

## Sorption of $^{237}\text{Np}$ by $\text{UO}_2$ under Repository Conditions

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**Abstract** – The primary radioisotope contributor to the calculated long-term radiation dose to the public at the Yucca Mountain spent nuclear fuel (SNF) repository site boundary is neptunium-237 ( $^{237}\text{Np}$ ). Russian experiments have shown that  $\text{Np(V)}$  and  $\text{Np(IV)}$  are sorbed onto  $\text{UO}_2$ . If  $\text{Np}$  were sorbed by  $\text{UO}_2$  in spent fuel rather than being transported to the site boundary, the site boundary dose would be more than an order of magnitude lower than that calculated. Early Russian experiments also show that  $^{99}\text{Tc(IV)}$  is sorbed by  $\text{UO}_2$ . If this is so, the remaining primary contributors to site boundary dose would be  $^{129}\text{I}$  and the decay products of  $^{238}\text{U}$ . One could provide an additional barrier, a chemical barrier, to radionuclide release by surrounding the SNF with  $\text{UO}_2$ . Russian experiments indicate that a relatively thin layer of  $\text{UO}_2$  essentially stops water penetration. Such a barrier would deny water access to the SNF. Such a repository SNF configuration would provide reduced radionuclide transport from the drift as well as sorbing released nuclides from failed SNF pins.

### I. INTRODUCTION

Figure 1 shows the radioisotopic contributors to the proposed Yucca Mountain (YM) geologic repository site boundary dose to one million years. This figure, a modification of one from Ref. 1, plots both the total site boundary dose and the dose from some important radionuclides as well as the dose resulting when the  $\text{Np}$  and  $\text{Np}$  daughter contributions are subtracted. The primary contributor to the long-term (>30,000 years) site boundary dose is  $^{237}\text{Np}$ . By removing most of the  $^{237}\text{Np}$ , the calculated long-term site boundary dose would be reduced by more than an order of magnitude. The second most important contributor to site boundary dose is  $^{99}\text{Tc}$ . If both  $^{237}\text{Np}$  and  $^{99}\text{Tc}$  were removed, the remaining primary contributors to site boundary dose would be  $^{129}\text{I}$  and the decay products of  $^{238}\text{U}$ . Consequently, studies have been directed toward understanding the behavior of  $\text{UO}_2$ ,  $\text{Np}$ , and  $\text{Tc}$  in a repository environment. This work summarizes recent experiments on the sorption characteristics of  $\text{Np}$  and  $\text{Tc}$  by  $\text{UO}_2$  and the implications of these experiments.

### II. SORPTION OF $^{237}\text{Np}$ BY $\text{UO}_2$

Russian experiments have shown that  $\text{Np(IV)}$  and  $\text{Np(V)}$  are strongly sorbed onto  $\text{UO}_2$ . As  $\text{Np}$  migrates from the waste package, it goes from reducing to more oxidizing conditions that tends to convert  $\text{Np}$  from the +4 to the +5 valence state. In these experiments,  $\text{Np(IV)}$  sorption equilibrium is reached within 2 h, while  $\text{Np(V)}$  sorption equilibrium is reached within ~24 h, as shown in Fig. 2. The amount of  $\text{Np(V)}$  sorbed is determined by the degree of deprotonation of the OH-group surface.  $\text{Np(V)}$  sorption onto  $\text{UO}_2$  is nominally irreversible and is

