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Neptunium interaction with uranium dioxide in aqueous solution

O.N. Batuk [a,*], St.N. Kalmykov [a], V.G. Petrov [a], E.V. Zakharova [b], Yu.A. Teterin [c], A.Yu. Teterin [c], V.I. Shapovalov [d], M.J. Haire [e]

[a] *Chemistry Department, Moscow State University, Moscow, Russia*
[b] *Frumkin Institute of Physical Chemistry and Electrochemistry, RAS, Moscow, Russia*
[c] *Research Centre 'Kurchatov Institute', Moscow, Russia*
[d] *Russian Federal Nuclear Centre – VNIIEF, Sarov, Russia*
[e] *Oak Ridge National Laboratory, USA*

Abstract

Neptunium, Np(V) and Np(IV), sorption onto uranium dioxide surface was studied at various values of pH. Sorption was studied in two sets of experiments with different redox conditions that correspond to either Np(V) (*Set 1*) or Np(IV) (*Set 2*) in solution. In *Set 1* the reduction of Np(V) was established when low pH solution covered a UO_2 surface. When the pH increased, the sorption of neptunium is decreased. At pH > 5.5 neptunium sequestration from solution is governed by Np(V) sorption onto $UO_{2.25}$. In *Set 2* (the more anoxic conditions) complete neptunium sorption is established at pH > 2: it is present in the tetravalent form over the whole pH range. The proposed mechanisms of neptunium sorption was suggested by using pH sorption edges of Th(IV) as an analog to Np(IV) onto UO_2 and Np(V) onto ThO_2. The UO_2 surface was characterized by X-ray photoelectron spectroscopy (XPS) after equilibration with aqueous solutions at different pH values.

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1. Introduction

Direct disposal of spent nuclear fuel (SNF) is considered now in many countries as an alternative to its reprocessing. The partial oxidation of UO_2 that is the main component of SNF upon exposure to atmosphere will occur [1,2]. This will lead to the formation of alteration products that may incorporate other radionuclides [3,4] and therefore reduce their mobility. The importance of the radionuclide retention to SNF alteration phases was discussed in several papers [1,5].

Previous studies of the potential HLW repository at Yucca Mountain have identified ^{237}Np (and ^{99}Tc) as a radionuclide of primary concern at long times [6]. Although sorbing minerals like zeolites are present between the repository and the water table, the zeolites may be thermally altered, and that may

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[*] Corresponding author.
E-mail address: batuk@radio.chem.msu.ru (O.N. Batuk).

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diminish their radionuclide sorptivity [7]. Under Yucca Mountain conditions, ^{237}Np will be present in the relatively mobile pentavalent form with $Np_2O_5 \cdot xH_2O$ as the solubility limiting phase [8]. Its solubility is found to be in the order of 10^{-5}–10^{-6} M at neutral pH conditions [9].

On the basis of crystal-chemical arguments Burns et al. [1] predicted that Np(V) may be incorporated into uranyl compounds. In another paper [3] they studied Np incorporation into the structure of different U(VI) compounds including meta-schoepite ($UO_3 \cdot 2H_2O$), Na-compreignacite ($Na_2[(UO_2)_3O_2(OH)_3]_2(H_2O)_7$), uranophane ($Ca(UO_2)_2(SiO_3OH)_2(H_2O)_5$) and β-$(UO_2)(OH)_2$. It was established that only Na-compreignacite and uranophane which interlayers contain cations and H_2O were able to incorporate Np(V). In the paper by Douglas et al. [4] the incorporation of Np(V) to U(VI) peroxide, metastudtite ($UO_4 \cdot 4H_2O$) was studied and further batch dissolution studies were done to test Np partitioning. They established that despite Np was incorporated into the metastudtite structure, it was released to the solution over time.

This paper deals with another phenomenon that may impact mobility of Np that is its surface sorption onto UO_2 or its oxidation products. Taking into consideration that both Np and U could be present at least in two valence states, it is supposed that mechanism of Np sorption would be governed by its redox reactions.

