007) at pH 8−9 under ambient air and CO_2-free conditions. In all cases, the Np-L_2-edge extended XAFS (EXAFS) spectra were fitted with two axial (O_{ax}) and four equatorial oxygen (O_{eq}) neighbors. Although the Np−O_{ax} distance was constant for all samples (1.84−1.85 Å), the Np−O_{eq} distance increased from 2.45 to 2.56−2.57 Å in the presence of CO_2. This increase was attributed to the presence of two carbonate ligands in the coordination sphere of NpO_2^+. The carbon and distal oxygen of carbonate were located at 2.97−3.00 Å and 4.25−4.28 Å, respectively, indicating a bidentate binding of carbonate to NpO_2^+. As a result, $NpO_2(CO_3)_2^{3-}$ was found to be the sorbed species on kaolinite.

The distribution coefficients (if determined) from all studies are summarized in Table 2. In cases where the SSA of the clay is known, values for both log K_d and log K_a are given. Good agreements were found in most cases when comparing the log K_d and log K_a values for NpO_2^+ sorption on kaolinite of different origin. At ambient air conditions, the maximum values are

Table 2. Sorption data of Np(IV) and Np(V) on various clay minerals.

Origin/Batch	pH	Solution	Specific experimental conditions	Log (K_d)[1]	Log (K_a)[2]	Reference
KAOLINITE						
	9.0	$[NaClO_4]$ = 0.1 M	$[NpO_2^+]$ = 8×10^{-6} M, s-l ratio = 0.5−20 g/L, ambient air	2.65 ± 0.09	−1.35 ± 0.09	Amayri *et al.* (2011)
	9.0	$[NaClO_4]$ = 0.1 M	$[NpO_2^+]$ = 5×10^{-12} − 1×10^{-7} M, s-l ratio = 4 g/L, ambient air	2.56 ± 0.07	−1.44 ± 0.07	
KGa-1b	6−11	$[NaClO_4]$ = 0.01 M	$[NpO_2^+]$ = 1×10^{-5} M, s-l ratio = 4 g/L, ambient air	0.1 − 2.6	−4.0 to −1.5	Schmeide *et al.* (2010)
	6−11	$[NaClO_4]$ = 0.01 M	$[NpO_2^+]$ = 1×10^{-5} M, s-l ratio = 4 g/L, CO_2 free, [Humic Acid] = 0 and 50 mg/L	0.4 − 3.6	−4.5 to −0.5	
Iwamoto Mineral Co.	6−11	$[NaClO_4]$ = 0.1 M	$[NpO_2^+]$ = 7×10^{-6} M, s-l ratio = 5 g/L, [Humic Acid] = 0−40 mg/L, CO_2 free	0.9 − 3.9	−3.5 to −0.5	Niitsu *et al.* (1997)
Glukhovets, Ukraine	6.5	$[CaCl_2]$ = 0.005−0.15 M	$[NpO_2^+]$ = 1×10^{-7} − 1×10^{-5} M, s-l ratio = 20−40 g/L, CO_2 free	0.92 − 2.18	−3.08 to −1.82*	Mironenko *et al.* (2006a)
	6.5	$[MgCl_2]$ = 0.005−0.1875 M	$[NpO_2^+]$ = 5×10^{-8} − 1×10^{-5} M, s-l ratio = 20−40 g/L, CO_2 free	1.20 − 2.49	−2.80 to −1.51*	
Zettlitz, former Czechoslovakia	1.5 and 7.6	Säckingen groundwater	$[NpO_2^+]$ = 1×10^{-9} − 1×10^{-6} M, ambient air	1.36 (pH 1.5) 3.04 (pH 7.6)	—	Aksoyoglu *et al.* (1991)

