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Incorporation of Neptunium(VI) into a Uranyl Selenite

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S *Supporting Information*

ABSTRACT: The incorporation of neptunium(VI) into the layered uranyl selenite Cs[$(UO_2)(HSeO_3)(SeO_3)$] has yielded the highest level of neptunium uptake in a uranyl compound to date with an average of 12(±3)% substitution of Np^{VI} for U^{VI}. Furthermore, this is the first case in nearly 2 decades of dedicated incorporation studies in which the oxidation state of neptunium has been determined spectroscopically in a doped uranyl compound and also the first time in which neptunium incorporation has resulted in a structural transformation.

A primary concern for the disposal of nuclear waste is the presence of high activity and/or long-lived radionuclides in used nuclear fuel. Among the radionuclides of greatest concern are ^{237}Np ($t_{1/2}$ = 2.14 × 10^6 years), ^{129}I ($t_{1/2}$ = 1.57 × 10^7 years), ^{135}Cs ($t_{1/2}$ = 2.30 × 10^6 years), and ^{79}Se ($t_{1/2}$ = 6.50 × 10^5 years).[1] The potential release of these radionuclides during corrosion of the waste form has led to investigations into a means of limiting their environmental mobility.[2]

Burns et al. proposed that uranium compounds that form during oxidation and corrosion of used nuclear fuel may be able to host transuranium elements and other radionuclides by incorporation into the structure via appropriate charge-balancing substitutions.[3] Several studies have shown that neptunium(V) can substitute for uranium(VI) in a variety of compounds. However, the oxidation state of neptunium has not been identified in these studies.[4] Additional studies have shown the successful incorporation of iodine and selenium oxoanions and cesium by exchange for anions or cations, respectively, within the structure.[5] Most notably, Wu et al. showed that cosubstitution of neptunium(V) and iodate increases the uptake of both species by providing an intrinsic charge balance.[6]

The uranyl selenite Cs[$(UO_2)(HSeO_3)(SeO_3)$] (CsUSeO) forms anionic layers that consist exclusively of vertex-sharing UO_2^{2+} pentagonal bipyramids and $HSeO_3^-$ and SeO_3^{2-} polyhedra.[7] Neptunium(V) and iodate cosubstitution into this compound was studied following the procedure for CsUSeO by adding NpO_2^+ and IO_3^- at 10% of the UO_3 and SeO_2 amounts, respectively.

The reaction yielded yellow prismatic crystals. Crystallographic data for the doped and undoped crystals are given in Table 1. Additional information can be found in the Supporting Information. Black crystals of molecular iodine were also observed, but these immediately dissolved upon rinsing of the product with methanol.

Table 1. Crystallographic Information for CsUSeO and CsUSeO+Np^{VI}

sample	CsUSeO	CsUSeO+Np^{VI}
descriptions	yellow plate	yellow prism
space group	$P2_1/c$ (No. 14)	$P2_1/n$ (No. 14)
a (Å)	13.8169(5)	8.4966(2)
b (Å)	10.5942(4)	10.3910(3)
c (Å)	12.5411(5)	10.2087(3)
β (deg)	100.845(2)	93.693(1)
V (Å^3)	1799.1(1)	899.44(4)
Z	8	4

This is the first observation of a structural transformation following neptunium incorporation because, while the anionic sheet topology remains the same, the compound crystallizes in a different space group when neptunium(VI) is incorporated. It is interesting to note that, in the original structure, there are two unique uranium sites, whereas in the doped structure, only one site is observed. Furthermore, it was not possible to solve the doped structure in $P2_1/c$ with two unique sites.

