

ACTINIDE OXIDE DISSOLUTION IN TRIBUTYL PHOSPHATE

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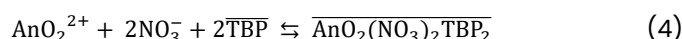
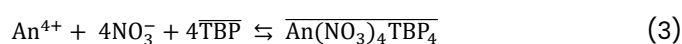
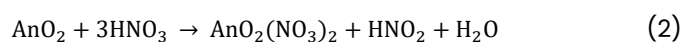
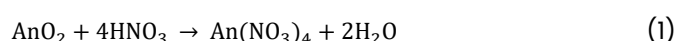
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Abstract. An alternative to dissolving used nuclear fuel (UNF) in an acidic solution during reprocessing is direct dissolution in an organic solution, which would eliminate an aqueous dissolution step, decrease the amount of nitrate needed, and reduce the facility size. The flowsheet for this potentially less expensive alternative is first to voloxidize the UNF to remove fission product gases and form an oxide. After voloxidation, the UNF is then dissolved in an organic solution containing an extractant mixed with an aliphatic diluent and pre-equilibrated with nitric acid. The organic solution then goes through a solvent extraction process to recover the uranium and/or other desired radionuclides. This work qualitatively studied the dissolution of actinide oxides (UO_2 , NpO_2 , and PuO_2) in tributyl phosphate using UV-Vis-NIR absorbance spectroscopy to ascertain dissolution behavior. Initial studies included material that is otherwise difficult to dissolve in only nitric acid, specifically CeO_2 , that is sometimes used as a dissolution surrogate for PuO_2 . This work confirmed that CeO_2 , NpO_2 , and PuO_2 are difficult to dissolve in 30 vol% TBP-dodecane pre-equilibrated with 10 M HNO_3 and will readily dissolve when co-precipitated with U (i.e., the mixed oxides U-Ce, U-Np, and U-Pu), surrogates for voloxidized nuclear fuel.

1. Introduction

Used nuclear fuel (UNF) from commercial power reactors contains approximately 95% of the initial uranium (U) after being irradiated to generate power [1]. Transuranics are formed from the neutron capture and decay of the U isotopes, which can be recovered for other applications. Reprocessing UNF with current technology, based on conventional two-phase solvent extraction, is costly. For instance, the only large-scale facility capable of reprocessing UNF in the United States is the Savannah River Site's H-Canyon, but the facility is not equipped for chopping and dissolving commercial fuels. Furthermore, the reprocessing equipment has been placed in cold standby for eventual decommission. The voloxidation of UNF, which removes the gaseous fission products, may potentially be a more economical alternative by reducing the capital and operating costs by requiring less equipment, reagent chemicals, and thermal energy.

The voloxidation process can create oxide powders, which could then be directly dissolved in an organic solution pre-equilibrated with nitric acid (HNO_3), complexed with tributyl phosphate (TBP) as a nitrate compound, and then processed using a solvent extraction flowsheet [2-4]. The limiting reagent is the HNO_3 present in the organic phase [5-7]. Eqns. 1 and 2 represent an idealized dissolution. In this case, HNO_3 does not freely dissociate in organic solutions. Instead, the HNO_3 is hydrogen-bound to TBP and is present in the organic phase after a pre-equilibration step where TBP extracts HNO_3 and reaches equilibrium. The $\text{An(IV)-NO}_3\text{-TBP}$ complex ratio will be 1:4:4 and the $\text{An(VI)-NO}_3\text{-TBP}$ complex ratio as 1:2:2, as shown in Eqns 3 and 4, respectively [8; 9]. The overhead bar denotes the organic phase and An symbolizes the actinide: U, Np, or Pu. Nitrous acid (HNO_2) has been observed to be generated during the dissolution of UO_2 [10] as shown as a product in Eqn. 2, but not for PuO_2 nor NpO_2 .



