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Uranium dioxide interaction with groundwater – Leaching behavior and sorption tests

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Abstract

The solubility of three UO$_2$ samples that were synthesized at different temperatures in reducing atmosphere and having different composition of surface oxidized layer was studied in distilled water and tuff groundwater (J-13). The solubility of the samples was governed by the presence of U(VI) in the surface oxidized layer. The sorption of Np(V) on those samples was accompanied by its partial reduction upon contact with UO$_2$ (samples). For Np(IV) a partial oxidation was observed at pH values between 4.5 and 6.5. The most oxidized sample, with the highest U(VI) content in the surface layer, despite the highest solubility, was more efficient in the sorption of Np(V).
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1. Introduction

The behavior of uranium dioxide is important while modeling radionuclide release from irradiated nuclear fuel in primary coolant circuits and in deep underground waste repositories. A first review of the published thermodynamic data of uranium compounds has been carried out by Langmuir [1]. A more recent compilation of thermodynamic data was published by Grenthe et al. [2], while an update of this work within the frame of the same NEA-

TDB project has been recently published [3]. The role of pH, *pe* and carbonate concentration on the kinetics and thermodynamics of dissolution of UO$_2$ has been reported in several papers including those by Casas et al. [4,5].

This work was focused on the study of the behavior UO$_2$ samples with different composition of surface oxidized layer. In general, the U/O system is quite complex with a variety of stoichiometric and non-stoichiometric oxides. The UO$_2$ has a fluorite type crystal lattice and is thermodynamically stable. Upon heating in reducing media at 1873 K several sub-stoichiometric oxides are formed, e.g., UO and UO$_{1.75}$. In the presence of oxygen UO$_2$ is oxidized with formation of oxide products which

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stoichiometry depends on the temperature and oxygen partial pressure [6]. At the temperatures below 423 K oxides with compositions up to $UO_{2.25}$ are formed. Absorption of oxygen by UO_2 starts at relatively low temperatures (143 K) and is accompanied by the formation of a surface oxidized layer of several tens of Angstroms. The required charge compensation is achieved through partial oxidation of U(IV) to U(VI) that leads to a decrease of the crystal lattice parameter. This surface alteration changes the properties of UO_2 samples including their solubility and sorption properties.

The aim of the present work was to study the solubility of UO_2 samples with different U(IV)/U(VI) ratios in the surface oxidized layer as well as the sorption of Np(IV) and Np(V) by those samples. Neptunium was taken since [237]Np is of a special interest for nuclear waste management. Neptunium redox chemistry is quite complex due to the presence of various states – from Np(IV) to Np(VI) for natural waters conditions. However, the most stable valence state of this element is Np(V) that is present in the form of NpO_2^+ that is rather mobile due to low charge density. Degueldre [7] developed a simple algorithm of Kd calculations for Np sorption by various oxides as a function of pH and Eh.

2. Experimental

2.1. Sample synthesis and characterization

Uranium dioxide samples were synthesized from UF_6 at different temperatures: at 898 K (Sample 1), 973 K (Sample 2), and 1073 K (Sample 3) in Ar/H_2 mixture. Samples were characterized by X-ray powder diffraction (XRD Enraf Nonius Delft) and X-ray photoelectron spectroscopy (XPS MK II VG Scientific). The particle morphology and size were characterized by dynamic light scattering (Fritsch Analysette 22), scanning electron microscopy (SEM-JEOL JSM 840A) and transmission electron microscopy (TEM-Leo 912). The pore distribution and free surface area were determined by BET technique using N_2 (ASAP-2000). Surface acidic properties were studied by potentiometric titration in $NaClO_4$ suspensions of different ionic strengths (0.001–0.1 M) under N_2 atmosphere.

2.2. Solubility experiments

The solubility of the samples was studied in J-13 reference groundwater that is a simulated low ionic

Table 1
Composition of J-13 reference groundwater [8]

Species	Concentration (mM)	Species	Concentration (mM)
Ca	0.29	SiO_2	1.07
Mg	0.072	F^-	0.11
Na	1.96	Cl^-	0.18
K	0.136	SO_4^{2-}	0.19
Li	0.009	NO_3^-	0.16
Fe	0.0008	pH	7.0
Mn	0.00002	Eh (mV)	+430
Al	0.001	CO_3^{2-}/HCO_3^-	2.81

strength groundwater with the composition presented in Table 1 [8]. Aliquots of solution were taken periodically in time, were filtered through 5 nm ultrafilters ('Vladisart', Russia) and the uranium concentration was subsequently determined by ICP-AES of the filtrated phase.