UV−vis−near-IR (NIR) spectra of several crystals were obtained using a microspectrophotometer. An example spectrum is shown in Figure 1. The peak occurring at 1200 nm is characteristic of neptunium(VI), indicating that the initial neptunium(V) in solution was oxidized by iodate (NpO_2^{2+} + e^-

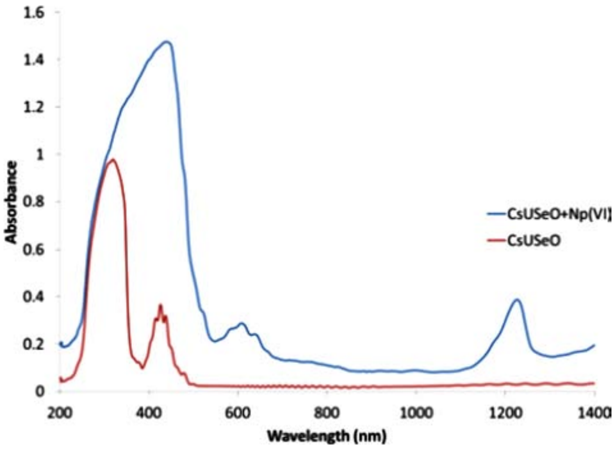

Figure 1. UV−vis−NIR spectra for CsUSeO and CsUSeO+Np^{VI}, which shows the characteristic peak for neptunium(VI) at 1200 nm.

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$\rightarrow NpO_2^+$, $E° = 1.16$ V; $2IO_3^- + 12H^+ + 10e^- \rightarrow I_2 + 2H_2O$, $E° = 1.195$ V).[9,10] The given potentials are for reactions at 25 °C and 1 atm and should only be considered as a guide because the reaction was conducted at 180 °C. This is the first study since Burns et al. first proposed neptunium incorporation in spent fuel corrosion products in which the oxidation state of neptunium doped into a uranyl compound was able to be determined spectroscopically.

Three crystals were selected for laser-ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) analysis. Because of the size of the crystals, only one ablation was conducted per sample. In a typical measurement, a 60 s background ion signal was obtained with the laser shutter in place followed by a 60 s ablation conducted at a single spot on the crystal using a 15 μm spot size. As seen in Figure 2, the neptunium signal is consistent with the signals for uranium, cesium, and selenium, indicating that it is uniformly incorporated within the structure.

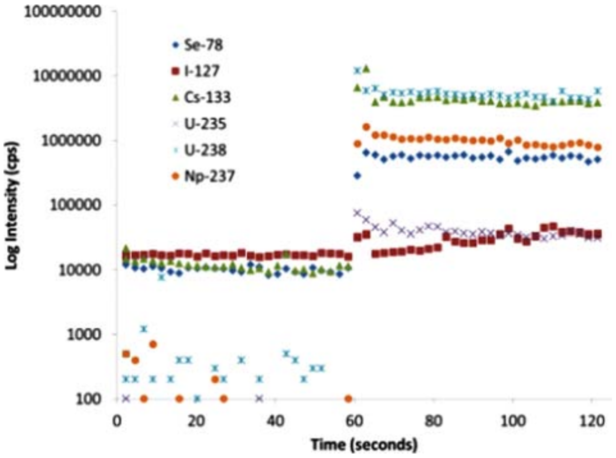

Figure 2. Typical LA-ICP-MS spectrum for CsUSeO+Np^{VI} showing the initial 60 s background with the laser shutter in place followed by the 60 s ablation measurement. The relatively flat profile of the ablation data indicates that the constituent elements are present uniformly in the crystal.

The signal intensities obtained from the LA-ICP-MS measurements were used to calculate ratios of the elements present in the crystals (Table 2). According to these results, between 10.3(±0.8)% and 16.4(±0.6)% of the uranium in CsUSeO+Np^{VI} has been replaced by neptunium. This is the highest level of neptunium uptake by a uranyl phase to date, with the previous maximum value being 7.93(±0.83)% substitution.[6] A small presence of iodine [0.33(±0.05)% to 1.5(±0.2)%] was also observed.

The high level of neptunium uptake in this compound may be attributed to the presence of neptunium(VI), as the NpO_2^{2+} cation, which may substitute directly for UO_2^{2+} in the structure without the need for a cosubstituent to maintain charge neutrality (Figure 3). NpO_2^{2+} is slightly smaller than UO_2^{2+}, which may account for the observed unit-cell transformation.[8] In fact, the doped phase adopts a unit cell similar to those of $M[(UO_2)(HSeO_3)(SeO_3)]$ (M = K, Rb, Tl, NH_4), which are isotypic with CsUSeO.[7] The axes of the doped phase are all slightly longer than those for the structures containing smaller cations, while the β angle is smaller, as would be expected with the larger Cs^+ cation.

