Sorption of Np and Tc in Underground Waters by Uranium Oxides

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Abstract –*The production of nuclear fuels results in the accumulation of large quantities of depleted uranium (DU) in the form of uranium hexafluoride (UF_6), which is converted to uranium oxides. Depleted uranium dioxide (DUO_2) can be used as a component of radiation shielding and as an absorbent for migrating radionuclides (especially ^{237}Np and ^{99}Tc). These may emerge from casks containing spent nuclear fuel (SNF) that are stored for hundreds of thousands of years in high-level wastes (HLW) and SNF repositories (e.g. Yucca Mountain Project). In this case DU oxides serve as an additional engineered chemical barrier.*

This work is a part of the joint Russian –American Program on Beneficial Use of Depleted Uranium. This paper describes the UO_2 transformations that take place in contact with various aqueous media (deionized water (DW), J-13 solution that simulates Yucca Mountain ground water, etc.) and sorption of long-lived radionuclides (^{237}Np and ^{99}Tc) from these media by depleted uranium dioxide.

Samples of depleted uranium dioxide used in this work originated from the treatment of UF_6 in a reducing media to form UO_2 (DUO_2-1 at 600 °C, DUO_2-2 at 700 °C, and DUO_2-3 at 800 °C). The investigations on DUO_2 transformations were performed under dynamic and static conditions. Increasing the DUO_2 pretreatment temperature resulted in formation of less oxidized uranium compounds. Under static conditions the solubility of the DUO_2 samples in J-13 solution is considerably higher than in DW. When the pretreatment temperature is decreased, the solubility of DUO_2 samples raises regardless of the media.

The experiments on interaction between depleted uranium dioxide and aqueous media (DW and J-13 solution) under dynamic conditions demonstrated that during 30-40 days the penetration / filtration rate of DW and J-13 solution through a thin DUO_2 layer decreased dramatically, and then slowed and stabilized. This can be explained by the forming of a secondary particulate phase that clogs the pores and reduces the filtration capacity. The filtration rate of J-13 solution through DUO_2 layer is several times lower than that of DW.

The sorption of neptunium in two valence states – Np(IV) and Np(V)- was also investigated. Various species of depleted uranium dioxide sorb Np(V) and Np (IV) from aqueous media. Equilibrium was achieved in 24 hours for Np (V) and in 2 hours for Np (IV). Increasing the pretreatment temperature leads to increased sorption . Np(V) sorption is accompanied with partial reduction of Np(V) to Np(IV), while Np (IV) sorption onto DUO_2 is accompanied by its partial oxidation to Np (V). Increasing the temperature up to 95ºC intensifies sorption. The sorption of Np(V) onto DUO_2 surfaces is irreversible.

Finally, Tc sorption experiments were carried out for two valence states of technetium – Tc(VII) and Tc(IV) . There was no significant sorption of Tc(VII) from DW and J-13 solution: However, depleted uranium oxide sorption of Tc(IV) from aqueous solutions was observed. In the pH range from 2.5 to 6, Tc(IV) sorption increases from 30 to 80%, while in neutral medium, sorption increases to 90%.

Experimental results obtained indicate that depleted uranium oxide can be successfully used as an additional chemical barrier in HLW and SNF repositories.

I. INTRODUCTION

The development of the nuclear power industry is closely related to the disposition of high-level wastes (HLW) and spent nuclear fuel (SNF). All wastes must ultimately be put into underground HLW and SNF repositories.

One of the principal safety requirements of HLW and SNF repositories is to minimize radionuclide release to the public over geological time. Two key radionuclides

that are long-lived and mobile are [237]Np and [99]Tc. SNF repositories system of multi-barriers contain radionuclides and mitigate their migration.