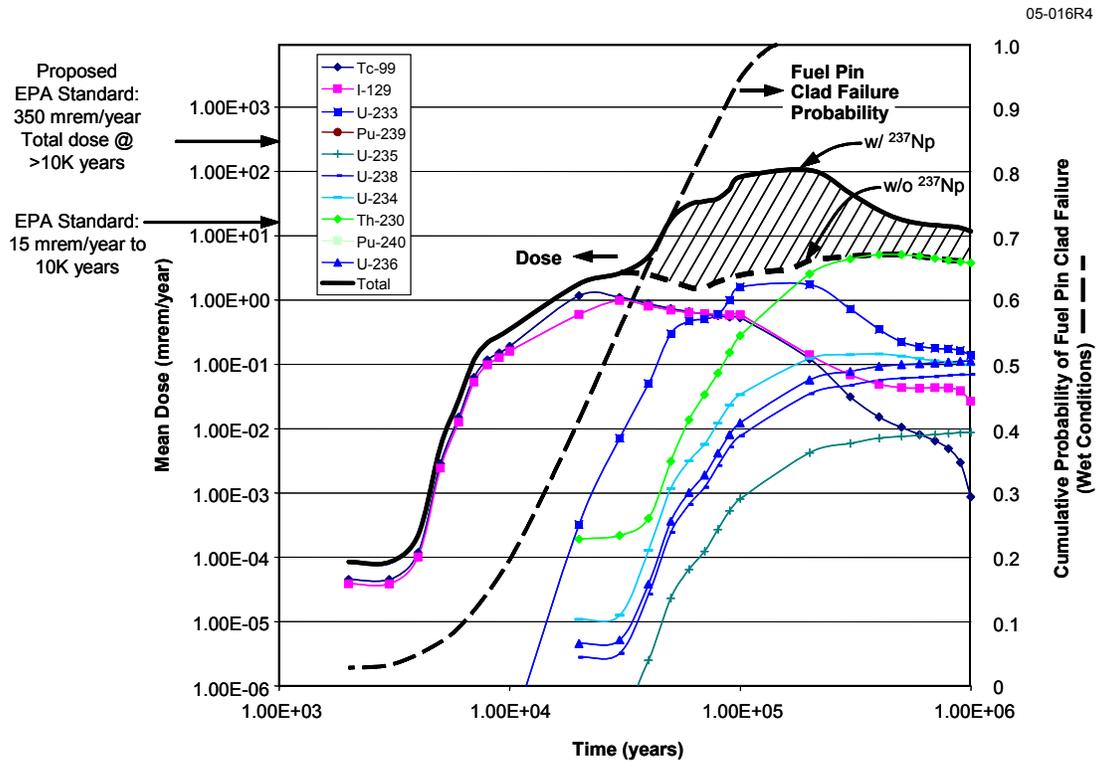
accompanied by partial reduction of  $\text{Np(V)}$  to  $\text{Np(IV)}$ . The sorption of  $\text{Np(V)}$  onto schoepite,  $(\text{UO}_2)_8\text{O}_2(\text{OH})_{12} \cdot 12(\text{H}_2\text{O})$ , (the primary product of  $\text{UO}_2$  corrosion) is less than the sorption of  $\text{Np(V)}$  onto  $\text{UO}_2$ .

Experiments involving sorption of neptunium as  $\text{Np(V)}$  and  $\text{Np(IV)}$  on samples of  $\text{UO}_2$ , prepared several different ways, have demonstrated that uranium oxides have a high potential for significantly attenuating the movement of  $\text{Np}$  in both valence states<sup>2</sup> from either dionized water (DW) or groundwater present in the repository environment (J13). In Figs. 2, 3, and 4, the DUO1 sample was prepared from  $\text{UF}_6$  by the gas-flame method (temperature 650–750°C followed by treatment in reducing conditions) with an F and Cl impurity content <0.0012 wt %. The samples designated as DUO2 and DUO3 were prepared at 700 and 800°C, respectively.

Sorption of  $\text{Np}$  in both valence states is a strong function of pH, as shown in Figs. 3 and 4.

### III. SORPTION OF $^{99}\text{Tc}$ ONTO $\text{UO}_2$

Russian experiments also show that  $^{99}\text{Tc}$ , the primary contributor to the short-term site boundary dose, is sorbed by  $\text{UO}_2$  when  $\text{Tc}$  is present as  $\text{Tc(IV)}$  (see Fig. 5).  $\text{Tc(IV)}$  may be formed by the reducing action of iron in the repository.



(Ref. Scientific and Technical Priorities at Yucca Mountain, EPRI Report No. 1003335, December 2003).

Fig. 1. Contribution of <sup>237</sup>Np to the YM total site boundary dose.