MONTMORILLONITE

Material	pH	Ionic medium	Conditions			Reference
SAz-1	5–11	$[NaNO_3] = 0.1$ M	$[NpO_2^+] = 9 \times 10^{-7}$ M, s-l ratio = 4.0–4.2 g/L, CO_2 free	1.0 – 3.0	−4.0 to −2.0	Turner et al. (1998)
	5–11	$[NaNO_3] = 0.1$ M	$[NpO_2^+] = 9 \times 10^{-7}$ M, s-l ratio = 4.0–4.2 g/L, ambient air	1.0 – 2.0	−4.0 to −3.0	
	2.5–12	$[NaClO_4] = 0.01$ M	$[NpO_2^+] <1 \times 10^{-13}$ M, s-l ratio = 0.6–3.2 g/L, CO_2 free	2.0–4.5	−2.5 to −0.003**	Bradbury and Baeyens (2006)
SWy-1	4–12	$[NaClO_4] = 0.1$ M	$[NpO_2^+] <1 \times 10^{-13}$ M, s-l ratio = 1.2 g/L, CO_2 free	1.0–4.5	−3.5 to −0.003**	
	3–5	$[NaCl] = 0.01$ M	$[NpO_2^+] = 3 \times 10^{-9}$ M, s-l ratio = 1.8 g/L, ambient air	1.38 ± 0.09	−3.05 ± 0.09	Zavarin et al. (2012)
	3–5	$[NaCl] = 1.0$ M	$[NpO_2^+] = 3 \times 10^{-9}$ M, s-l ratio = 1.8 g/L, ambient air	<0.78	<−3.66	
SWy-2	4.5	$[NaCl] =$ 0.001, 0.01, 0.1 M $[KCl] =$ 0.001, 0.01, 0.1 M $[CaCl_2] =$ 0.001, 0.01, 0.1 M	$[NpO_2^+] = 2 \times 10^{-8} - 5 \times 10^{-6}$ M, s-l ratio = 2 g/L, ambient air	<2.32	<−2.18	Benedicto et al. (2014)
	4.5	$[MgCl_2] =$ 0.001, 0.01, 0.1 M	$[NpO_2^+] = 2 \times 10^{-8} - 5 \times 10^{-6}$ M, s-l ratio = 2 g/L, ambient air	<1.90	<−2.60	
The Clay Minerals Society Batch not stated	8.2	J-13 ground water (Yucca Mt.)	$[NpO_2^+] = 2 \times 10^{-7}$ M, ambient air	2.18	−3.74	Runde et al. (2002)
Kunipia-F®	2–8	$[NaClO_4] = 0.01$ M	$[NpO_2^+] = 6 \times 10^{-7}$ M, ambient air	1.3–2.5	−3.4 to −2.2***	Kozai et al. (1993)
Kunipia-F®	2–5	$[NaClO_4] = 0.01$ M,	$[NpO_2^+] = 6 \times 10^{-7}$ M, homoionic Li, Na, K, Cs, Mg, or Ca clay, ambient air	0.3–2.5	−4.4 to −2.2***	Kozai et al. (1996)
Extract from bentonite (Askanite, Georgia)	6.5	$[CaCl_2] =$ 0.005–0.15 M	$[NpO_2^+] = 4 \times 10^{-7} - 3 \times 10^{-5}$ M, s-l ratio = 20–40 g/L, CO_2 free	0.60–1.35	—	Mironenko et al. (2006b)
	6.5	$[MgCl_2] =$ 0.005–0.187 M	$[NpO_2^+] = 4 \times 10^{-7} - 3 \times 10^{-5}$ M, s-l ratio = 20–40 g/L, CO_2 free	0.47–1.27	—	

ILLITE

Material	pH	Ionic medium	Conditions			Reference
Purified from illite-containing material	2.5, 8.5, 10.4	J-13 groundwater (Yucca Mt.)	$[NpO_2^+] <1 \times 10^{-7}$ M, ionic strength 0.2 M	<2.3	—	Torstenfelt et al. (1988)
Du Puy	2.7–9.9	$[NaCl] = 0.1$ M	$[NpO_2^+] = 3.6 \times 10^{-8} - 9.7 \times 10^{-7}$ M, s-l ratio = 2 g/L, CO_2 free	1.11–4.40	−4.01 to −0.72	Marsac et al. (2015)
	2–11	$[NaClO_4] =$ 0.025 – 1 M	$[NpO_2^+] = 1 \times 10^{-6}$ M, s-l ratio = 10 g/L	−0.2–3.5	—	Gorgeon (1994)

BENTONITE

Material	pH	Ionic medium	Conditions			Reference
Kunigel-V1	6–10	$[NaClO_4] = 0.01$ M $[CO_3^{2-}] = 0.001$ M	$[Np^{4+}] = 1 \times 10^{-7}$ M, s-l ratio = 500 g/L, CO_2 free	4.00–4.43	—	Nagasaki et al. (1999)
	9	0.1 M $NaClO_4$	$[Np^{4+}/ NpO_2^+] = 1 \times 10^{-8}$ M, Eh = −100 − 200 mV, CO_2 free	1.00–4.78	—	Nagasaki et al. (1996)
not stated	2.5, 8.5, 10.4	J-13 groundwater (Yucca Mt.)	$[Np] <1 \times 10^{-7}$ M, ionic strength 0.2 M	<2.48	—	Torstenfelt et al. (1988)