The use of depleted uranium (DU) as an additional geochemical barrier in SNF repositories is currently being evaluated. DU is a residual product of the enrichment process of natural uranium to produce [235]U for nuclear fuel. At present over 1.2×10^6 tons of DU with an assay of content of 0.25-0.35 wt % [235]U, in the form of toxic uranium hexafluoride (DUF_6), has accumulated worldwide. As a rule DUF_6 is stored in steel cylinders near power stations [1,2] in Russia, and at uranium enrichment plants in the U.S. It is desirable to convert the UF_6 to stable uranium oxides. It would be a significant contribution if DU oxides can be shown to substantially inhibit the transport of important actinide elements and fission products from repositories, both for the repository licensing process and for safety.

This paper describes UO_2 transformations while in contact with various aqueous media under static and dynamic conditions, and, sorption of long-lived radionuclides ([237]Np and ^{99}Tc) from these media by DUO_2 under various conditions.
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II. EXPERIMENTAL ASPECTS

II.A. Samples

The following three kinds of depleted uranium oxides were used in this work:

DUO_2-1 depleted uranium oxide was made from depleted uranium hexafluoride according to standard manufacturing techniques using the gas-flame method (at temperatures of 650°C followed by treatment in reducing conditions). The impurities (fluorine + chlorine) content was <0.0012 wt.%.

DUO_2-2 and DUO_2-3 samples containing 1.2 wt.% of fluorine were annealed, for 1 hour in reducing atmosphere at 700°C and 800°C, respectively, to remove the excess fluorine [3].

II.B. Methods

Samples were characterized by a number of methods, including dynamic light–scattering laser method in aqueous medium, transmission electron microscopy (TEM), scanning electron microscopy (SEM), X-ray phase analysis (RPA), and X-ray photoelectron spectroscopy (RHES).

The composition of the solution simulating the ground water from the J-13 well (YM repository) is given in reference [4].

The investigation on DUO_2 solubility was performed with a solid /liquid phase ratio of 0.002 g/ml under static and dynamic conditions using DW and J-13 simulated water. Experiments on pH effects were carried out in DW

during 100 days of exposure. For phase separation, a suspension was percolated through a filter system with pore a diameter of 5, 50 and 170 nm. The uranium concentration in the filtrates was analyzed using atom-emission spectroscopy

To investigate the sorption of radionuclides, a DUO_2 suspension in a liquid phase (containing various radionuclide) was prepared. The suspensions were mixed until equilibrium was achieved. To determine the amount of radionuclide sorption, the suspensions were percolated through filters with 170 nm pore diameter and a sample of the filtrate was analyzed using a liquid scintillation spectroscopy. The concentration of [237]Np(V) and [237]Np(IV) was equal to 1.2 and 4.0×10^{-7} mole/l units, respectively. The short-living [239]Np isotope was used as a nuclear tracer and the concentration of Tc(VII) was 1.5×10^{-10} mole/l and Tc(IV) was 8×10^{-9} mole/l.

III. RESULTS AND DISCUSSION

III.A. Properties of DUO₂ Samples

The average particle size of the different types of uranium dioxide samples used in this work was the following: DUO_2-1 – 1.5 microns, DUO_2-2 – 1.9 microns, and DUO_2-3 – 2.1 microns.

There was no significant difference among the various kinds of DUO_2. When the pretreatment temperature was raised, the number of large particles increased.

To determine the lattice parameters and uranium oxidation level at the surface, RFA and RPES methods were used (see Table I) . Partial oxidation of U(IV) to U(VI) was detected for all samples. In the row DUO_2-1 to DUO_2-2 to DUO_2-3 the value of oxygen /uranium ratio reduces and content of U(IV) increases.

Consequently, the pretreatment temperature of uranium dioxide significantly effects the oxygen content and U(IV) / U(VI) ratio. Pretreatment in a reducing atmosphere under higher temperatures leads to formation of less oxidized surfaces.

Table I – Parameters of various DUO_2 samples.