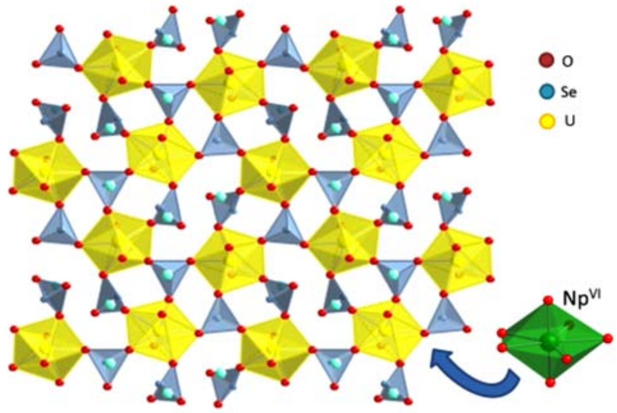

Figure 3. Illustration of the potential substitution of NpO_2^{2+} for UO_2^{2+} in CsUSeO.

Several possible mechanisms exist for the incorporation of iodine. The first could be intercalation of iodic acid into the interlayer, as has previously been observed in uranyl iodate.[9] Two other possibilities are based on the substitution of iodate for selenite. The substitution, $IO_3^- \leftrightarrow HSeO_3^-$, maintains a charge balance and results in iodate with one terminal oxygen atom. Alternatively, IO_3^- may exchange with SeO_3^{2-} with three bridging oxygen atoms. This substitution results in an excess of positive charge, which may be relieved by the stoichiometric removal of a Cs^+ cation or cosubstitution with some remaining Np^{V} for U^{VI}. Further exploration is needed to evaluate the likelihood of each of these proposals.

Neptunium incorporation in CsUSeO has revealed several new observations that have not been observed in previous incorporation studies. In addition to the highest level of neptunium uptake to date, this study is the first in which the oxidation state of neptunium was determined by UV−vis−NIR spectroscopy and also the first observation of a significant change in the unit cell parameters of the crystal structure in a doped compound. This work reinforces the critical role of

Table 2. LA-ICP-MS Results for Neptunium-Doped CsUSeO

	sample			
	Se/(U + Np)	Cs/(U + Np)	Np/(U + Np)	I/(Se + I)
CsUSeO[a]	0.38 ± 0.10	0.72 ± 0.26		
CsUSeO+Np^{VI}	0.372 ± 0.009	0.71 ± 0.06	0.164 ± 0.006	0.0056 ± 0.0007
	0.38 ± 0.01	0.71 ± 0.04	0.107 ± 0.005	0.0033 ± 0.0005
	0.34 ± 0.02	0.69 ± 0.06	0.103 ± 0.008	0.015 ± 0.002

[a] Ratio averaged from six measurements (three ablations × two crystals). Three crystals were originally analyzed; however, one fractured upon ablation, giving anomalous measurements (Se/U ≈ 0.20, for example), and was therefore excluded.

charge balance with respect to uptake levels of neptunium in uranium compounds.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details, X-ray diffraction collection parameters, laser-ablation parameters, scanning electron microscopy and optical images, energy-dispersive X-ray analysis data, and X-ray crystallographic files in CIF format for CsUSeO and CsUSeO +Np^{VI}. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Bruno, J.; Ewing, R. C. *Elements* **2006**, *2*, 343−349.

(2) (a) Finch, R. J.; Ewing, R. C. *J. Nucl. Mater.* **1992**, *190*, 133−156. (b) Forsyth, R. S.; Werme, L. O. *J. Nucl. Mater.* **1992**, *190*, 3−19. (c) Wronkiewicz, D. J.; Bates, J. K.; Gerding, T. J.; Veleckis, E.; Tani, B. S. *J. Nucl. Mater.* **1992**, *190*, 107−127. (d) Wronkiewicz, D. J.; Bates, J. K.; Wolf, S. F.; Buck, E. C. *J. Nucl. Mater.* **1996**, *238* (1), 78−95. (e) Shoewsmith, D. W. *J. Nucl. Mater.* **2000**, *282*, 1−31. (f) Finn, P. A.; Hoh, J. C.; Wolf, S. F.; Slater, S. A.; Bates, J. K. *Radiochim. Acta* **1996**, *74*, 65−71.

