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SORPTION OF LONG-LIVED RADIONUCLIDES FROM GEOLOGIC REPOSITORY UNDERGROUND WATERS BY URANIUM OXIDES

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ABSTRACT

Uranium dioxide (UO_2) from unburned nuclear fuel is present in large quantities in spent nuclear fuel geologic repositories. Furthermore, depleted uranium dioxide (DUO_2) can be used as a component of the geologic repository waste package as an absorbent for migrating radionuclides.. A potentially important use of DU oxides is to provide an additional engineered chemical barrier in the Yucca Mountain repository. If the DU oxides can be shown to substantially inhibit transport of important actinide elements and fission products, especially [237]Np and ^{99}Tc, out of the repository, then that would be a significant contribution to the repository safety. Interaction of cask material, SNF and depleted uranium dioxide with ground waters is the main natural factor, defining failure of cask and migration of radioactive products of SNF.

This work is a part of joint Russian –American Program on Beneficial Use of Depleted Uranium. It is funded by the International Scientific Technical Center (the ISTC Project #2694). The U.S. Yucca Mountian geological repository was chosen as being representative of SNF repositories, in general. The paper describes DUO_2 transformations in contact with various aqueous media (deionized water, J-13 solution - simulated Yucca Mountain ground water etc.) and sorption of long-lived radionuclides ([237]Np and ^{99}Tc) from ground waters by depleted uranium dioxide.

The samples of depleted uranium dioxide differed in the temperature of DUF_6 pretreatment in the reducing media (600°C, 700°C, and 800°C respectively). The investigation was performed in static conditions under various pH. Samples were characterized by XRD, XPS, potentiometric titration, BET analysis, TEM and SEM. Increase of the pretreatment temperature results in formation of less oxidized DU compounds. The solubility of DUO_2 samples in J-13 solution is considerably higher than in deionized water. When pretreatment temperature decreases, the solubility of DUO_2 samples raises regardless of media. Neptunium is sorbed from aqueous solutions onto all samples.

INTRODUCTION

The development of nuclear power engineering is closely connected with the problem of high-level wastes (HLW) and spent nuclear fuel (SNF) utilizing. According to conception of nuclear powers, ultimately all wastes must be put into underground HLW and SNF repositories.

One of the principal safety requirements of HLW and SNF repositories is to reduce radionuclide release in geological time. The most long-lived and mobile radionuclides are ^{237}Np and ^{99}Tc. The system of multi-barrier shielding in SNF repositories will help to solve the problem of radionuclide seepage.

Currently the problem of development of depleted uranium use as an additional geochemical barrier in SNF repositories is being evaluated. Depleted uranium is a residual product of the enrichment process of natural uranium to product ^{235}U used as nuclear fuel. At present over 1.2 10^6 tons of depleted uranium with content of ^{235}U 0.25-0.35 wt % in the form of toxic uranium hexafluoride (DUF_6) is accumulated in the world. As a rule, DUF_6 is stored in steel cylinders near power stations [1,2]. It is expedient to convert the UF_6 to stable uranium oxides. Potentially beneficial uses of DU oxides are the following: an oxidation catalyst, a radiation-shielding material, a concrete componentin casks[3-6], and, an additional engineered barrier in geological repositories. If the DU oxides can be shown to substantially inhibit transport of important actinide elements and fission products, out of a repository then that would be a significant contribution, both to the repository licensing process and to the safety of the repository
.

The preliminary data review allowed to draw the following conclusions:

- there is practically no experimental data on sorption of any radionuclides from aqueous solutions onto depleted uranium dioxide;

- in the system DU – ground waters the Np and Tc sorption would be determined by uranium (VI) compounds, formed during dissolution of depleted uranium oxides. At the same time, formation of uranium hydroxides will significantly reduce the filtration rate of ground waters through DUO_2 geochemical barrier.

- The most stable ionic form of neptunium in liquid phase (Yucca-Mountain ground waters) is NpO_2^+ due to mostly oxidation conditions in Yucca Mountain (YM) Repository.

The paper presents data on DUO_2 solution in various aqueous media and on ^{237}Np sorption from ground waters onto depleted uranium dioxide. The investigation was conducted assuming that the geochemical conditions of Yucca Mountain repository are representative of geologic repositories in general.