Sample	x in UO_{2+x}	U(IV) content, %	U(VI) content, %	a , Å
Method	RPES	RPES	RPES	RPA
DUO2-1	0,28	71,5	28,5	5,4661
DUO2-2	0,27	73,0	27,0	5,4695
DUO2-3	0,17	82,4	17,6	5,4718

III.B. DUO₂ Solubility

III.B.1. Static Conditions

The experiments on solubility in static conditions were performed in J-13 solution (aerobic atmosphere) and in DW (aerobic and nitrogen atmosphere) simulated oxidizing and reducing conditions of a repository.

Fig.1 presents kinetic curves for DUO_2-1 solubility in J-13 solution (pH=7.15) and DW (pH=6.5). The data indicate that under aerobic conditions DUO_2 solubility in DW is lower than in J-13 solution. This observation is connected with the presence of complex reagents in the J-13 solution (carbonate and fluoride ions). The leach rate of uranium after 100 days of exposure in J-13 solution is significantly higher (2.19 x 10^{-6} g/cm^2·day) than in DW (4.79 x 10^{-7} g/cm^2·day)[3].
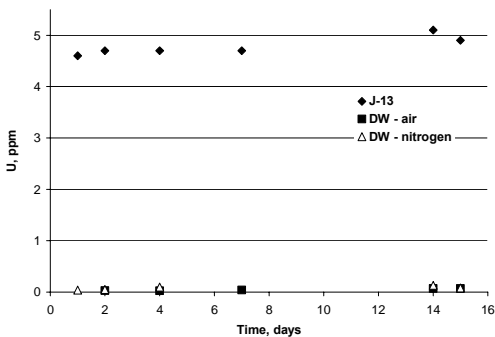
Fig.1. Solubility kinetics of DUO_2-1 in J-13 solution and DW.

Although the solubility of DUO_2-2 and DUO_2-3 in DW was lower than the sensitivity (~0,01 ppm) of our analysis method, it must be noted that the solubility of DUO_2-2 and DUO_2-3 is considerably lower than that of DUO_2-1. After 14-days of contact with J-13 simulated well , the solubility of DUO_2-2 and DUO_2-3 was equal to micro ppm; whereas, the solubility of DUO_2-1 was equal to 5 ppm. The equilibrium for the various types of DUO_2 used in this work was established over 14 days (both in DW and in J-13 solutions).

As a rule, the valence state of uranium in solution is six. It is proposed that secondary phases of U(VI) (which has a considerably higher solubility than U(IV) compounds) are formed. The main secondary phase is shoepite ($UO_2(OH)_2$) and is a primary product of DUO_2 corrosion. Its formation is more typical for DUO_2-1, in which U(VI) content is considerably higher than in DUO_2-2 and DUO_2-3.

The decrease of the uranium content in the filtrates may be indicative of the presence of uranium molecular colloids or that the suspension was filtered through filters with different pore sizes (5, 50 and 170 nm).

III.B.2. Dynamics Conditions

The investigation of the filtration of DW and J-13 solution through a thin DUO_2-1 sample layer under dynamic conditions was conducted. The experimental parameters were as following: filtration area - 8 cm^2, thickness of DUO_2-1 layer - 0.5 mm, filtration pressure – 400 millimeters of water, sample mass – 1 g. The filtration rate curves are presented in Fig. 2 for DW and J-13 solution through the thin DUO_2 layer. One can see that during 30-40 days the filtration rate decreases rapidly. Then, the filtration rate through the DUO_2 layer for both DW and J-13 solutions slows down and stabilizes. The filtration rate of the J-13 solution through the DUO_2 layer is several times lower than that of DW.
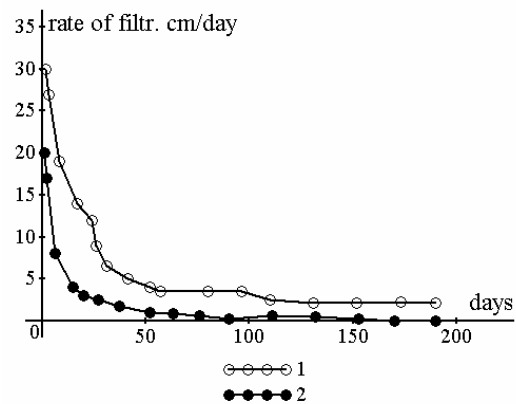

Fig.2. Filtration rate of deionized water (#1) and J-13 solution (#2) through a DUO_2-1 sample layer.