Table 2 continued

Origin/Batch	pH	Solution	Specific experimental conditions	Log (K_d)[1]	Log (K_a)[2]	Reference
Kunibond	4.6–12.8	$[NaClO_4]$ = 0.1 M $[CO_3^{2-}]_{Initial}$ = 0.1 M	$[Np^{4+}]$ = 10^{-6} M, Eh = 296 to −296 mV, s-l ratio = 25 g/L, ambient and CO_2 free conditions	0.5–5.5	—	Pratopo et al. (1993)
Gaomiaozi, China	8.5	$[NaCl]$ = 0.1 M	$[NpO_2^+]$ = 4×10^{-4} M, s-l ratio = 0.5–20 g/L, contact time = 0–250 h, CO_2 free	2.00 ± 0.25	−2.69 ± 0.25	Li et al. (2015)
BOOM CLAY						
not stated	10	Milli-Q water	$[NpO_2^+]$ = 8×10^{-7} M, s-l ratio = 25 g/L, Eh = −150 to −50 mV, CO_2 free	<5.85	<0.55	Hart et al. (1994)
not stated	10	Milli-Q water	$[NpO_2^+]$ = 3×10^{-4} M, s-l ratio = 25 g/L, Eh = 50 − 200 mV, CO_2 free	<4.70	<−0.60	
OPALINUS CLAY						
	8.2	Saturated calcite solution	$[NpO_2^+]$ = 8×10^{-6} M, s-l ratio = 2–20 g/L, ambient air	2.10 ± 0.05	−2.52 ± 0.05	Froehlich et al. (2011)
	8.2	Saturated calcite solution	$[NpO_2^+]$ = 1×10^{-8} − 1×10^{-13} M, s-l ratio = 15 g/L, ambient air	3.16 ± 0.01	−1.46 ± 0.01	
	7.7–7–8	$[NaCl]$ = 0.1–0.4 M $[NaClO_4]$ = 0.1–0.4 M $[CaCl_2]$ = 0.033–0.133 M	$[NpO_2^+]$ = 9×10^{-6} − 1×10^{-5} M, s-l ratio = 2–20 g/L, ambient air	2.12 − 2.36	−2.49 to −2.25	
	7.2–7.8	$[MgCl_2]$ = 0.033–0.133 M	$[NpO_2^+]$ = 8 − 9×10^{-6} M, s-l ratio = 2–20 g/L, ambient air	1.53 − 1.73	−3.09 to −2.88	
BHE-24/1	7.6	synth. OPA pore water	$[NpO_2^+]$ = 1×10^{-5} M, s-l ratio = 2–20 g/L, T = 40 °C, ambient air	1.36 ± 0.08	−3.25 ± 0.08	Froehlich et al. (2012b)
	7.5	synth. OPA pore water	$[NpO_2^+]$ = 8×10^{-6} M, s-l ratio = 2–20 g/L, T = 60 °C, ambient air	1.75 ± 0.04	−2.87 ± 0.04	
	7.5	synth. OPA pore water	$[NpO_2^+]$ = 1×10^{-5} M, s-l ratio = 2–20 g/L, T = 70 °C, ambient air	2.37 ± 0.13	−2.25 ± 0.13	
	7.5	synth. OPA pore water	$[NpO_2^+]$ = 8×10^{-6} M, s-l ratio = 2–20 g/L, T = 80 °C, ambient air	2.83 ± 0.16	−1.79 ± 0.16	
	7.6	synth. OPA pore water	$[NpO_2^+]$ = 8×10^{-6} M, s-l ratio = 2–20 g/L, ambient air	1.40 ± 0.09	−3.18 ± 0.09	Wu et al. (2009)
	7.6	synth. OPA pore water	$[NpO_2^+]$ = 8×10^{-6} M, s-l ratio 6–20 g/L, ambient air	1.48 ± 0.06	—	
BLT-14	7.6	synth. OPA pore water	$[NpO_2^+]$ = 8×10^{-6} M, s-l ratio = 6–20 g/L, [Humic Acid] = 10 mg/L, ambient air	1.34 ± 0.02	—	Froehlich et al. (2013)

[1] Logarithm when K_d is reported in L/kg; [2] Logarithm when K_a is reported in L/m^2.
* calculated with SSA = 10 m^2/g given by López-Galindo et al. (2008); ** calculated with SSA = 31.82 m^2/g given by Van Olphen and Fripiat (1979);
*** calculated with SSA = 45 m^2/g given by Kozaki et al. (1999)

~2.5 (log K_d when K_d is reported in L/kg) and ~−1.5 (log K_a when K_a is reported in L/m^2), respectively (Schmeide and Bernhard, 2010; Amayri et al., 2011). In the absence of CO_2, sorption is more pronounced due to the absence of negatively charged NpO_2-carbonate species at high pH. The maximum values reported by Niitsu et al. (1997) and Schmeide and Bernhard (2010) are ~−0.5 for log K_a (when K_a is reported in L/m^2). The values reported by Mironenko et al. (2006a) cannot be compared easily, because 1:2 background electrolytes were used. This leads to a strong dependence of the K_d/K_a value on ionic strength, unlike the studies summarized above which used $NaClO_4$ solutions. The values reported by Aksoyoglu et al. (1991) were obtained using a groundwater of complex composition. Because no specific surface area for the Czechoslovak clay used was reported, these values cannot be compared to other literature data.

Smectite, bentonite, and illite

Studies of the sorption of neptunium on 2:1 clay minerals have focused largely on the smectite clay mineral montmorillonite. Montmorillonite has a large cation exchange capacity, favoring the exchange of radionuclides in solution with interlayer cations. Montmorillonite is also a main constituent of natural clay (mostly included in mixed-layer smectite-illite) and bentonite (60−80%), which is a potential backfill material and will also be discussed here. There are few studies of neptunium uptake by illite.

Whereas no sorption data for Np^{4+} can be found in the literature, sorption of NpO_2^+ on montmorillonite has been investigated by variation of a range of experimental parameters, mostly using the well characterized Source Clays. The clay SWy-1 was studied by Bradbury and Baeyens (2006) and Zavarin et al. (2012). Bradbury and Baeyens studied the sorption of $<1 \times 10^{-13}$ M NpO_2^+ as a function of pH (2.5−12) and ionic strength (0.01 and 0.1 M $NaClO_4$) in the absence of CO_2. At both ionic strengths, NpO_2^+ sorption increased continuously with increasing pH, reaching the same maximum value (log K_d = 4.5 when K_d is reported in L/kg). At acidic to neutral pH (2−7) the K_d decreased by up to one order of magnitude when the ionic strength was increased from 0.01 to 0.1 M. The same trend was observed by Zavarin et al. (2012) when comparing NpO_2^+ ($[NpO_2^+] = 3 \times 10^{-9}$ M) sorption at pH 3−5 in 0.01 M and 1.0 M NaCl solution. At the greater ionic strength, the distribution coefficient was >0.5 log units lower than data at I = 0.01 M.