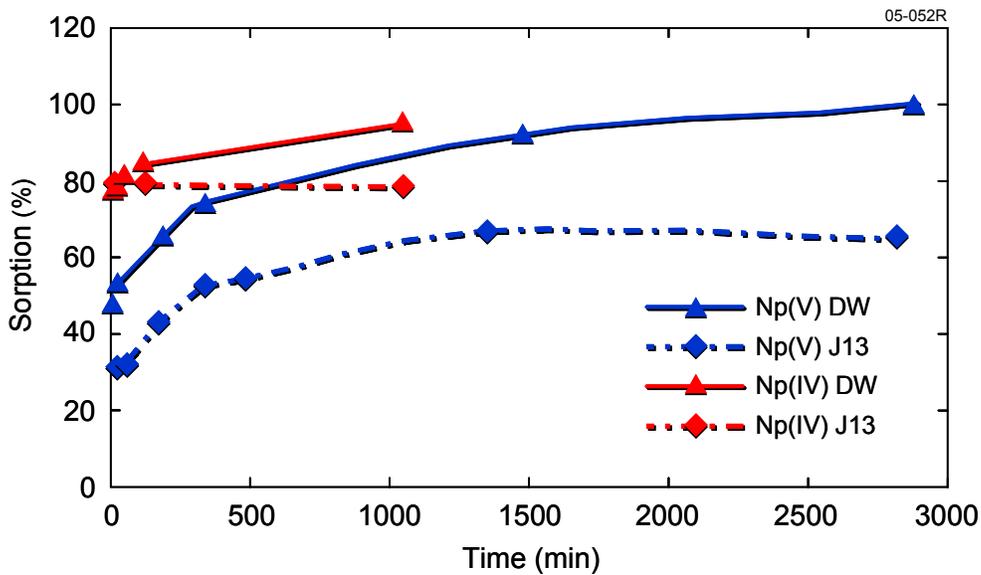


Fig. 2. Neptunium sorption onto UO<sub>2</sub>.

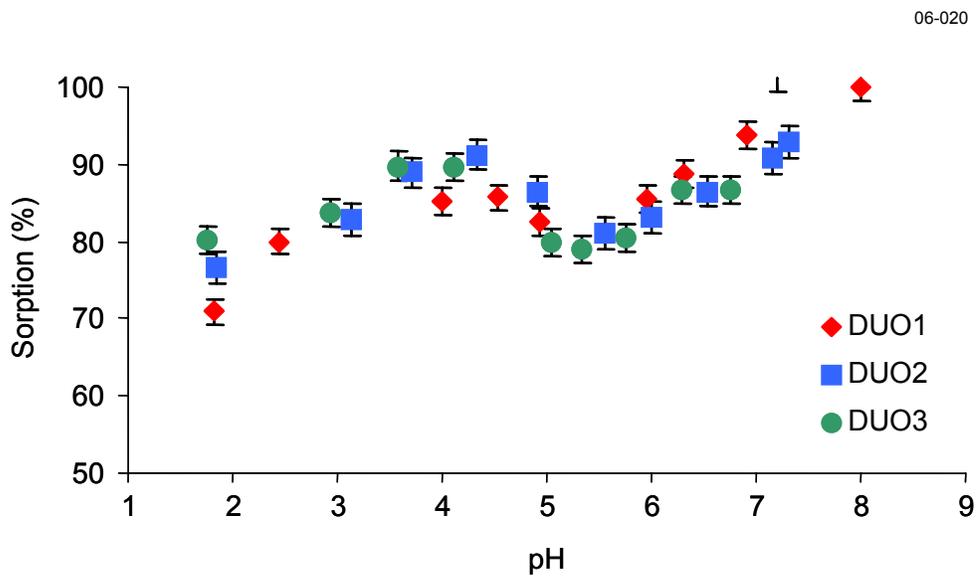


Fig. 3. Np(IV) sorption onto DUO<sub>2</sub> vs pH.