This work investigated the dissolution of several actinide oxides: UO_2 , NpO_2 , PuO_2 and mixes of U with Ce (U-Ce), Np (U-Np), and Pu (U-Pu). The mixes of U were prepared using a co-precipitation method to simulate voloxidized material. Single actinide oxides were studied as a reference point for comparison with mixed oxides. Previous studies have investigated the dissolution of U, Pu, Np, or mixed actinide oxides in supercritical carbon dioxide with TBP or pure TBP and determined the dominant oxidation states to be U(VI), Np(IV), and Pu(IV) [11; 12]. Yet, neither study tracked the actinide oxide dissolving in the organic solution via absorbance spectroscopy and within process scale conditions (i.e., 30 vol% TBP-aliphatic diluent). A previous study showed that oxides that are generally difficult to dissolve in mildly acidic conditions ($<1\text{ M HNO}_3$), like CeO_2 , would also be difficult to dissolve in 30 vol% TBP pre-equilibrated with 10 M HNO_3 (approximately 1.4 M HNO_3 in organic phase), unless co-precipitated with U [13]. As will be discussed later, this was shown to be true for NpO_2 and PuO_2 . The dissolution of these materials was tracked using a single pass transmission probe with UV-Vis-NIR capability. The final mixed solutions of CeO_2 and U-Ce were compared with x-ray fluorescence (XRF) to qualitatively illustrate the amount of Ce dissolved in both solutions.

2. Experimental

The actinide oxides (UO_2 , NpO_2 , and PuO_2) were prepared at least several years prior to this work. The UO_2 were fragments from a UO_2 pellet (i.e., not ball-milled to form a fine powder). The NpO_2 was a legacy item from HB-Line at H-Canyon at Savannah River Site and an extremely fine powder. The PuO_2 was prepared by purifying the Pu by anion exchange and precipitating with oxalic acid. The Pu oxalate solids were then calcined at $650\text{ }^\circ\text{C}$ in air for 8 h, providing a coarse PuO_2 powder with a specific surface area of $5\text{ m}^2/\text{g}$. The U-Ce, U-Np, and U-Pu were made using a hydroxide co-precipitation method and then calcined at $600\text{ }^\circ\text{C}$ in air for 2 h (the U-Pu was calcined at $450\text{ }^\circ\text{C}$ in air for 3 h) to form a mixed oxide [13]. The voloxidation process has been demonstrated to produce a fine powder, the potentially lower surface area of the mixed oxides synthesized as described would therefore be conservative [4; 14]. The mole ratios of U-Ce, U-Np, and U-Pu were approximately 1:1, 1:0.07, and 1:0.015, respectively. These mixed oxides, prepared by the co-precipitation method, were used as surrogates to represent voloxidized fuel. The starting materials for U-Ce, U-Np, and U-Pu were ceric ammonium nitrate ($\geq 98.5\%$, Fisher), uranyl nitrate hexahydrate ($\geq 98\%$, Spectrum Chemical), and dissolved neptunyl or plutonium nitrate from a previously made stock solution. The CeO_2 was obtained from Sigma Aldrich ($\geq 99.0\%$).

The organic solutions were prepared by pre-equilibrating 30 vol % TBP ($\geq 99\%$, Sigma Aldrich) diluted in *n*-dodecane ($>99\%$, Sigma Aldrich) with either 4 or 10 M HNO_3 (certified ACS plus, Fisher Chemical, diluted to target concentration with deionized water) and repeating the pre-equilibration a second time with fresh acid. The solutions were vigorously mixed for at least two minutes with a 2:1 volume ratio of aqueous to organic, respectively. Typically, the actinide oxides were added to 10 mL of organic solution and mixed using a stir bar and dissolution of the metal oxides were monitored by using a single pass transmission probe. Note, the U-Ce and UO_2 were dissolved in 100 mL of organic solution, mixed using an air sparge technique, and monitored using an *in situ* probe. In addition to the UV-Vis analysis previously used in prior work [13], the spectroscopy of the AnO_2 dissolutions also include a near-infrared (NIR) absorbance spectrometer (Avantes; Avaspec-NIR512-1.7-HSC-EVO) to monitor changes in the NIR region (900 - 1600 nm). Cerium nitrate cannot be easily quantified using the available absorbance spectrometers, as Ce(IV) has an absorbance at 320 nm [15; 16]. Therefore, XRF (Amptek, X-123SDD detector, 50 kV, 15 μA source, Ag target) was used to detect that species.

3. Results and Discussion

Cerium(IV) was used as a NpO_2 and PuO_2 dissolution surrogate to help ascertain dissolution characteristics in an organic solution. Admittedly, their dissolution chemistries are not truly analogous. However, CeO_2 , NpO_2 , and PuO_2 all do not readily dissolve at low HNO_3 concentrations in an aqueous

solution, which is approximately the same environment as 30 vol% TBP-dodecane pre-equilibrated with 10 M HNO₃ (i.e., a low HNO₃ concentration). As shown in previous work, XRF analysis detected dissolved Ce after leaving the CeO₂ in the organic solution for 7 – 8 months [13]. It is possible, but difficult to demonstrate, that the CeO₂ had consumed the available HNO₃ and stopped dissolving earlier. Separate XRF analysis of CeO₂ mixed in the organic solution for days to weeks did not detect any dissolved Ce.