2. Experimental

2.1. Synthesis and characterization of samples

Samples of UO_2 were prepared from UF_6 and then annealed at 900 K in H_2/Ar mixture for use in this study. The average particle size was 1.5 μm as determined by dynamic light scattering technique. The sample free surface area was measured to be 1.5 $m^2\ g^{-1}$ and the sample was nonporous as determined by BET-analysis. The bulk sample stoichiometry was determined by X-ray diffraction (XRD) using the dependence of the lattice parameter on U(IV)/U(VI) ratio [10]. The degree of surface oxidation of U(IV) that occurs, even at ambient temperatures, was measured by X-ray photoelectron spectroscopy (XPS). The bulk composition of the sample was measured to be UO_2 while the surface composition corresponds to $UO_{2.25}$.

ThO_2 was synthesized and characterized in order to model the sorption behavior of neptunium onto UO_2 at different pH values. ThO_2 was prepared by precipitating the oxalate and annealing at 775 K as described earlier [11]. The samples were characterized by the same methods as for UO_2. The phase composition was confirmed by XRD. The free surface area was 0.8 $m^2\ g^{-1}$.

2.2. Sorption and solubility experiments

Solubility and sorption tests were done in aqueous solutions in batch mode at controlled Eh and pH conditions in a glove box with N_2 atmosphere. All experiments were done in deionized water at solid: solution ratio of 2.5 $g\ L^{-1}$. The total concentration of ^{237}Np was maintained at 1×10^{-10} M and ^{239}Np tracer was added to increase the sensitivity of Np determination by liquid scintillation spectrometry. Th(IV) was used as an analog to Np(IV) and its sorption onto UO_2 was studied under the same conditions as for neptunium. The total Th(IV) concentration was maintained at 1×10^{-10} M using a ^{232}Th and ^{234}Th mixture. Solid were separated from solution by ultra-filtration using 50 nm filters. The separate experiments were done to ensure that sorption of both radionuclides by ultra-filters were negligible and were not taken into consideration in sorption calculations. The valence of uranium and neptunium in solution was determined by a solvent extraction technique with 1-(2-thenoyl)-3,3,3-trifluoracetone (TTA) [12].

3. Results and discussion

It was postulated earlier [13] that the properties of UO_2, e.g. dissolution rate, solubility, and surface charge, are coupled with the degree of surface oxidation of UO_2. For the U–O systems the number of stoichiometric oxides and solid solutions with various compositions are known [10]. The first step of UO_2 oxidation is the formation of UO_{2+x} ($0 < x \leqslant 0.25$) having the same fluorite structure type, *Fm3m*. Oxygen diffusion into the lattice of UO_2 leads to the formation of an oxidized surface layer, whose thickness depends on temperature and the partial pressure of oxygen. Further oxidation of $UO_{2.25}$ (U_4O_9) may lead to the formation of UO_{2+x} oxides with $0.25 < x \leqslant 0.33$ accompanied by a changing of the crystal structure. Subsequent oxidation may proceed through the formation of $UO_{2.5}$ (U_2O_5) and $UO_{2.67}$ (U_3O_8) until UO_3 is formed. However no anhydrous oxides above $UO_{2.33}$ are known to exist in nature [14]. The UO_2

sample used in this study was stored at ambient air conditions for the few months that lead to the oxidation of its surface to $UO_{2.25}$.

Experiments were done at different pH values and two redox conditions, *Set 1* and *Set 2*, respectively, that correspond to the stability of Np(V) and Np(IV) as dominant redox forms in solution. In *Set 1* the experiment was done in aqueous solutions purged with N_2 or Ar. Neptunium was present in pentavalent form that was demonstrated by solvent extraction. In *Set 2* the small addition of hydrazine was used to stabilize neptunium in tetravalent state that was also confirmed by solvent extraction.