2.3. Sorption experiments

The sorption experiments with either Np(V) or Np(IV) were performed from J-13 groundwater and from deionized water as a function of pH. Solid–solution separation was performed using 5 nm ultrafiltration after which [237]Np in solution was measured using liquid scintillation spectrometry. In the experiments with Np(IV), the neptunium total concentration was maintained at 1.2×10^{-10} M and [239]Np tracer was used to increase the sensitivity of Np determination. In the case of Np(V) the total metal ion concentration was 4.0×10^{-7} M.

3. Results and discussion

The samples that were studied represent different degrees of surface oxidation. The bulk composition of the samples was studied by powder XRD and indicates that the treatment in reducing media at 973 and 1073 K leads to the formation of UO_x where x is slightly less than 2. The reported crystal lattice parameter for UO_2 is 5.4704(8) Å [6] while for Sample 1, Sample 2, and Sample 3 the corresponding values were 5.4661(2), 5.4695(4), and 5.4718(5) Å, respectively. This indicated that bulk composition of all samples was close to UO_2, however, only for Sample 1 the value of x in UO_x is higher than 2. Fig. 1 demonstrates the dependency of crystal lattice parameter upon oxygen to uranium ratio. The straight lines correspond to literature data for UO_2 and $UO_{2.25}$.
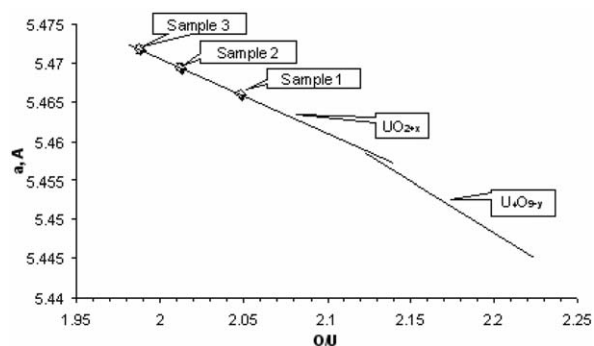
Fig. 1. The dependence of crystal lattice parameter upon O/U ratio for uranium oxides. Straight lines correspond to literature data while the points indicate experimental data for the studied samples.

Table 2
Characterization of UO_2 samples used in the experiments

Sample	Average particle size (μm)[a]	Lattice constant (Å)[b]	U(VI) on the surface $(\%)$[c]	pHpzc[d]
1	1.5	5.4661(2)	28.5 ± 2.9	6.5
2	1.9	5.4695(4)	27.0 ± 2.7	7.0
3	2.1	5.4718(5)	17.6 ± 1.8	7.0

[a] Determined by dynamic light scattering.
[b] Determined by XRD.
[c] Determined by XPS.
[d] Determined by potentiometric titration.

XPS was used to characterize the surface composition of the samples as presented in Table 2. Despite that the bulk stoichiometry of the samples was close to UO_2, their surface layer was partially oxidized and is represented by oxides with stoichiometry close to $UO_{2.25}$. The corresponding U(IV)/U(VI) ratios decrease in the following sequence: Sample 3–Sample 2–Sample 1, as presented in Table 2.

According to the dynamic light scattering data, the average particle size varied from 1.5 to 2.1 μm. For all studied samples low values of free surface area were determined by BET, they varied from 0.5 to $2.2\ m^2\,g^{-1}$ testifying that the particles were non-porous. According to potentiometric titrations, the pH of point of zero charge were different for Sample 1 compared to Sample 2 and Sample 3 as presented in Table 2. This could potentially effect the sorption of radionuclides by surface hydroxyl groups.