EXPERIMENTAL ASPECTS

Samples

Three kinds of depleted uranium oxide were used:

DUO_2-1– depleted uranium oxide was fabricated from depleted uranium hexafluoride according to manufacturing technology using gas-flame method (under temperature equal to 650-750°C with following treatment in reducing conditions). Impurities (fluorine + chlorine) content equals to <0.0012 wt.%.;

DUO_2-2 and DUO_2-3 - initially these samples contained 1,2 wt.% of fluorine. To remove the excess fluorine uranium dioxide was annealed for 1 hour in reducing atmosphere at 700°C and 800°C, correspondingly.

Methods

Particle size and their distribution were detected using dynamic light–scattering laser method in aqueous medium. Particle size range was equal 0.2 - 30 microns. Ad interim, the samples were affected by ultrasound during 30 seconds.

Preparation of DUO_2 samples for transmission electron microscopy (TEM) includes the following steps: at first aqueous suspension of powder was treated by ultrasound during 5 minutes, then suspension was applied to copper grating with 2-μm through.

The surface morphology was analyzed using scanning electron microscopy (SEM). To use this method DUO_2 powders were applied onto carbon substrate. To reduce electrostatics the samples were covered with a thin layer of aurum (~30Å).

For X-ray phase analysis (RPA) of polycrystalline samples, a focused three-shot monochromator with high resolution ($CuK_{\alpha 1}$ radiation) was used. Germanium served as a standard (a=5,6574(9)Å. Experiments were carried out at room temperature.

X-ray photoelectron spectroscopy (RHES) was conducted using electrostatic spectrometer MK II VG Scientific with AlK_{α} (1486,6 eV) exciting radiation in vacuum (P=10^{-7} Pa) at room temperature.

The composition of solution simulating ground water of J-13 well (YM repository) is shown in the table I [7].

Table I - Chemical composition of J–13 well water

Ion	J–13 well water (mg/l)
Na^+	45.8
K^+	5.04
Mg^{2+}	2.01
Ca^{2+}	13.0
SiO_2	61
HCO_3^-	128.9
SO_4^{2-}	18.4
Cl^-	7.14
NO_3^-	8.78
F^-	2.18
pH	7.41

The investigation on DUO_2 solubility was performed under static conditions in J-13 simulated water (aerobic atmosphere) and in deionized water (aerobic and nitrogen atmosphere) . Solid /liquid phase ratio was equal to 0.002 g/ml. Experiments on pH effect were carried out in deionized water during 100 days. For phase separation a suspension was percolated through filters with pore diameter, equal to 5, 50 and 170 nm. The uranium concentration in filtrates was analyzed using atom-emission spectroscopy.

To investigate sorption of radionuclides DUO_2 suspension in deionized water or J-13 solution (with radionuclide aliquot introduced into liquid phase) was prepared. Prepared suspensions were mixed until system equilibrium was achieved. To determine sorption, suspensions were percolated through filters with 170 nm pore diameter. The filtrate aliquot was measured using liquid scintillation spectroscopy. $^{237}Np(V)O_2^+$ concentration was equal to 4,0·10^{-7} mole/l, (short-living ^{239}Np was used as a nuclear tracer).

RESULTS AND DISCUSSION

Properties of DUO$_2$ samples.

Particle size distribution, specific surface.

The average particle size detected by dynamic light–scattering method in aqueous medium for different types of uranium dioxide was the following: DUO_2-1 – 1.5 microns, DUO_2-2 – 1.9 microns, DUO_2-3 – 2.1 microns (see table II)..

TEM method showed that ultrasound pretreatment of water- DUO_2 suspension resulted in formation of more regular agglomerates with smaller size.

SEM indicated that every type of DUO_2 included particles of nano-size, but their amount was rather insignificant. There was no significant difference between various kinds of DUO_2. When pretreatment temperature was raised, the number of large particles increased.

Table II - Free surface and average particle size

Sample	Free surface, m^2/g	Average particle size, microns
DUO_2-1	2.2	1.5
DUO_2-2	0.5	1.9
DUO_2-3	1.0	2.1

Volume and surface O/U ratio

There are a great number of stoichiometric oxides and solid solutions for U-O system. When UO_2 oxidizes, isostructural oxides UO_{2+x} ($0<x\leq0,25$) are formed. The oxidation rate is based on oxygen diffusion into structure of uranium dioxide (UO_2 has a cubic lattice structure of the fluorite type) . Thickness of forming oxidized layer depends on temperature. Oxygen dissolution begins under temperature equal to minus 183^0C [8], Up to t=+ 60^0C partial oxidation of surface layer occurs. When temperature exceeds + 60^0C, oxidation takes place both at surface and in volume. Oxygen penetration is accompanied by lattice parameter reduction, connected with substitution of U^{4+} to U^{6+}. Under temperature above +150^0C U_3O_7 ($UO_{2,33}$) with tetragonal lattice forms [9]. Following oxidation results in formation of $U_4O_9 \rightarrow U_3O_8$ ($UO_{2,67}$).