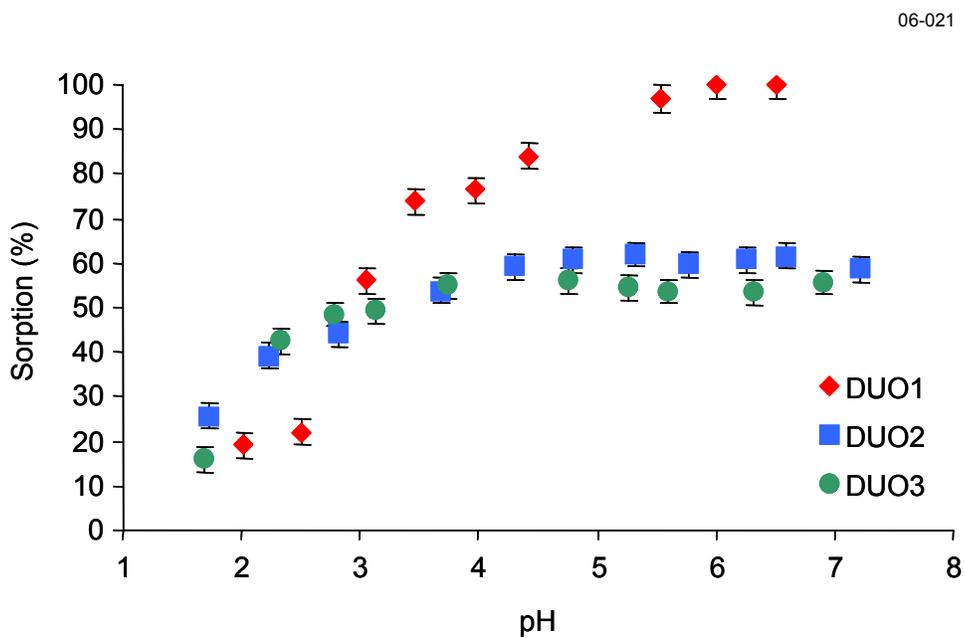


Fig. 4. Np(V) sorption onto DUO<sub>2</sub> vs pH.

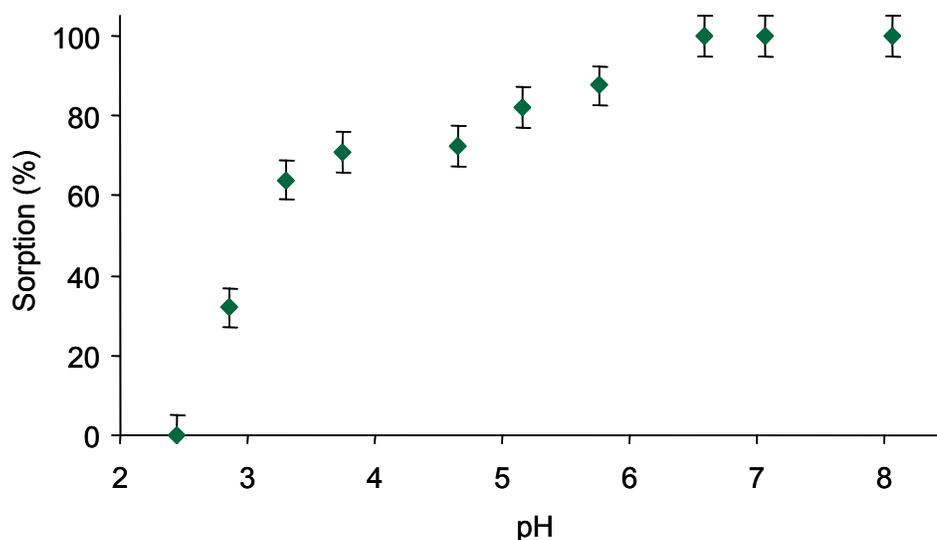


Fig. 5. Tc(IV) sorption onto DUO<sub>2</sub> surface vs. pH (in a nitrogen atmosphere).

#### IV. SOLUBILITY OF UO<sub>2</sub> IN WATER

Solubilization of the UO<sub>2</sub> would release sorbed Np, so it is important to know UO<sub>2</sub> solubility. The solubility of UO<sub>2</sub> in deionized water and YM J13 simulated water was determined by measuring the U(VI) content in the surface layer and by the O/U ratio. It was found that the solubility of UO<sub>2</sub> samples formed at lower temperatures (~700°C) is ten times greater than that formed at higher temperatures (~800°C). Fuel pellets are fired at even higher temperatures (~1200°C).

#### V. THE PENETRATION OF WATER THROUGH UO<sub>2</sub>

Russian experiments have shown that water transport through UO<sub>2</sub> slows and in a relatively short time stops almost completely (see Fig. 6). Thus, UO<sub>2</sub> in SNF, and any surrounding DUO<sub>2</sub>, may have self-sealing properties above and beyond those previously reported as being due to formation of surface compounds such as silicates.

#### VI. ADD UO<sub>2</sub> TO SNF SURROUNDINGS

Because Np and Tc radionuclides are sorbed on the UO<sub>2</sub> component of the SNF, or on engineered barriers containing UO<sub>2</sub>, this sorption could significantly attenuate

movement of the radionuclides and thus have a large effect on the radiation dose from these radioisotopes at the YM site boundary.