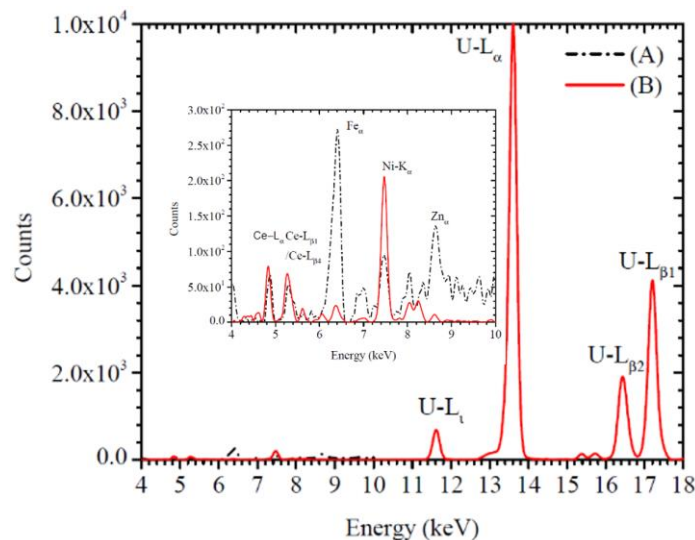


Fig. 1: The XRF of (A) CeO₂ and (B) U-Ce oxide dissolved in 30 vol% TBP-dodecane pre-equilibrated with 10 M HNO₃ and 4 M HNO₃, respectively. The inset figure is a focused portion from 4 to 10 keV to improve the resolution of the Ce peaks.

When Ce was co-precipitated with U and calcined to make Ce_{0.50}U_{0.50}O₂, the Ce was detected after being dissolved for only several hours in an organic solution pre-equilibrated with a lower HNO₃ concentration (Fig. 1). Note that the much smaller (~125x) fluorescence peaks observed for Ce compared to U can be attributed to a combination of an intrinsically lower Ce L_α fluorescence cross section (~20x for 22 keV excitation from a Ag x-ray source) and greater attenuation in the sample at the Ce fluorescence lines than the U lines [17]. Despite the differences in peak intensities, Ce and U may be present in comparable amounts in solution. This observation supports earlier findings that when a refractory oxide (i.e., CeO₂) is co-precipitated with another metal (i.e., U) to form a mixed oxide, the mixed oxide will readily dissolve.

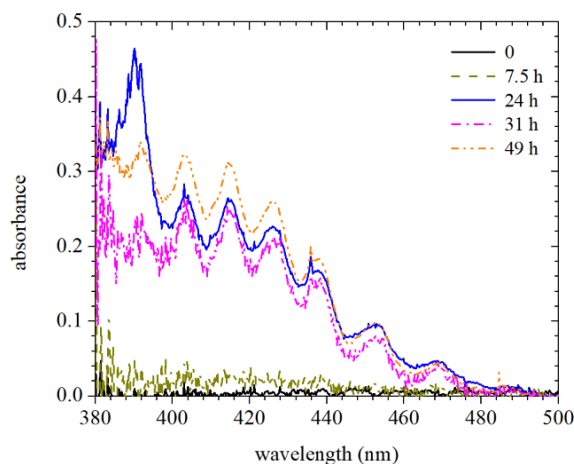


Fig. 2: Direct dissolution of UO₂ in 30 vol% TBP-dodecane pre-equilibrated with 10 M HNO₃. Note: The short time gaps (0 to 7.5 h) had active air sparge mixing and the large time gaps (7.5 to 24 h) had passive mixing.