The kinetics of neptunium sorption onto UO_2 was studied at different pH values. It was shown that the sorption became constant in about a day and was not dependent on pH. All further sorption data were obtained after at least one day of equilibration, the time at which sorption becomes constant.

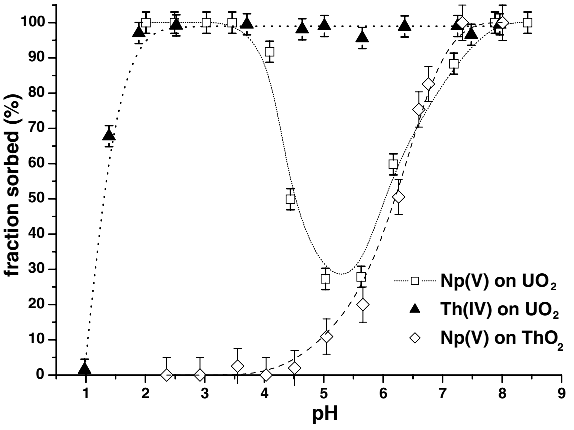

Fig. 1. The pH dependence of Np (initially in pentavalent form) and Th(IV) sorption onto UO_2 and Np(V) sorption onto ThO_2 (experimental *Set 1*).

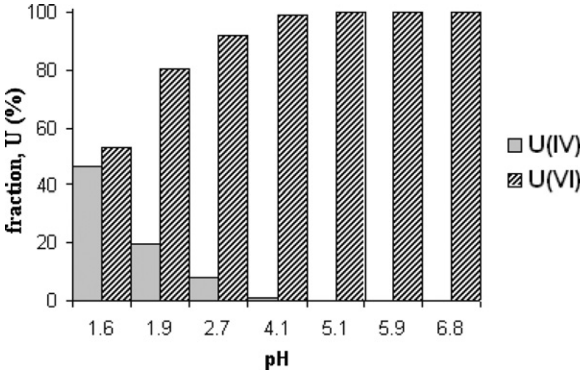

Fig. 2. The pH dependence of uranium oxidation state in solution (experimental *Set 1*).

The dependence of neptunium sorption as a function of pH in experimental *Set 1* is presented in Fig. 1. The sorption has a minimum near neutral pH values: this is not typical for cation sorption onto oxides or oxyhydroxides. The sorption of plutonium and neptunium onto UO_2 was studied extensively in Chalmers University of Technology [15–17]. However, a difference in radionuclide sorption to UO_2 used in this study is expected due to its different degree of surface oxidation. The shape of the sorption curve presented in Fig. 1 can be explained by redox reactions that occur at different pH values, either in solution or on the UO_2 surface. At low pH values the dissolution of the surface oxidized layer of UO_2 leads to the dissolution of both U(IV) and U(VI) and also to alteration of the UO_2 surface. The fraction of U(IV) in solution varies between 30% and 50% (Fig. 2), as determined by uranium redox speciation measured by solvent extraction. The presence of U(IV) in solution, or on the surface, stabilizes neptunium in its tetravalent state that is readily sorbed to the surface. This is confirmed by solvent extraction as presented in Table 1. It should be noted that according to redox potentials (see for example Ref. [18]) one would expect higher Np(IV) fraction than U(IV). This is the case in our study but Np(IV) is readily sorbs onto UO_2 and only small fraction is found in solution. The reduction of Np(V) to Np(IV) and Pu(IV) to Pu(III) by freshly washed UO_2 under anoxic conditions and a subsequent sorption was suggested earlier [17,19]. In our case, at pH 4–5.5, two possible redox scenarios are conceivable: (1) oxidation of Np(IV) and stabilization of Np(V) in the presence of U(VI) in solution, and (2) precipitation of U(VI) solids from solution onto the UO_2 surface, thus negating surface reduction of Np(V). The fraction of U(VI) on the surface is increased systematically, according to the XPS of UO_2 samples that