The solubility of UO_2 samples were studied in J-13 simulated groundwater and in deionized water
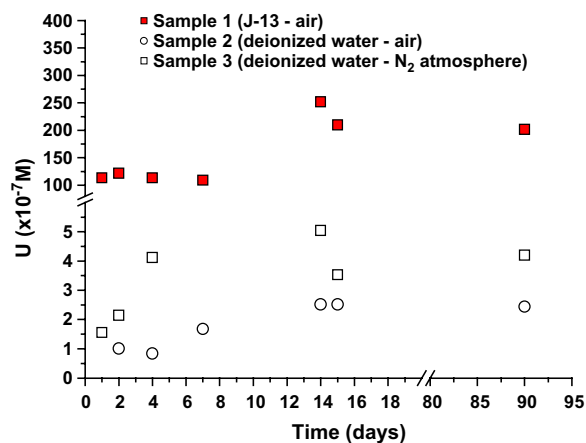

Fig. 2. Time evolution of Sample 1 apparent solubility in J-13, deionized water under N_2 atmosphere and under ambient atmospheric conditions.

under N_2 atmosphere or under ambient atmosphere. The steady state was reached in a few days as demonstrated in Fig. 2 for Sample 1. Due to the carbonate complexation of U(VI) in solution, the solubility in J-13 groundwater was significantly higher than for deionized water. The difference in solubility between aerobic and anaerobic conditions is less than the uncertainty of the values.

For the same type of leaching solution the apparent solubility increased with increasing U(VI) content in the surface oxidized layer of the samples. The U aqueous concentrations upon interaction with J-13 groundwater vary between 0.8×10^{-6} and 1.7×10^{-6} M for Sample 2 and Sample 3, while for Sample 1 this value was about 2.9×10^{-5} M. The pH dependency of U apparent solubility for Sample 1 in deionized water is shown in Fig. 3 together with
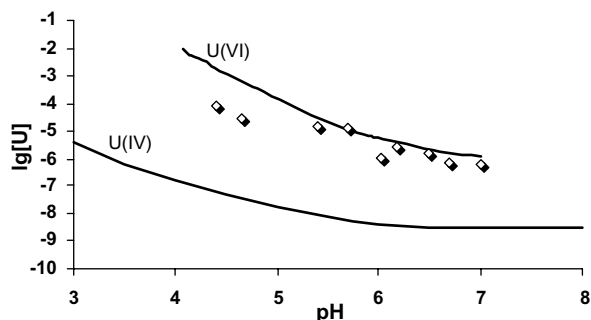

Fig. 3. The pH dependence of uranium apparent solubility in deionized water. Lines correspond to calculated curves for U(IV) and U(VI) solid oxides while the points represent experimental data for Sample 1.
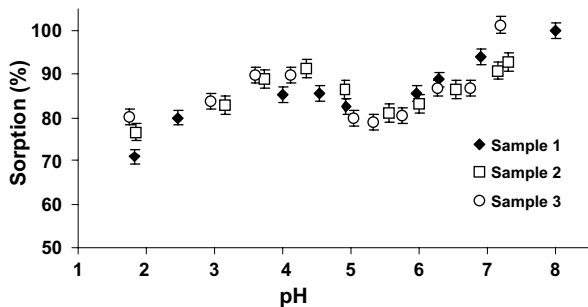
Fig. 4. The pH dependence of Np(IV) sorption by UO_2 samples (DW under N_2 atmosphere, $Eh = +50$ mV).

the calculated solubilities of UO_2 and $UO_2(OH)_2$. The experimental U concentrations are close to U(VI), however, they are systematically lower than the theoretical line that indicate influence of U(IV) on samples apparent solubility.

The sorption of Np(IV) and Np(V) was studied from deionized water (DW) under N_2 atmosphere and under ambient atmospheric conditions, and from J-13. At neutral pH values the steady state was reached in about 2 and 24 h for Np(IV) and Np(V) correspondingly for all studied solutions.

The pH dependency of Np(IV) sorption on the studied UO_2 samples is presented in Fig. 4. The sorption of Np(IV) increased with increasing of pH; however, for all samples a decrease of sorption at pH values between 4.5 and 6.5 was observed. Redox speciation of Np was performed using solvent extraction technique [9] after its leaching in 0.1 M HCl. Partial oxidation of Np(IV) into Np(V) was observed at this pH interval as presented in Table 3.