The results could be explained by "silting" of the DUO_2 filtration layer; in this case secondary phases may precipitate on the DUO_2 particles and reduce the filtration capacity. The filtration rate of J-13 solution through DUO_2 layer is several times lower than of DW.

Preliminary experimental data justify the use of highly-dispersive DUO_2 in HLW and SNF repositories, both as sorption and filtration barriers.

III.C. Neptunium Sorption onto DUO_2

[237]Np is one of most ecologically dangerous radionuclides because of its long radioactive decay half-life (2.26×10^6 years) and its high migration ability.

The most stable Np(V) form in water solutions is the dioxy-cation NpO_2^+ [5]. It is the dominant form in neutral or near neutral oxidizing environments (Eh 100-800 mV) [6].

In reducing conditions (Eh <100 mV) neptunium exists in the form of Np(IV), which could form multi-

nuclear hydrox-complexes [7]. In natural waters $Np(OH)_4$ or $NpO_2 \cdot H_2O$ are the most common compounds.

III.C.1 Kinetics

Experiments were performed in DW (nitrogen and aerobic atmosphere) and in J-13 solution (aerobic atmosphere). System equilibrium is reached in 24 hours for Np(V) and in 2 hours for Np(IV) (Figs. 3, 4).

There were no significant differences between the sorption of Np(V) from DW under nitrogen and air atmosphere ($P(CO_2)=10^{-3,5}$ atm) in spite of the possible formation of complexes between Np(V) and carbonate – ions.

In J-13 solution the dioxide solubility raises whereas Np(V) sorption decreases. Vice versa, when DUO_2 solubility goes down, sorption increases. In an anaerobic (nitrogen) atmosphere, sorption is characterized by the surface activity of the samples. The surface activity (and correspondingly the sorption) of DUO_2-1 is higher than for other kinds of depleted uranium oxide. This effect facilitates the Np(V) sorption from J-13 solution in the presence of carbonate ions [3].
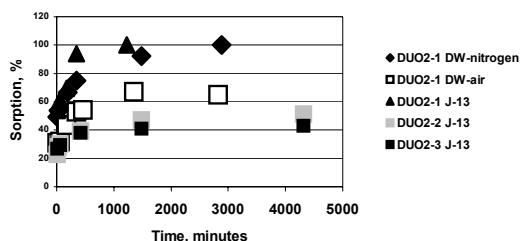
Fig.3. Sorption of Np(V) onto various DUO_2 samples
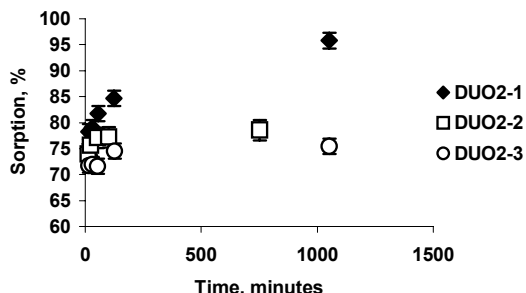
Fig.4. Sorption of Np(IV) from DW onto various DUO_2 samples

III.C.2. Temperature Effect

Considering that temperature in the YM repository could rise significantly during the first one thousand years, the dependence of Np (V) sorption on temperature (Fig. 5) was investigated.