(3) Burns, P. C.; Ewing, R. C.; Miller, M. L. *J. Nucl. Mater.* **1997**, *245* (1), 1−9.

(4) (a) Klingensmith, A. L.; Burns, P. C. *Am. Mineral.* **2007**, *92* (11−12), 1946−1951. (b) Klingensmith, A. L.; Deely, K. M.; Kinman, W. S.; Kelly, B.; Burns, P. C. *Am. Mineral.* **2007**, *92* (4), 662−669. (c) Burns, P. C.; Deely, K. M.; Skanthakumar, D. *Radiochim. Acta* **2004**, *92* (3), 151−159. (d) Douglas, M.; Cark, S. B.; Friese, J. I.; Arey, B. W.; Buck, E. C.; Hanson, B. D.; Utsunomiya, S.; Ewing, R. C. *Radiochim. Acta* **2005**, *93*, 265−272. (e) Schuller, L. C.; Ewing, R. C.; Becker, U. *J. Nucl. Mater.* **2011**, DOI: 10.1016/j.jnucmat.2011.04.016. (f) Buck, E. C.; Finch, R. J.; Finn, P. A.; Bates, J. K. Scientific Basis for Nuclear Waste Management XXI. In*Materials Research Society Symposium Proceedings*; McKinley, I. G., McCombie, C. H., Eds.; Materials Research Society: Warrendale, PA, 1998; pp 87−94. (g) Buck, E. C.; Douglas, M.; McNamara, B. K.; Hanson, B. D. *Possible Incorporation of Neptunium in Uranyl(VI) Alteration Phases*; Pacific Northwest National Laboratory: Richland, WA, 2003.

(5) (a) Wu, S.; Chen, F.; Kang, M.; Yang, Y.; Dou, S. *Radiochim. Acta* **2009**, *97* (8), 459−465. (b) Ling, J.; Wu, S.; Chen, F.; Simonetti, A.; Shafer, J. T.; Albrecht-Schmitt, T. E. *Inorg. Chem.* **2009**, *48* (23), 10995−11001. (c) Wu, S.; Wang, S.; Simonetti, A.; Chen, F.; Albrecht-Schmitt, T. E. *Radiochim. Acta* **2011**, *99*, 573−579. (d) Chen, F.; Burns, P. C.; Ewing, R. C. *J. Nucl. Mater.* **1999**, *275* (1), 81−94. (e) Douglas, M.; Blars, S. B.; Utsunomiya, S.; Ewing, R. C. *J. Nucl. Sci. Technol.* **2002**, *3*, 504−507. (f) Burns, P. C. *J. Nucl. Mater.* **1999**, *265*, 218−223.

(6) Wu, S.; Chen, F.; Simonetti, A.; Albrecht-Schmitt, T. E. *Environ. Sci. Technol.* **2010**, *44*, 3192−3196.

(7) (a) Almond, P. M.; Albrecht-Schmitt, T. E. *Inorg. Chem.* **2002**, *41*, 1177−1183. (b) Koskenlinna, M.; Valkonen, J. *Acta Crystallogr.* **1996**, *C52*, 1857−1859.

(8) Forbes, T. Z.; Wallace, C.; Burns, P. C. *Can. Mineral.* **2008**, *46*, 1623−1645.

(9) Ling, J.; Albrecht-Schmitt, T. E. *Inorg. Chem.* **2007**, *46*, 346−347.

(10) Bray, T. H.; Ling, J.; Choi, E. S.; Brooks, J. S.; Beitz, J. V.; Sykora, R. E.; Haire, R. G.; Stanbury, D. M.; Albrecht-Schmitt, T. E. *Inorg. Chem.* **2007**, *46*, 3663−3668.