To determine lattice parameters and uranium oxidation level at surface RFA and RPES methods were used (see table III) . The composition of all kinds of DUO_2 is near stoichiometric UO_2, nevertheless O/U ratio reduces in the row DUO_2-1 $\rightarrow$ DUO_2-2 $\rightarrow$ DUO_2-3. It means that pretreatment in reducing atmosphere under higher temperature leads to formation of less oxidized surface

Partial oxidation of U(IV) to U(VI) is detected for all samples. In the row DUO_2-3 $\rightarrow$ DUO_2-2 $\rightarrow$ DUO_2-1 the value of oxygen coefficient increases (error of RPES method is approximately 10%).

Consequently, pretreatment temperature of uranium dioxide significantly effects the oxygen content and U(IV) / U(VI) ratio

Table III – Parameters of various DUO_2 samples.

Sample/ method	x in UO_{2+x}/ RPES	Content U(IV), %/ RPES	Content U(VI), %/ RPES	a , Å/ RPA
DUO_2-1	0.28	71.5	28.5	5.4661
DUO_2-2	0.27	73.0	27.0	5.4695
DUO_2-3	0.17	82.4	17.6	5.4718

Solubility of DUO_2

The experiments on solubility were performed under static conditions in J-13 simulated water (aerobic atmosphere) and in deionized water (aerobic and nitrogen atmosphere). This way the authors simulated oxidizing and reducing conditions of repository

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In the fig.1 curves of DUO$_2$-1 solubility in J-13 solution (pH=7,0) and in deionized water (pH=6,4) are presented. The data indicated that solubility in deionized water is lower than in J-13 solution under aerobic conditions. It is connected with the presence of complex reagents in J-13 solution (carbonate and fluoride ions). The leaching rate of uranium after 100 days exposure in J-13 solution is significantly higher ($2.19 \cdot 10^{-6}$ g/cm$^2 \cdot$day) than in deionized water ($4.79 \cdot 10^{-7}$ g/cm$^2 \cdot$day).
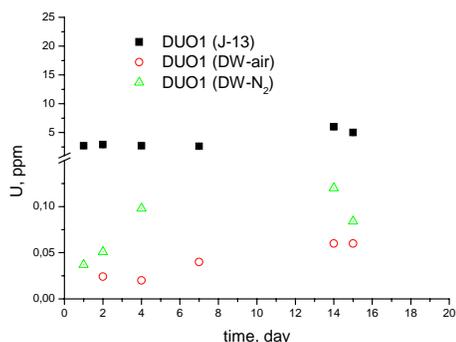
Fig.1. Solubility kinetics of DUO$_2$-1 in J-13 solution and deionized water

Solubility of DUO$_2$-2 and DUO$_2$-3 in deionized water is beyond method sensibility (~0,01 ppm). It must be noted that solubility of DUO$_2$-2 and DUO$_2$-3 is considerable, lower than that of DUO$_2$-1. After 14-days contact with J-13 simulated water, the solubility of DUO$_2$-2 and DUO$_2$-3 equals to micro ppm. Whereas, the solubility of DUO$_2$-1 is equal to 5 ppm. The system equilibrium for all types of DUO$_2$ is being settled during 14 days (both in deionized and in J-13 simulated water).

To detect the possibility of U(IV) colloid particles formation after 100-days contact of DUO$_2$ and J-13 solution (equilibrium system), the suspension was filtered through filters with different pore size (5, 50 and 170 nm). The results are presented in the table IV. The experiments indicated that in YM ground waters uranium could be present in the form of colloid particles.

Table IV Equilibrium uranium content in J-13 solution after filtration

Sample	Uranium content, ppm		
	170-nm filter	50 -nm filter	5 -nm filter
DUO$_2$-1	10,0	4,7	0,5
DUO$_2$-2	2,3	0,8	0,4
DUO$_2$-3	1,0	0,2	0,3

The decrease of uranium content in filtrates might indicate the presence of uranium molecular colloids or the formation of secondary uranium-containing phases at DUO$_2$ surface (pseudo-colloids).

Liquid extraction method testifies that uranium exists in filtrates in the form of U(VI) (see table V).