Table 1
Neptunium redox speciation in solution equilibrated with UO_2

pH	Fraction Np(IV) (%)	Fraction Np(V) (%)
1.85	24	76
3.03	6	94
5.73	0	100
6.16	0	100
7.16	0	100

Table 2
The pH dependence of uranium speciation on the surface of UO_2

pH	Phase stoichiometry
2.54	$UO_{2.14}$
4.35	$UO_{2.17}$
7.04	$UO_{2.25}$

were contacted with aqueous solutions at different pH values. However, no oxides with stoichiometries that exceed $UO_{2.25}$ are formed (Table 2). This supports our conclusion that at pH > 4 the oxidation of Np(IV) occurs in solution while no U(VI) solids are precipitated from solution. Precipitation could only occur upon oxidative leaching of UO_2, as previously described [20]. Under oxic conditions, used in the cited work, the oxides with a stoichiometry close to $UO_{2.5}$ were formed at neutral and alkaline conditions: at acidic pH, it was close to UO_2 as determined by XPS. The corrosion potential responsible for surface reduction decreased with increasing the pH. In our study at pH > 3.0–3.5 neptunium in solution is present only in the pentavalent state (Table 1). The shape of the curve at pH above 5.5 corresponds to the Np(V) sorption onto UO_2 by a surface complexation mechanism.

The sorption of Th(IV) onto UO_2 and Np(V) onto ThO_2 were studied to support our thesis than different redox reactions govern neptunium behavior in this system.

The sorption curves obtained are presented in Fig. 1 together with neptunium sorption onto UO_2. At pH between 2 and 3.5 the sorption of neptunium is comparable to the sorption of Th(IV). This is an indirect indication that at low pH values the sorption of Np(IV) onto UO_2 is the dominant mechanism of its sequestration from solution. The sorption of Np(V) onto ThO_2, an non oxidisable analog for UO_2, agrees well with the sorption of neptunium onto UO_2 at pH >5.5. This experimental data indicates that the sorption of neptunium above pH 5.5 is governed by Np(V) sorption onto UO_2. The simplified schematic representation of the surface processes that occur at acidic and neutral pH are presented in Fig. 3.

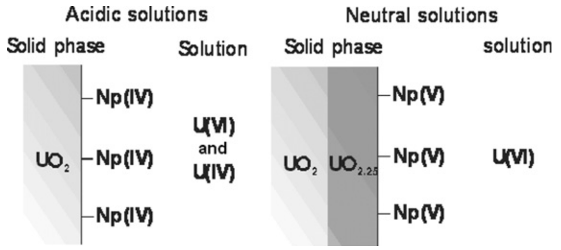

Fig. 3. Schematic representation of sorption processes onto UO_2 surface.

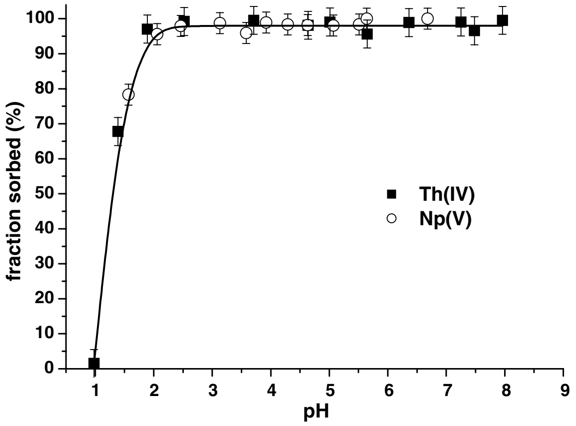

Fig. 4. The pH dependence of neptunium (initially in pentavalent form) and Th(IV) sorption onto UO_2 (experimental *Set 2*).

In experimental *Set 2* (the more reducing conditions) the high sorption is established through the whole pH range (Fig. 4) without any decrease of sorption at pH between 3.5 and 5.5. The sorption of neptunium agrees well with sorption of Th(IV). This indicates that it is present only in tetravalent state. This conclusion is also supported by solvent extraction with TTA: no Np(V) was found.