Experiments to date indicate that there are important potential advantages to adding UO<sub>2</sub> to the immediate surroundings of the SNF. For example, potential uses of depleted uranium (DU) in a repository or in a storage facility are as (1) a particulate fill material in the void spaces in the WP—including the SNF coolant channels,<sup>3</sup> (2) a component of a Richards barrier, and (3) a component of the invert. (The invert is the proposed support structure for the WP in the repository disposal tunnels.) The U.S. Department of Energy has a vast surplus of DU from years of uranium enrichment that will be converted to uranium oxides and that could be used in these applications. Some of the potential advantages afforded by DUO<sub>2</sub> (partially supported by the Russian experiments) are as follows:

- *Nuclear criticality control.* The DU reduces the probability of nuclear criticality over geological time by isotopic dilution with the DUO<sub>2</sub> of the low-enriched uranium in the SNF.
- *Chemically reducing conditions.* The DUO<sub>2</sub> fill helps maintain chemically reducing conditions near the SNF as the WP degrades—slowing long-term SNF degradation.

- *Solubilization minimization.* The  $\text{DUO}_2$  will saturate incoming water with uranium species before it reaches the SNF, thus minimizing solubilization of the SNF.
- *Reduced water flow.* The  $\text{DUO}_2$  may significantly reduce water flow through the degraded WP into and out of the SNF and thus may reduce radionuclide transport from the WP (see Fig. 6).
- *Pore blockage.* By blockage of the pores in  $\text{DUO}_2$  the rate of water transport may be reduced to near-zero, thus significantly reducing the rate of movement of all radionuclides to the site boundary (see Fig. 6).
- *Sorption.*  $\text{DUO}_2$  may slow the uptake and movement of Np and Tc in water by sorption/ion-exchange processes (see Figs. 2, 3, 4, and 5).

## VII. SUMMARY

It appears that  $\text{UO}_2$  present within SNF and elsewhere in the repository may sorb Np and Tc, thereby

reducing radiation dose to the public at the repository site boundary. Ongoing experiments indicate that it may be possible to surround SNF with additional  $\text{UO}_2$  (e.g., in the form of  $\text{DUO}_2$ ) to provide an additional chemical barrier to the release of these radionuclides.

## REFERENCES

1. T. V. Kazakovskaya et al., "Sorption of Long-Lived Radioisotopes in Geological Repository Underground Waters by Depleted Uranium Oxides," 10<sup>th</sup> International Conference on Environmental Remediation and Radioactive Waste Management, Glasgow, Scotland, September 4–8, 2005.
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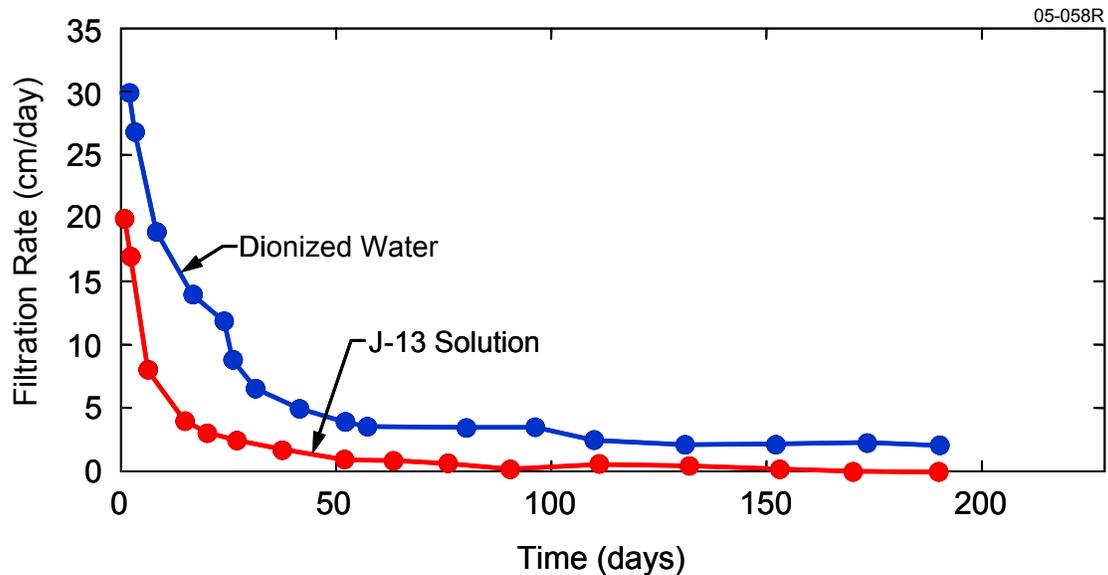


Fig. 6. Penetration of DW and J13 solutions through a thin bed of  $\text{DUO}_2$ .