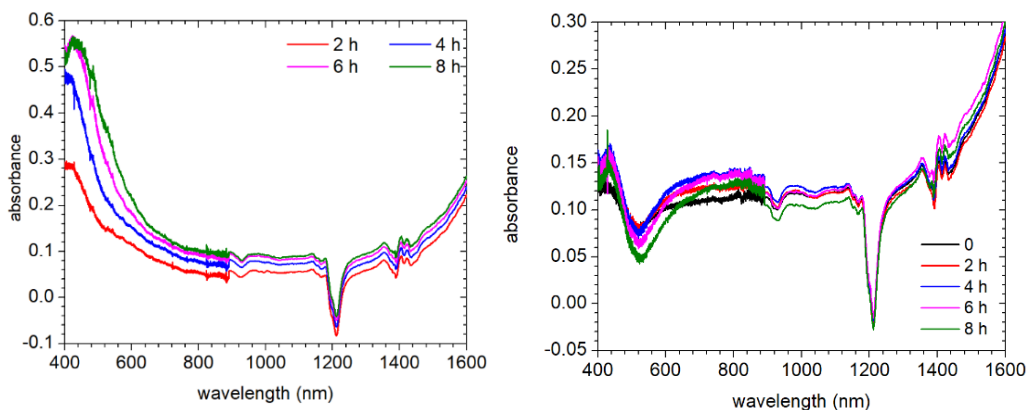


Fig. 3: Direct dissolution of NpO_2 (left) and PuO_2 (right) in 30 vol% TBP-dodecane pre-equilibrated with 10 M HNO_3 .

The UO_2 fragments dissolved slowly over time in the 30 vol% TBP-dodecane pre-equilibrated with 10 M HNO_3 , as shown in Fig. 2. It also seems that the U(IV) immediately oxidized to U(VI) when binding the TBP because a U(IV) peak was not observed around 640 nm [18]. To clarify, Fig. 2 omits the spectra past 500 nm because there were no other observed peaks. The disproportionately large peak observed at ~ 385 nm corresponds to HNO_2 being formed within the organic phase, which has been observed with other organic extractants [19; 20]. Interestingly, the UO_2 continued to dissolve overnight even without active mixing (i.e., no air sparge). The air sparge seemed to expedite the decomposition of the HNO_2 within the organic phase as the spectrum taken at the end of day showed no distinct HNO_2 peak. The HNO_2 , or a similar catalytic species, has been observed to aid in the dissolution of UO_2 and will oxidize the U(IV) [21]. The air sparging technique could therefore impact the UO_2 dissolution rate.

The spectra for the direct dissolutions of NpO_2 and PuO_2 are peculiar (Fig. 3), because while there are distinct spectral shifts, the characteristic Np and Pu peaks are not present. Albeit, the spectra of Np and Pu in organic solutions will be different from aqueous solutions, there should be distinct similarities to at least conclude a dominant oxidation state [11; 19]. The uncertain oxidation state, particularly for Np, was compounded by the interference in the NIR region from the spectral peaks for TBP- HNO_3 and TBP- H_2O near 1200 nm [22]. Separately, the dissolution spectra for NpO_2 and PuO_2 omit the region < 400 nm due to the significant noise. It is possible that HNO_2 was being formed, as seen for the UO_2 , but the spectra were inconclusive. The dissolution spectra in Fig. 3 used 30 vol% TBP-dodecane without pre-equilibration as the reference to help capture spectral changes of consumed HNO_3 and produced H_2O . Several hundred milligrams of NpO_2 and PuO_2 were previously added to 100 mL of organic solution and an aqueous bubble was observed to have formed amongst the NpO_2 undissolved solids. According to Eqns. 1 and 2, H_2O would only form when at least some of NpO_2 dissolved.

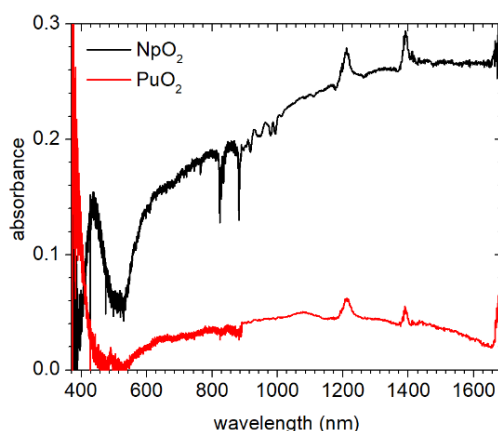


Fig. 4: Spectra of NpO_2 and PuO_2 in organic solution after one month with solids present.