The sorption of Np(V) at neutral pH values was less than that of Np(IV) (Fig. 5). It depended on the degree of oxidation of the samples and was significantly higher for Sample 1 than for Sample 2 or

Table 3
Neptunium redox speciation on UO_2 samples

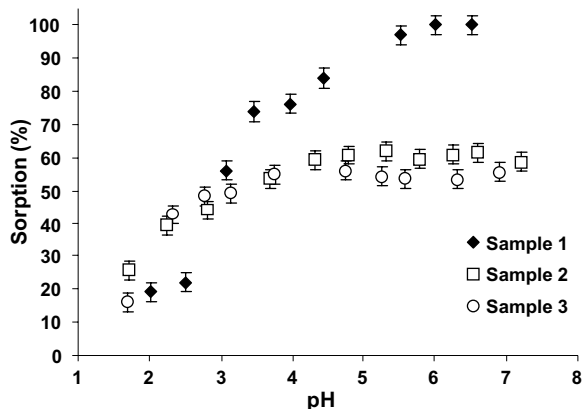| Sample	pH	Np(IV) (%)	Np(V) (%)
Initially Np(IV)			
3	3.24	93	7
3	4.40	91	9
3	5.35	59	41
3	6.27	87	13
3	7.33	86	14
Initially Np(V)			
1	7.30	64	36
2	7.37	70	30
3	7.39	71	29

Fig. 5. The pH dependence of Np(V) sorption by UO_2 samples (DW under N_2 atmosphere, $Eh = +50$ mV).

Table 4
Equilibrium distribution of Np sorbed by UO_2 samples

Sample	pH	Conditions	Sorption (%)
Initially Np(V)			
1	6.02	DW (N_2)	100 ± 3
1	6.05	DW (air)	100 ± 3
1	7.25	J-13 (air)	65 ± 3
2	6.75	DW (N_2)	59 ± 3
2	7.05	J-13 (air)	48 ± 3
3	6.59	DW (N_2)	56 ± 3
3	7.09	J-13 (air)	41 ± 3
Initially Np(IV)			
1	6.02	DW (N_2)	95 ± 3
1	7.25	J-13 (air)	79 ± 3
2	6.75	DW (N_2)	79 ± 3
2	7.05	J-13 (air)	78 ± 3
3	6.59	DW (N_2)	79 ± 3
3	7.09	J-13 (air)	82 ± 3

Sample 3. At a fixed pH value the sorption of either Np(IV) or Np(V) was higher in DW that in J-13 due to the strong carbonate complexation in the last case (Table 4). According to the redox speciation of Np on the UO_2 surface, a partial reduction of Np(V) to Np(IV) was observed as presented in Table 3. A similar reduction of Np(V) on UO_2 was observed by Albinsson et al. [10].

4. Conclusions

It was shown that the investigated UO_2 properties were dependent upon the presence of U(VI) in the surface oxidized layer that is governed by the temperature of treatment under reducing conditions. The apparent solubility of the samples with different degrees of surface oxidation varied from

about 0.8×10^{-6} to about 2.9×10^{-5} M. The apparent solubility of the samples was due to the presence of U(VI) on the surface layer and changed in the following sequence: Sample 1 > Sample 2 $\approx$ Sample 3.

The sorption of Np(V) was higher on sample for which higher U(VI) concentration was found. For all samples sorption of Np(V) accompanied by its partial reduction to Np(IV) as determined by solvent extraction. If Np(IV) is taken initially decrease of sorption was observed at pH values between 4.5 and 6.5 and was probably due to a partial oxidation of Np(IV) to Np(V). The sorption of both Np(IV) and Np(V) was higher from deionized water than from J-13 simulated groundwater.

The sorption of Np(V) was accompanied by its partial reduction to Np(IV) and was higher for Sample 1. In the case of Np(IV), a decrease of sorption was observed at pH values between 4.5 and 6.5 and was probably due to a partial oxidation of Np(IV) to Np(V). The sorption of both Np(IV) and Np(V) was higher from deionized water than from J-13 simulated groundwater may be because of the formation of carbonate complexes.

Acknowledgements

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