When temperature increases, the sorption of neptunium both onto DUO_2-2, and onto DUO_2-3 also raises. This phenomenon is probably connected with the increase of superficial activity of these samples under these conditions. Considering the anti-migration properties of a DUO_2 barrier, such a relationship between sorption and temperature is favorable for radionuclide retention.
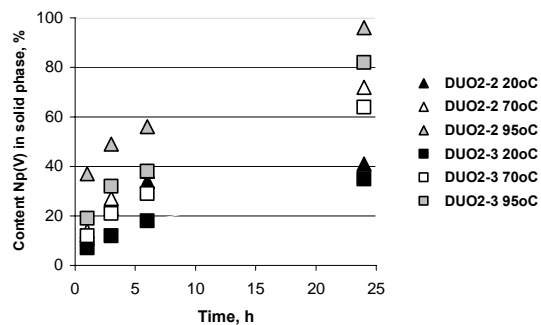
Fig.5. Np(V) sorption from J-13 solution onto DUO_2-2 and DUO_2-3 versus temperature

III.C.3. pH Effect

It is well known that if cation sorption is the result of formation of a complex on the surface (not physical absorption or ion exchange), there is a S-shaped sorption dependence on pH. It should be noted that in this case sorption under alkaline conditions is higher than in acid one. One could observe the same dependence for Np(V) sorption onto DUO_2 surfaces (Fig.6).

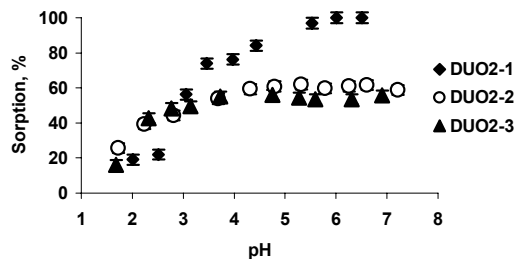Fig.6 Np(V) sorption in deionized water (nitrogen) onto DUO_2 surface versus pH

The dependence of Np(IV) sorption on pH differs from a similar Np(V) dependence (Fig.7). Under acidic conditions Np (IV) sorption is greater than Np(V) sorption. Most probably, the mechanisms for Np(IV)

sorption under acid and alkaline conditions are different. It is likely that the Np(IV)→Np(V) transition in the pH range of 4.5-7.0 have an influence on Np sorption.
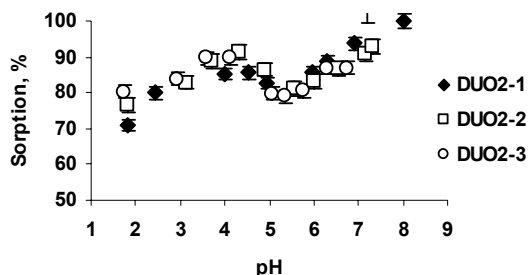

Fig. 7 - Np(IV) sorption from DW onto DUO2 surface versus pH (N_2 atmosphere)

III.C.4. Neptunium Fixation onto DUO_2

Desorption experiments using DW were performed to estimate neptunium fixation onto DUO_2 surface. The experiments lasted for 55 days. No neptunium was discovered in the desorption solutions. This fact indicates that sorption of neptunium onto DUO_2 surface, as a result of surface complex formation (not physical absorption), is irreversible.

Solid phase desorption experiments with hydrochloric acid (0.01M HCl) were carried out to determine existing forms of Np(V).

It should be noted that the desorption process from DUO_2-1 surface is faster than from DUO_2-2 or DUO_2-3 surfaces. This fact indicates different Np(V)- DUO_2 surface bonding strengths for various types of depleted uranium dioxides, may be because of the different valence states of neptunium at the DUO_2 surface.

To determine the valence of sorbed neptunium on the DUO_2 surface, a liquid extraction method was used, which indicates the presence of both Np(V) and Np(IV) complexes.

When considering DUO_2 as a geochemical barrier, the fact that uranium dioxide can reduce actinides sounds positive, because actinides with a oxidation state of 4+ are less mobile and their affinity for the solid phase is higher.

It is known that U(IV) in solution reduces Np(V) to Np(IV) [8]. The results obtained indicate that the reduction occurs not only under homogeneous conditions but also in a heterogeneous system of uranium dioxide –water solution as well.