Table V. U(VI) content in J-13 solution after filtration
(DUO$_2$-1)

Filter pore size, nm	Content U(VI), %
170	70 ± 10
50	100 ± 10
5	100 ± 10

As a rule, uranium valency in solution is 6. It may be proposed that in the investigated system secondary phases of U(VI) (which solubility is considerably higher than solubility of U(IV) compounds) is formed. The main secondary phase is shoepite ($UO_2(OH)_2$) - 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.

Neptunium sorption onto DUO_2

[237]Np is one of most ecologically dangerous technogenic radionuclides because of long half-life period (2.26×10^6 years) and its high migration ability. The most stable Np(V) form in water solutions is dioxy-cation NpO_2^+ [10]. It is the dominating form in neutral or close to neutral oxidizing environments (Eh 100-800 mV) [11].

In reducing conditions (Eh <100 mV) neptunium exists in the form of Np(IV), which could form multi-nuclear hydroxo-complexes [12]. In natural waters $Np(OH)_4$ or $NpO_2 \cdot H_2O$ are the most common compounds

Kinetics
Experiments were performed in deionized water (nitrogen and aerobic atmosphere) and in J-13 solution (aerobic atmosphere). System equilibrium is reached in 24 hours for all kinds of DUO_2 (fig. 2).
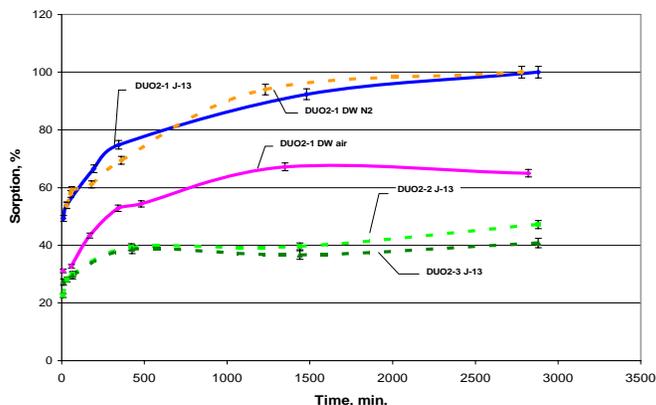
Fig.2. Neptunium sorption onto various kinds
of depleted uranium oxide.

There are no significant difference between sorption of Np(V) from deionized water under nitrogen and air atmosphere ($P(CO_2)=10^{-3,5}$ atm) in spite of possible complex formation between Np(V) and carbonate –ion.

In J-13 solution dioxide solubility raises whereas Np(V) sorption decreases. Vice versa, when DUO_2 solubility goes down, sorption increases. In anaerobic (nitrogen) atmosphere sorption is characterized by surface activity of samples. The surface activity (and correspondingly the sorption) of DUO_2-1 is higher than of other kinds of depleted uranium oxide. This effect specifies the Np(V) sorption from J-13 solution in the presence of carbonate ions.

Table VI includes data on Np(V) sorption from neutral solutions onto DUO_2 in equilibrium. Under these conditions DUO_2-1 is the best sorbent of Np(V). At the same time Np(V) sorption from deionized water is higher than from J-13 solution. This act could be explained by formation of stable complexes of Np(V) with carbonate-ions presented in J-13 solution.

Table VI. Sorption of Np(V) in equilibrium system

uranium dioxide – water solution.

Sample	Medium , pH	Np sorption, %
DUO$_2$-1	Deionized water (N$_2$), pH=6,02	100±3
	Deionized water (air) pH=6,05	100±3
	J-13 solution, pH=7,25	65±3
DUO$_2$-2	Deionized water (N$_2$), pH=6, 75	59±3
	J-13 solution, pH=7,05	48±3
DUO$_2$-3	J-13 solution, pH=7,09	41±3
	Deionized water (N$_2$), pH=6,59	56±3

Temperature effect
Considering, that temperature in the YM repository could rise [13, 7], the dependence of Np (V) sorption on temperature (fig. 3) was investigated.