The effects of different cations (Na^+, K^+, Ca^{2+}, Mg^{2+}) on NpO_2^+ ($[NpO_2^+] = 2 \times 10^{-8} − 5 \times 10^{-6}$ M) uptake by homoionic SWy-2 montmorillonite at pH = 4.5 under variable ionic strength (0.001, 0.01, and 0.1 M) was investigated by Benedicto et al. (2014; the same research group as Zavarin et al., 2012, mentioned above). In NaCl and KCl solutions, NpO_2^+ sorption decreased with increasing ionic strength. Sorption of NpO_2^+ was distinctly lower in background electrolytes containing divalent cations. The maximum K_d values obtained either in NaCl and KCl or $CaCl_2$ and $MgCl_2$ solutions differed by almost 0.5 log units. Because cation exchange is the dominant uptake mechanism at acidic pH, the lower sorption in the presence of divalent cations was explained by lower selectivity coefficients for the ion exchange between Ca^{2+}/Mg^{2+} and NpO_2^+.

The effect of contact time (5 min−6 h) on the sorption of 10^{-14} M NpO_2^+ on SWy-1 montmorillonite, in deionized water or seawater, was investigated by Keeney-Kennicutt and Morse (1984). In both solutions, sorption remained very small (<3%). Distribution coefficients were not reported.

CMS Source Clay montmorillonites other than SWy-1/2 were studied by Turner et al. (1998) (SAz-1) and Runde et al. (2002) (batch not stated). Turner et al. (1998) investigated the effect of pH on the sorption of 9×10^{-7} M NpO_2^+ on ~4 g/L of SAz-1 in 0.1 M $NaNO_3$ solution in the presence or absence of ambient CO_2. Under ambient air conditions, NpO_2^+ sorption increased up to pH $\approx$ 8 (log $K_{d \ (max)} \approx$ 2 when K_d is reported in L/kg at pH 8) and decreased at higher pH due to formation of negatively charged NpO_2-carbonate species. In the absence of CO_2, the sorption increased continuously with increasing pH (log $K_{d \ (max)} \approx$ 3 when K_d is reported in L/kg at pH 10.5). Runde et al. (2002) determined NpO_2^+ ($[NpO_2^+] = 2 \times 10^{-7}$ M) sorption on montmorillonite at pH 8.2 in J-13 Yucca Mountain groundwater (log K_d = 2.18 when K_d is reported in L/kg).

Sorption of NpO_2^+ ($[NpO_2^+] = 4 \times 10^{-7} − 3 \times 10^{-5}$ M) on montmorillonite (separated from Askanite bentonite, West Georgia) using $CaCl_2$ and $MgCl_2$ solution as background electrolyte was investigated by Mironenko et al. (2006b) at pH = 6.5 in the absence of CO_2, varying the ionic strength between 0.005 and 0.15 M ($CaCl_2$) or 0.005 and 0.187 M ($MgCl_2$). In general, NpO_2^+ sorption was very low ($K_{d \ (max)}$ < 23 L/kg) and decreased with increasing ionic strength.

The sorption of 6×10^{-7} M NpO_2^+ on different homoionic montmorillonites (Li^+, Na^+, K^+, Cs^+, Mg^{2+}, and Ca^{2+} type Kunipia-F$^{®}$) was investigated by Kozai et al. (1996) in the pH range 2−5 in 0.01 M $NaClO_4$ solution. For Na- and Li-montmorillonite, NpO_2^+ sorption decreased with increasing pH from 300 to 20 L/kg (values estimated from graphics). For Ca-, Mg-, and K-montmorillonite, the distribution coefficients were discernably smaller, decreasing from 60−80 to 5−6 L/kg. For Cs-montmorillonite, the NpO_2^+ sorption was <10 L/kg over the whole pH range. Differences were explained by different affinities of the exchangeable cations for the clay. For the homoionic Na-form, the sorption of NpO_2^+ was also investigated up to pH 8 (Kozai et al., 1993). The K_d values obtained in that work are also comparable to distribution coefficients obtained from diffusion experiments in the absence of carbonate

using the same batch of clay, as reported by Tachi *et al.* (2010).

Kasar *et al.* (2014) studied NpO_2^+ sorption ($[NpO_2^+] = 8 \times 10^{-14}$ M) on a clay from western India containing ~90% montmorillonite as a function of the ionic strength ($[NaCl] = 0.01-1$ M) and pH values ranging from 2 to 10 under ambient air conditions. Whereas no significant effect of ionic strength was observed, sorption on 3 g/L of clay increased with increasing pH from 0 to >80% ($I = 0.1$ M). Aksoyoglu *et al.* (1991) investigated the sorption of NpO_2^+ on a Molasse clay containing 65−70% montmorillonite and 5−10% illite at pH = 1.5 and 7.6. In that study, the K_d value increased only slightly with increasing pH. Kozai *et al.* (2014) recently investigated the effect of minor amounts of calcite (1−5%) and apatite (2−4%) added to montmorillonite (Kunipia−F®). NpO_2^+ sorption on montmorillonite was less after the addition of calcite than for the calcite-free montmorillonite. No sorption on the calcite fraction was observed. In the presence of apatite at mild pH (apatite dissolved only minimally), NpO_2^+ sorption on montmorillonite decreased, while NpO_2^+ accumulated on the apatite moiety. At low pH (apatite completely dissolved), absolute NpO_2^+ sorption onto montmorillonite was not affected significantly when apatite was added to the system. NpO_2^+ sorption data, on a montmorillonite of unstated origin, was reported by Allard *et al.* (1984). In their study, sorption of $1-5 \times 10^{-11}$ M NpO_2^+ increased continuously from pH 5 to 9 and then decreased toward higher pH. Because this experiment was carried out in equilibrium with air, the sorption curve can again be explained by the successive formation of negatively charged NpO_2^+-carbonate complexes with increasing pH.