All the aforesaid is proof that neptunium sorption onto a DUO_2 surface is a result of the formation of surface complexes. At the same time neptunium is strongly fixed at the surface of an oxide particle. During the sorption

process onto a DUO_2 surface Np(V) is partly reduced to Np(IV) and results in increased sorption.

III.D. *Technetium Sorption onto DUO_2*

The most stable ionic form of technetium in the liquid phase (Yucca-Mountain ground waters) is TcO_4. Nevertheless, it is very likely that there will be local reducing conditions in the repository resulting in the formation of Tc (IV).

Tc(VII) sorption experiments were carried out in DW and J-13 solution. Technetium (VII) was introduced into the liquid phase in the form of the pertechnetate – ion (TcO_4^-). System equilibrium was reached within three hours. During the first 24 hours, it was noticed that both in DW and in J-13 solution that there was no significant sorption of TcO_4^- onto the solid phase. After one-month of exposure at 30°C, a low Tc sorption (4-6%) was registered. But after 8-hours of rinsing with ground water, the sorbed technetium completely returned to the liquid phase.

Sorption experiments with low-valent technetium (Tc(IV)) were carried out with a solid/liquid phase ratio of 0.05 g/ml. System equilibrium was reached in 3 hours. as in the case of Tc (VII). Fig. 8 presents the sorption of Tc(IV) onto DUO_2-1 as a function of pH. Experiments were performed in a nitrogen atmosphere.
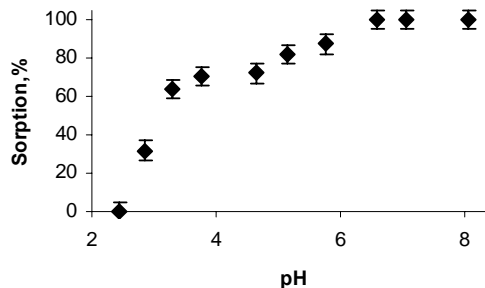

Fig.8. Tc(IV) sorption from DW onto DUO_2 surface versus pH (N_2 atmosphere)

In the pH range from 2.5 to 6.0 Tc(IV) sorption increases from 30 to 80%, and neutral medium sorption increases essentially 90%.

This data shows that depleted uranium oxide sorbs technetium from aqueous solutions.

IV.CONCLUSIONS

The use of depleted uranium dioxide as a chemical sorption barrier in HLW and SNF repositories was evaluated. Experiments were performed using three kinds of depleted uranium dioxide (DUO_2), which were prepared using different annealing temperatures (DUO_2-1 - 650°C DUO_2-2 - 700°C, and DUO_2-3 - 800°C). The conclusions from these experiments are as follows:

1) The solubility of DUO_2 in Yucca Mountain J-13 ground water and in deionized water was determined by measuring the U(VI) content in the surface layer of DUO_2. The solubility rate depends on O/U ratio.

2) The data from this work showed that in the row DUO_2-1 - DUO_2-2 - DUO_2-3 U(VI) content decrease Solubility of DUO_2- 1 is ten times higher than DUO_2-3.

3) All of the specimens of depleted uranium dioxide sorb Np(V) and Np (IV) both from DW and from solution simulating J-13 well Yucca Mountain ground water. The system was shown to equilibrate in 24 hours for Np (V) and in 2 hours for Np (IV). Increase in the DUO_2 pre-treatment temperature lead to decrease in Np sorption.

 4) Np(V) sorption is accompanied with partial reduction of Np(V) to Np(IV). Vice versa, Np (IV) sorption onto DUO_2 is accompanied with its partial oxidation to Np (V). Increasing the temperature up to 95°C intensifies the sorption process.

5) Sorption of Np(V) onto DUO_2 surfaces as a result of complex formation on the surface is irreversible.

6) Sorption experiments with low-valent technetium show that depleted uranium oxide sorbs Tc(IV) from aqueous solutions.

The results obtained indicate that depleted uranium oxide can be successfully used as a chemical and physical barrier in HLW and SNF repositories to reduce radionuclide releases in geological time.

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