When temperature increases, the sorption of neptunium both onto DUO$_2$-2, and onto DUO$_2$-3 raises too. It is probably connected with increase of superficial activity of these samples under these conditions. Considering anti-migration properties of DUO$_2$ barrier, such relationship between sorption and temperature is the positive fact.
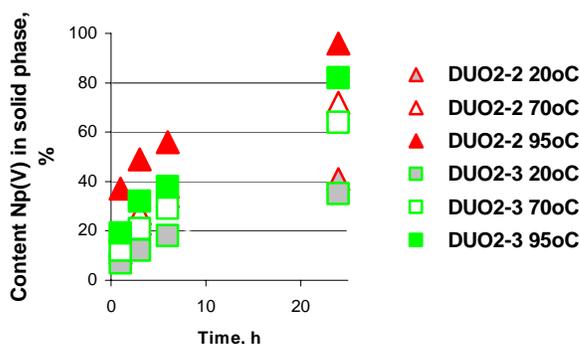
Fig.3 Np(V) sorption from J-13 solution onto DUO_2-2 and DUO_2-3 versus temperature

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pH effect

It is well known that if cation sorption is the result of complex formation on the surface (not physical absorption or ion exchange), there is a S-shaped sorption dependence on pH. It is necessary to note that in this case sorption in alkaline area is higher than in acid one. One could observe the same dependence for Np(V) sorption onto DUO_2 surface (fig.4).
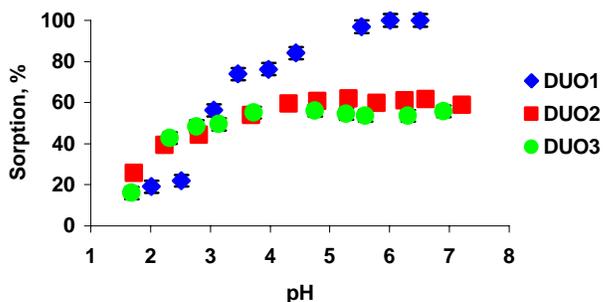
Fig.4 Np(V) sorption in deionized water (nitrogen)
onto DUO_2 surface versus pH

Neptunium fixation onto DUO_2

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

To determine existing forms of Np(V) in solid phase desorption with hydrochloric acid (0.01M HCl) was carried out.

It is necessary to note that desorption process from DUO_2-1 surface is faster in comparison with DUO_2-2 и DUO_2-3. This fact indicates different Np(V)- DUO_2 surface bonding strength for various types of depleted uranium dioxide, maybe because of different neptunium valency at DUO2 surface.

To determine valency of sorbed neptunium, a liquid extraction method was used, which indicated surface presence of both Np(V) and Np(IV) complexes..

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Considering DUO_2 geochemical barrier, the fact that uranium dioxide can reduce actinides sounds positive, because actinides with oxidation number 4+ are less mobile and their fixation in solid phase is higher.

It is known that U(IV) in solution reduces Np(V) to Np(IV) [14] The results obtained indicate that the reduction is occurred not only under homogeneous conditions but alos in heterogeneous system uranium dioxide –water solution as well. This fact indicates the necessity of further investigations of low-valency neptunium

Thus, considering the aforesaid, it is one more proof that neptunium sorption onto DUO2 surface is a result of surface complex formation. At the same time neptunium is strongly fixed at the surface of an oxide particle. During sorption process onto DUO2 surface Np(V) is partly reduced to Np(IV), and as a whole sorption raises.

In YM repository oxidizing atmosphere prevails, but there is a prosibility that YM waters will seep to the horizon located below repository to reducing conditions [12]. Recall also that there will be large amounts of iron used in the building the repository. Due to corrosion processes, magnetite (α-Fe_3O_4) formation is possible. The presence of significant amounts of Fe (II) will create local reducing conditions in which radionuclides will be in the oxidation ~~degree~~ (state?).

CONCLUSIONS

The use of depleted uranium dioxide as a geochemical shielding barrier in HLW and SNF repository was evaluated. Experiments were performed using three kinds of depleted uranium dioxide (DUO_2), which differed in temperature of reducing annealing (DUO_2-1 - 630-650°C, DUO_2-2 - 700°C, DUO_2-3 - 800°C)

The solubility of DUO_2 in Yucca Mountain ground water and in deionized water as determined by U(VI) content in surface layer wase measured.. The solubility rate depends on O/U ratio.

In the row DUO_2-1 - DUO_2-2 - DUO_2-3 U(VI) content decreases. Solubility of DUO_2- 1 is ten times higher than DUO_2-3.

All kinds of depleted uranium dioxide sorb Np(V) from deionized water and water simulating J-13 well (Yucca Mountain repository). System equilibrium occurred over a 24 hour time period
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Np(V) sorption is accompanied with partial reduction of Np(V) to Np(IV). In the system J-13 solution – a DUO_2 rise of temperature to 95°C intensifies sorption.

Np(V) sorption onto DUO2 is irreversible.

The results obtained indicate that depleted uranium dioxide show great promise as an additional geochemical barrier in HLW and SNF repositories.

Preliminary results on partial formation of Np(IV) emphasize necessity of additional experiments on sorption of Np(IV).

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