The sorption kinetics for NpO_2^+ uptake by montmorillonite were studied by Nagasaki and Tanaka (2000), distinguishing a slow and a fast sorption process with apparent sorption enthalpies of 19 ± 2 and 23 ± 3 kJ/mol, respectively.

Montmorillonite has also been the topic of several sorption studies, indirectly in instances where it occurs as the main constituent of bentonite (which is being considered as a filling material in the engineered barrier in the multi-barrier concepts for high-level nuclear waste disposal). Bentonite is a rock consisting mainly of montmorillonite (60−80%). Minor (non-clay) mineral phases include quartz, calcite, feldspars, and iron-bearing minerals (*e.g.* pyrite).

Nasgasaki *et al.* (1996, 1999) investigated the sorption behavior of Np^{4+} and NpO_2^+ using Kunigel-V1 bentonite. When the pH was increased from 6 to 10 (0.01 M $NaClO_4$ solution) in the presence of 1×10^{-3} M carbonate, sorption of 1×10^{-7} M Np^{4+} increased, reached a plateau at pH = 7.5−9, and then decreased at higher pH due to the formation of Np^{4+}-carbonate species. The maximum K_d value was 2.7×10^4 L/kg (Nagasaki *et al.*, 1999). The effect of redox potential on the sorption behavior of 1×10^{-8} M Np^{4+} and NpO_2^+ was studied at pH = 9. The distribution coefficients remained constant at Eh = $-100-0$ mV ($K_d = 6 \times 10^4$ L/kg) and $100-200$ mV ($K_d = 30-100$ L/kg). The large change in K_d between Eh = $0-100$ mV can be explained by the change of oxidation state from tetra- to pentavalent when increasing or from penta- to tetravalent when decreasing the Eh value, respectively (Nagasaki *et al.*, 1996).

Pratopo *et al.* (1993) studied the sorption of 10^{-6} M Np^{4+} on the Kunibond bentonite (Kunimine Co. Ltd., Japan) at pH = 4.6−12.8 under reducing and oxidizing conditions. The initial carbonate concentration was 0.1 M; the final carbonate concentration in the samples varied between 1.6×10^{-4} and 9.1×10^{-2} M. Log K_d varied between 0.5 and 5.0 when K_d is reported in L/kg. Under reducing conditions a pronounced tendency to form colloids of >3 nm was observed.

The sorption of NpO_2^+ on a bentonite from the Khakassiya, Russia, was investigated by Sabodina *et al.* (2006a, 2006b). Under inert atmosphere, sorption of 3×10^{-8} M NpO_2^+ increased continuously with increasing pH (1.5−10) reaching a maximum sorption of ~90%. The variation of ionic strength (0.1, 0.01, 0.001 M $NaClO_4$ solution) showed only a minor effect at low pH. The large sorption of NpO_2^+ was explained by a reduction to Np^{4+} on the basis that the aqueous solution after equilibration with bentonite showed an Eh value of -150 mV (Sabodina *et al.*, 2006a). These findings were reproduced using slightly different experimental conditions (Sabodina *et al.*, 2006b). In the latter study, the oxidation state at the mineral surface was investigated by a combination of desorption and liquid-extraction techniques which showed that only Np^{4+} was present at the mineral surface. The occurrence of NpO_2^+ reduction at this Eh value is in agreement with the work of Nagasaki *et al.* (1996) mentioned above.

K_d values for the sorption of NpO_2^+ on a bentonite of unstated origin in J-13 Yucca Mountain groundwater at pH 2.3, 8.7, and 10.2 as function of centrifugation speed during phase separation were determined by Torstenfelt *et al.* (1988) and ranged between 0 and 300 L/kg, increasing with increasing pH.

In a recent study, Li *et al.* (2015) investigated the effect of pH, ionic strength, contact time, s-l ratio, temperature, and humic acid on the sorption of NpO_2^+ on Gaomiaozi bentonite under anaerobic conditions in NaCl solution. Whereas the pH was found to have a large effect, with NpO_2^+ sorption increasing from 0% to 100% between pH 6 and 11, ionic strength (0.01−0.3 M) had only a minor effect on NpO_2^+ sorption at pH 6.5 and 8.5. As discussed above, addition of humic acid resulted in an increase in NpO_2^+ sorption at low pH (<8) and lower NpO_2^+ sorption at high pH. Log K_d values were determined as a function of s-l ratio or contact time in 0.1 M NaCl solution at pH 8.5. Log K_d was almost constant in both experimental series (log $K_d = 2.00 \pm 0.25$ when K_d is reported in L/kg).