4. Conclusions

It was shown that redox reactions play a dominant role in neptunium sorption onto UO_2 with a surface oxidized layer of $UO_{2.25}$. At relatively low Eh values (*Set 2*), that correspond to Np(IV) stability in aqueous solutions, the quantitative sorption of neptunium is established at pH > 2. This is the case of Th(IV) that indirectly indicates that the former is sorbed as Np(IV). In another set of experiments at higher Eh values (*Set 1*), neptunium is sorbed as Np(IV) at low pH values and is oxidized with increasing pH. Increasing pH decreases sorption between a pH of 3.5 and 5.5. Further increase of sorption at pH > 5.5 is due to the surface complexation reaction of Np(V) on UO_2.

Despite the relatively low free surface area of the industrially produced UO_2 sample studied, it was shown that UO_2 can effectively sorb neptunium from solution, especially at low Eh values.

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References

[1] P.C. Burns, R.C. Ewing, M.L. Miller, J. Nucl. Mater. 245 (1997) 1.

[2] Ch. Cachoir, M.J. Guittet, J.-P. Gallien, P. Trocellier, Radiochim. Acta 74 (1996) 59.

[3] P. Burns, K.M. Deely, S. Skanthakumar, Radiochim. Acta 91 (2004) 151.

[4] M. Douglas, S.B. Clark, J.I. Friese, B.W. Arey, E.C. Buck, B.D. Hanson, Environ. Sci. Technol. 39 (2005) 4117.

[5] P.A. Finn, J.C. Hoh, S.F. Wolf, S.A. Slater, J.K. Bates, Radiochim. Acta 74 (1996) 65.

[6] H.S. Viswanathan, B.A. Robinson, A.J. Valocchi, I.R. Triay, J. Hydrol. 209 (1998) 251.

[7] T.S. Bower, R.G. Burns, Am. Mineral. 75 (1990) 601.

[8] D.W. Efurd, W. Runde, J.C. Banar, D.R. Janecky, J.P. Kaszuba, P.D. Palmer, F.R. Roensch, C.D. Tait, Environ. Sci. Technol. 32 (1998) 3893.

[9] J.P. Kaszuba, W.H. Runde, Environ. Sci. Technol. 33 (1999) 4427.

[10] N.M. Voronov, R.M. Safronova, E.A. Voitehova, High Temperature Chemistry of Uranium Oxides and their Compounds, Atomizdat, Moscow, 1971 (in Russian).

[11] V.A. Matyukha, S.V. Matyukha, Oxalates of Lanthanides and Actinides, 2nd Ed., Energoatomizdat, Moscow, Russia, 2004.

[12] R. Choppin, A.H. Bond, Russ. J. Anal. Chem. 12 (1996) 1240.

[13] M. Olsson, PhD theses, Sorption and surface complexation of plutonium, Chalmers University of Technology, Goteborg, Sweden, 2005.

[14] R.J. Finch, R.C. Ewing, Radiochim. Acta 52&53 (1991) 395.

[15] M. Olsson, A.-M. Jakobsson, Y. Albinsson, J. Colloid Interf. Sci. 266 (2003) 269.

[16] A.-M. Jakobsson, Y. Albinsson, R.S. Rundberg, Radiochim. Acta 92 (2004) 683.

[17] M. Olsson, H. Glanneskog, A.-M. Jakobsson, H. Nilsson, Y. Albinsson, Radiochim. Acta 93 (2005) 341.

[18] G.R. Choppin, Radiochim. Acta 85 (1999) 89.

[19] Y. Albinsson, H. Nilsson, A.-M. Jakobsson, Mater. Res. Soc. Symp. Proc. 663 (2001) 1109.

[20] S. Sunder, D.W. Shoesmith, R.J. Lemire, M.G. Bailey, G.J. Wallace, Corros. Sci. 32 (4) (1991) 373.