It was hypothesized that a mix of oxidation states had initially formed that could explain the spectra. The Np and Pu were expected to eventually reach equilibrium and a preferred oxidation state in the organic solution. A spectrum of the solutions was acquired a month after initial dissolution with 30 vol% TBP-dodecane pre-equilibrated with 10 M HNO₃ as the reference, shown in Fig. 4. A different reference was used to help determine if the peaks at 1200 and 1400 nm were most likely due to HNO₃ being consumed and H₂O formed. Interestingly, the spectra still do not clearly indicate Np or Pu's preferred oxidation state, but do indicate dissolution.

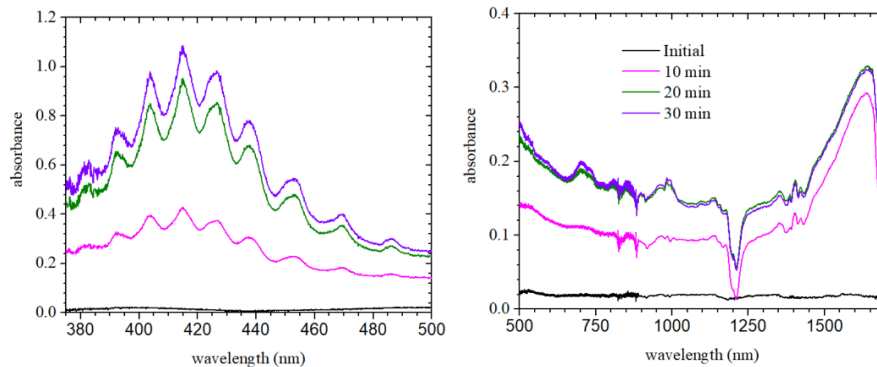


Fig. 5: Direct dissolution of U-Np in 30 vol% TBP-dodecane pre-equilibrated with 4 M HNO₃. The left figure (focused on U) and right figure (focused on Np) were scaled differently for clarity.

The mixed oxides of U-Np and U-Pu were dissolved in the organic solution to help elucidate the spectra of NpO₂ and PuO₂. As seen in Fig. 5 and 6, the Np and Pu were dissolving, along with the U, into solution. The U-Np and U-Pu readily dissolved in 30 vol% TBP pre-equilibrated with 4 M HNO₃, which was with less acid than the dissolutions of the single AnO₂ (approximately 0.7 M HNO₃ initially in the organic phase). Furthermore, Fig. 5 and Fig. 6 indicate that Np(IV) and Pu(IV) are the preferred oxidation states (+4) upon dissolution based on visible peaks around 750 nm and from 475 to 1100 nm for Np and Pu, respectively. This observation is consistent with findings in the literature [11; 12].

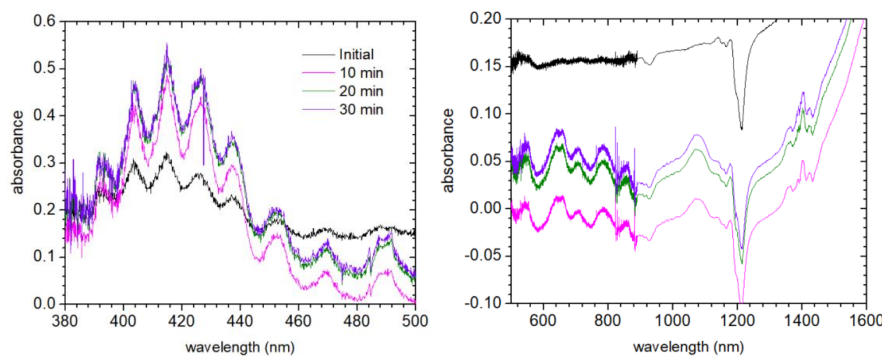


Fig. 6: Direct dissolution of U-Pu in 30 vol% TBP-dodecane pre-equilibrated with 4 M HNO₃. The left figure (focused on U) and right figure (focused on Pu) were scaled differently for clarity.

4. Conclusions

The spectra of UO₂, U-Np, and U-Pu dissolving in 30 vol% TBP-dodecane supports that U(VI), Np(IV), and Pu(IV) are primarily formed. It is therefore likely that NpO₂ and PuO₂ will also form Np(IV) and Pu(IV) while dissolving in solution at concentrations lower than can be detected with the current absorbance configuration. Mixed oxides of Np and Pu with U, formed by co-precipitation and calcination, might be more representative of solids following voloxidation and were significantly more amenable to dissolution than their single oxides. This study provides a qualitative foundation for the development of a process for the direct dissolution of voloxidized UNF in 30 vol% TBP-dodecane pre-equilibrated with nitric acid.

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