Unlike montmorillonite (which is a representative smectite clay and the main component of bentonite), only a few studies treating the sorption behavior of neptunium on illite are found in the literature. Nagasaki *et al.* (1998) studied the sorption kinetics of NpO_2^+ on illite (Rochester, New York, USA) at pH 6 as a function of the temperature and determined the apparent activation enthalpy and entropy (37 ± 3 kJ/mol and -69 ± 7 J/K $\times$ mol, respectively).

Thorstenfelt *et al.* (1988) determined distribution coefficients for the sorption of $<1 \times 10^{-7}$ M on illite at pH 2.5, 8.5, and 10.4 in Yucca Mountain groundwater as a function of centrifugation speed during phase separation. Whereas the centrifugation speed had no significant effect, the K_d value increased with increasing pH up to ~200 L/kg.

In a recent study, Marsac *et al.* (2015) studied the effect of pH ($2-10$), redox potential, initial NpO_2^+ concentration ($3 \times 10^{-8}-3 \times 10^{-4}$ M), and contact time ($7-63$ days) on the sorption of NpO_2^+ on 2 g/L purified illite (du Puy) in 0.1 M NaCl solution in the absence of CO_2 (Ar glove-box). NpO_2^+ sorption did not change with contact time after 7 days. In general, sorption increased with increasing pH. Whereas sorption at pH < 6 was independent of the initial radionuclide concentration, sorption at pH > 6 increased with decreasing metal concentration. Depending on the initial NpO_2^+ concentration, maximum log K_d values were between 3.3 and 4.4 when K_d is reported in L/kg. Furthermore, sorption at pH = 7.2 was determined as a function of the redox potential (pe = $3-7$). K_d values increased by more than four orders of magnitude as the redox potential decreased, due to reduction of NpO_2^+ to Np^{4+}. The reduction was verified using liquid-liquid extraction. Furthermore, two samples at pH 7.4 and 9.6 with an initial NpO_2^+ concentration of 3×10^{-4} M and a s-l ratio of 20 g/L were measured using X-ray absorption near-edge structure (XANES) spectroscopy also verifying the partial reduction of NpO_2^+ to Np^{4+}. In addition, the amount of reduction decreased with increasing pH. The reduction mechanism could not be clarified fully but might be related to an electron transfer from adsorbed or structurally bound Fe(II) to sorbed NpO_2^+.

NpO_2^+ sorption on illite (du Puy) has also been studied by Gorgeon (1994), as cited by Bradbury and Baeyens (2009) and Marsac *et al.* (2015). The log K_d values (when K_d is reported in L/kg) obtained increased from ~0 at pH $\approx$ 2 to 3.2 at pH = 11. Variation of the ionic strength between 0.025 and 1 M $NaClO_4$ had no significant effect.

Examining the literature data for montmorillonite shows that comparison of distribution coefficients is very difficult. Firstly, the investigated pH range is of great importance as different uptake mechanisms dominate depending on the experimental conditions. Secondly, at low pH, where cation exchange determines the uptake of NpO_2^+, the ionic strength is also very important. Thirdly, the composition of the aqueous phase strongly affects the extent of neptunium uptake as the presence of divalent cations decreases NpO_2^+ sorption significantly. Most studies concentrate on the acidic to neutral pH range to describe the cation exchange process only and to determine selectivity coefficients for the exchange of NpO_2^+ with various cations. When comparing the K_d and K_a values obtained at acidic pH for different montmorillonites, the agreement of the distribution coefficients does not improve significantly after normalization with respect to the SSA. In both cases, the distribution coefficients differ by up to two orders of magnitude. When comparing data for the same batch of clay and identical ionic strength, however, the agreement is very good (*e.g.* data of Bradbury and Baeyens, 2006 and of Zavarin *et al.*, 2012). Only Turner *et al.* (1998) and Bradbury and Baeyens (2006) investigated a wider range of pH values (up to pH = 12). The effect of carbonate (equilibrium with ambient CO_2) on the sorption of NpO_2^+ on montmorillonite was taken into account by Turner *et al.* (1998) only.

Compared to montmorillonite, data on NpO_2^+ sorption to illite is still sparsely documented in the open literature.

Clearly, insufficient literature data exist on the interaction between neptunium and montmorillonite and illite to enable proper description of the sorption behavior of neptunium under environmental conditions. Firstly, no data treating the sorption characteristics of Np^{4+} are found in the literature although, as stated above, the tetravalent oxidation state is of great importance with respect to nuclear-waste-repository conditions. In addition, carbonate is a very important complexing ligand, thus enhancing NpO_2^+ uptake as shown by Turner *et al.* (1998). As a result, additional sorption investigations should be more focused on high-pH studies in the presence of carbonate, because we know that partial pressures of CO_2 which are greater than those under ambient conditions can occur at deep geological conditions (Pearson *et al.*, 2003; Turrero *et al.*, 2006). In contrast to smectite and illite, sorption data for Np^{4+} have been reported for bentonite. In general, distribution coefficients for Np^{4+} are at least two orders of magnitude greater than the corresponding values for NpO_2^+ under the given experimental conditions. The SSA of the bentonite used has only been reported by Li *et al.* (2015), enabling the calculation of K_a.

Natural clays and heterogeneous sorbents based on clay

Whereas bentonite contains mainly a single clay mineral (*i.e.* montmorillonite), a number of sorption studies have focused on even more heterogeneous natural clays and synthetic mixtures.

Several studies have investigated the uptake of NpO_2^+ by different soils or sediments most of which contained only minor amounts of clay (Higgo *et al.*, 1986; Bidoglio *et al.*, 1987; Yamamoto *et al.*, 1990; Braithwaite *et al.*,

2000; Minchner *et al.*, 2003; Weijuan and Zuyi, 2003; Sabodina *et al.*, 2008). André *et al.* (1998) investigated the sorption of NpO_2^+ on a mixture of sand and natural clay (8%) in column experiments. The sorption behavior of NpO_2^{2+} by two clay-bearing sediments was studied by Nash *et al.* (1981). In that study, NpO_2^{2+} was reduced readily to NpO_2^+ under aerobic conditions.

Stammose *et al.* (1992) investigated NpO_2^+ sorption on a purified clay material selected as a potential engineered barrier for nuclear waste disposal. The material consisted of kaolinite and mixed-layer kaolinite/smectite. Between pH 3 and 9, sorption of 2.4×10^{-5} M NpO_2^+ increased continuously with increasing pH. Increase of the ionic strength ($NaClO_4$ solution) from 0.01 to 1 M led to larger K_d values at low pH and a decrease in K_d under basic conditions. Over the whole range of experimental conditions, log K_d values varied between 0.8 and 3.2 when K_d is reported in L/kg (log K_a = −4.3 to −1.9 when K_a is reported in L/m²), respectively.

Even more interesting are studies on the sorption behavior of natural clays which are being considered as potential host rocks for nuclear-waste disposal. The sorption of NpO_2^+ on Boom Clay, which is being investigated as a possible host-rock formation in Belgium, was investigated by Hart *et al.* (1994) and Henrion *et al.* (1985). Boom Clay consists of up to 60% clay minerals (10−45% illite, 10−30% mixed-layer smectite-illite, 5−20% kaolinite, 0−5% chlorite, 0−5% mixed-layer chlorite-smectite), ~20% quartz, ~10% feldspars and minor amounts of other mineral phases (De Craen *et al.*, 2004). Hart *et al.* studied NpO_2^+ sorption on the Boom Clay depending on initial Np concentration (3×10^{-4} and 8×10^{-7} M), contact time and Eh (50−200 mV and −150 to −50 mV) under anaerobic conditions. The maximum K_d values ranged up to 7×10^5 L/kg. In addition, experiments at low Eh showed a strong dependence of Np uptake on the filter pore size when separating the phases. The large distribution coefficients and the dependence on filter pore size indicate clearly that NpO_2^+ was reduced to Np^{4+}. This reduction is in agreement with Eh-pH diagrams reported in the literature (*e.g.* Lieser and Mühlenberg, 1988). According to these, Np^{4+} will be formed at Eh < 100 mV at pH = 10. The strong dependence on filter pore size can probably be attributed to the formation of Np(IV) colloids. Distribution coefficients for NpO_2^+ uptake by Boom Clay obtained by Henrion *et al.* (1985) were significantly smaller than those established by Hart *et al.* (1994). In the Henrion *et al.* (1985) case, no reduction of the pentavalent neptunium took place − no information on pH or atmospheric conditions was presented in that work.

A number of studies of the interaction between NpO_2^+ and Opalinus Clay (investigated as a potential host rock in Switzerland) were conducted by Fröhlich *et al.* (2011, 2012a, 2012b, 2013) who investigated the effects of pH,

initial NpO_2^+ concentration, partial pressure of CO_2, aerobic/anaerobic conditions, background electrolytes, temperature, and the presence of humic substances. Opalinus Clay from the rock laboratory, Mont Terri, Switzerland, consists of >65% clay minerals (kaolinite, illite, mixed-layer illite-smectite, chlorite), >10% quartz and calcite, ~4% iron-bearing minerals and minor amounts of albite, feldspar, and organic carbon (NAGRA, 2002). The effect of pH (6−10) on the sorption of 7×10^{-12} and 8×10^{-6} M NpO_2^+ has been studied under aerobic (atmospheric CO_2) and anaerobic conditions ($p(CO_2) = 10^{-2.3}$ atm) (Fröhlich *et al.*, 2011). The greater partial pressure of CO_2 was applied because the pore waters of the Opalinus Clay can be in equilibrium with partial pressures of up to $10^{-1.5}$ atm (Pearson *et al.*, 2003; Turrero *et al.*, 2006). Under aerobic conditions, NpO_2^+ sorption increased with increasing pH up to pH = 8−9 and decreased at higher pH due to the formation of negatively charged NpO_2^+-carbonate species. In addition, NpO_2^+ sorption increased significantly with decreasing initial neptunium concentration. The dependence between NpO_2^+ sorption and initial neptunium concentration was explained by different affinities of the minerals contained in Opalinus Clay for NpO_2^+. At greater partial pressure of CO_2 and in the absence of oxygen, the sorption edge and sorption maximum were shifted toward lower pH due to the greater carbonate concentration in solution. The maximum K_d value for 8×10^{-6} M NpO_2^+ in the absence of O_2 was more than twice as large as in the experiment under aerobic conditions; this was attributed to a partial reduction of NpO_2^+ to Np^{4+} under anaerobic conditions (verified by liquid-liquid extraction).

The reduction of NpO_2^+ on the surface of Opalinus Clay has also been verified spectroscopically using spatially resolved XANES and bulk-EXAFS spectroscopy (Fröhlich *et al.*, 2012a). Even under aerobic conditions, NpO_2^+ was found to be partially reduced to Np^{4+}. Under anaerobic conditions, this behavior was more pronounced. In addition, pyrite was identified by μ-X-ray diffraction as one of the redox-active phases in Opalinus Clay determining the speciation of neptunium on the mineral surface.

The influence of humic acid on NpO_2^+ sorption on Opalinus Clay has been studied at pH 6−10 for 8×10^{-6} and 7×10^{-12} M NpO_2^+ under ambient air conditions (Fröhlich *et al.*, 2013). At the higher NpO_2^+ concentration, humic acid showed no significant effect at pH < 7.5, whereas NpO_2^+ sorption decreased visibly at pH > 8.5. For $[NpO_2^+] = 7 \times 10^{-12}$ M, the presence of humic acid increased the neptunium uptake by >20% at low pH. The decrease in sorption at pH = 10 was comparable to the findings at higher initial NpO_2^+ concentration. As for kaolinite (Schmeide and Bernhard, 2010), greater sorption at low pH is explained by stronger sorption of the humic acid itself creating more potential sorption sites. Lower sorption at basic

conditions is addressed to the formation of NpO_2^+-humate or mixed NpO_2^+-humate-carbonate species.

As it is known that the near field of a nuclear-waste repository will heat up significantly due to the radioactive decay of the stored radionuclides (in the case of clay, up to 100ºC; Brasser *et al.*, 2008), Fröhlich *et al.* (2012b) studied NpO_2^+ sorption on Opalinus Clay at $T = 40-80$ºC using synthetic Opalinus Clay pore water as a background electrolyte (pH = 7.6, I = 0.4 M).

The distribution coefficient increased continuously with increasing temperature by ~1.5 orders of magnitude. The value obtained at 40ºC was comparable with the K_d value at room temperature determined by Wu *et al.* (2009). This value, which was obtained using synthetic pore water as the background electrolyte, can be compared to values determined in $NaClO_4$, NaCl, $CaCl_2$, and $MgCl_2$ solutions (I = 0.1 and 0.4 M) at the same pH (7.2–7.8) (Fröhlich *et al.*, 2012b). K_d values for electrolyte solutions containing divalent cations agreed well with the result in pore water, thus suggesting that divalent cations (*e.g.* Mg^{2+}, Ca^{2+}) determine the sorption behavior of NpO_2^+ in pore water. In the case of NaCl or $NaClO_4$ solutions, the distribution coefficient was up to ten times higher. Differences in the sorption behavior of NpO_2^+ were explained by a pronounced correlation between divalent cations and NpO_2^+ for sorption sites on Opalinus Clay, whereas Na^+ interaction with the clay is much weaker at pH $\approx$ 7.5.

The general effects of different experimental parameters (*e.g.* pH) are obviously found for both heterogeneous natural clays and for pure clay minerals. Nevertheless, the description of Np uptake by natural clays can be very complicated (*e.g.* due to reduction processes of minor Fe-bearing mineral phases) and, thus, in most cases, it will not be possible to predict Np sorption by simple addition of the distribution coefficients of the minerals of which it consists. As a result, careful investigation of the sorption properties of particular sorbents as they occur in potential host-rock formations is essential.

SUMMARY

The present review demonstrates the difficulties of comparing sorption data reported in the literature. General trends (*e.g.* pH dependency or effect of ionic strength) are generally reproducible. Also, data obtained for the same batch of clay (*e.g.* kaolinite, KGa-1, or montmorillonite, SWy-1), generally agree very well within the range of experimental error.

Nevertheless, comparison of distribution coefficients of NpO_2^+ sorbed on a distinct mineral from different origins can be challenging. In some cases, the agreement is better when comparing distribution coefficients of NpO_2^+ normalized with respect to the SSA of the mineral (*e.g.* data for different montmorillonites, Table 2). Every sorption study should report the SSA of the sorbent used, therefore.

This review also notes that the specific experimental conditions play an important role. For example, data obtained in $NaClO_4$ solution are not comparable with results of studies using background electrolytes containing divalent cations, due to the different affinity of the cations for sorption sites. Some minerals contain small amounts of redox-active phases which can lead to a reduction of NpO_2^+ to Np^{4+}, changing the sorption behavior of neptunium completely (*e.g.* Hart *et al.*, 1994; Sabodina *et al.*, 2006a, 2006b, Fröhlich *et al.*, 2012; Marsac *et al.*, 2015). Generally, data related to Np^{4+} are under-represented in the literature. As a result, an accurate evaluation of a potential storage site for high-level nuclear waste will almost always require detailed individual investigations of the local geologic material and geochemical characteristics (*i.e.* pH, Eh, ionic strength, *etc.*), and the use of data obtained for pure clays might not be sufficient in most cases. The use of the K_a concept, however, clearly improves the usability of the sorption data reported.

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