Chelates

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Glutarimidedioxime: A Complexing and Reducing Reagent for Plutonium Recovery from Spent Nuclear Fuel Reprocessing

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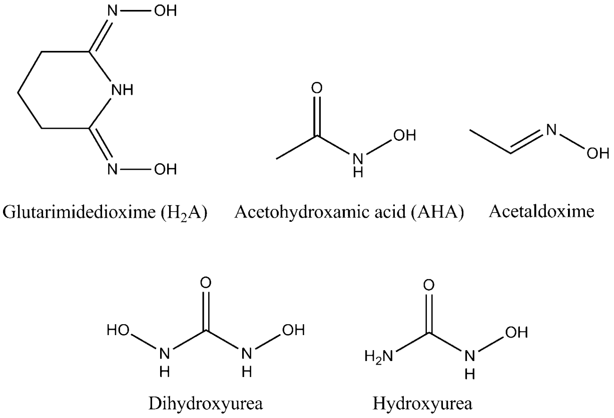
Abstract: *Efficient separation processes for recovering uranium and plutonium from spent nuclear fuel are essential to the development of advanced nuclear fuel cycles. The performance characteristics of a new salt-free complexing and reducing reagent, glutarimidedioxime (H_2A), are reported for recovering plutonium in a PUREX process. With a phase ratio of organic to aqueous of up to 10:1, plutonium can be effectively stripped from 30 % tributyl phosphate (TBP) in kerosene into 1 M HNO_3 with H_2A. The complexation-reduction mechanism is illustrated with the combination of UV/Vis absorption spectra and the crystal structure of a Pu^{IV} complex with the reagent. The fast stripping rate and the high efficiency for stripping Pu^{IV}, through the complexation-reduction mechanism, is suitable for use in centrifugal contactors with very short contact/resident times, thereby offering significant advantages over conventional processes.*

To efficiently use our natural uranium resources and to reduce the volume of high-level radioactive waste, the main components of spent nuclear fuel, that is, recyclable uranium (about 95 % in mass) and plutonium (about 1 % in mass), can be recovered by reprocessing. Furthermore, if the very small amount of long-lived minor actinides and radioactive fission products are separated during the reprocessing, the volume of high-level radioactive waste associated with geological storage can be dramatically reduced. The current method for reprocessing of commercial spent nuclear fuel is the PUREX (plutonium and uranium recovery by extraction) process, which was originally developed to extract plutonium for producing nuclear weapons, through a solvent–solvent extraction process. Uranium and plutonium are extracted independently of each other, thus leaving minor actinides and other fission products behind. In the PUREX process, a very important step is to selectively strip plutonium from the 30 % tributyl phosphate (TBP) in the kerosene (KO) phase after U and Pu coextraction. Within currently operating reprocessing plants, U/Pu separation has been conventionally achieved by the use of an aqueous-phase reductant (Fe^{II} or U^{IV}/hydrazine) to reduce Pu^{IV} to Pu^{III}. However, there are some obvious disadvantages in using either Fe^{II} or U^{IV}. The added Fe^{II} increases the amount of waste, while the use of U^{IV} increases the uranium load of the plants. Additionally, overly strong reductants, such as Fe^{II} and U^{IV}, will reduce some Np^{V} and Np^{VI} to Np^{IV}, which can be extracted with U^{VI}. Therefore, Np^{IV} will therefore follow the U^{VI} stream in the reprocessing plants and further complicate the process. Hence, an alternate method for purifying uranium products contaminated with Pu and Np is essential, preferably one with a reagent which neither adds a burden to the plants nor increases the volume of the waste.[1,2] For instance, salt-free organic reducing reagents consisting of C, H, O, and N elements may satisfy these criteria, if they can reduce Pu^{IV} to Pu^{III} efficiently. Because these salt-free organic reducing reagents and their degradation products can be completely incinerated after use, they will not increase the volume of the waste at the end.

In last two decades, considerable efforts have been made to explore new salt-free organic reagents for Pu separation in the PUREX process. Organic-phase-soluble hydroquinones and butyraldehyde have been reported as reductants for Pu^{IV} to Pu^{III} and Np^{VI} to Np^{V}. Several aqueous-phase-soluble reagents, such as hydroxylamine and its derivatives, acetohydroxamic acid, acetaldoxime, hydroxyurea, and dihydroxyurea, have also been evaluated for the reduction of Pu^{IV} and Np^{VI} in different media (Scheme 1).[3–9] Although some of these organic reagents have been very promising, the 1:1 phase ratio of organic to aqueous has always been employed in the previous studies and results in a relatively large volume



Scheme 1. Structures of some salt-free reducing reagents.

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of a Pu/Np aqueous stream which needs to be evaporated to reduce the volume for further treatment. We report another new organic reagent, glutarimidedioxime (H_2A), which demonstrates an impressive ability for stripping Pu^{IV} from 30 % TBP in kerosene.

The stripping efficiency of Pu^{IV} loaded in the organic phase increases as the H_2A concentration increases in the aqueous phase. As shown in Figure 1, with a 10:1 phase ratio of organic to aqueous, a contact time of 10 seconds, and using 0.02 M H_2A, only 23 % of Pu^{IV} can be stripped. Whereas using 0.4 M H_2A with same phase ratio results in 85 % of Pu^{IV} being stripped after a single contact. High stripping efficiency can also be obtained by increasing the times of contact or the volume of the stripping solution. For example, with a 10:1 phase ratio of organic to aqueous, a stripping efficiency of 99.5 % is achieved by two successive contacts with two aliquots of 0.4 M H_2A in 1 M HNO_3. With a 1:1 phase ratio, over 99.5 % Pu^{IV} can be stripped by 0.4 M H_2A in 1 M HNO_3. To our knowledge, this is the best result obtained thus far, in comparison with other reagents under similar reaction conditions.

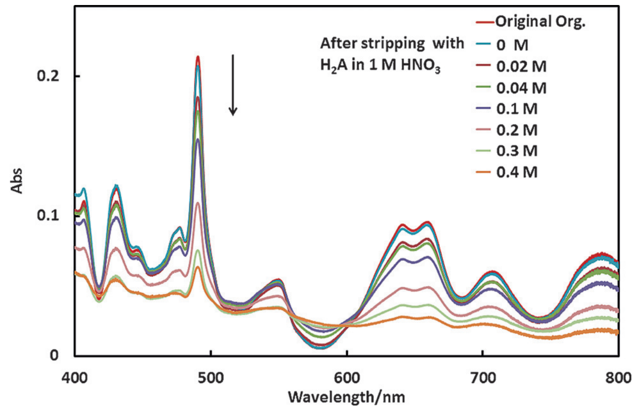


Figure 1. Spectra of Pu^{IV} ($[Pu^{IV}]_{\text{Original Org.}} = 3.4$ mM) in 30% TBP after stripping with H_2A in 1 M HNO_3 with a phase ratio of 10:1 for the organic phase to the aqueous phase.

Additionally, the stripping rate is very fast, and the efficiency varies less than 1 % when the contact time increases from 10 seconds to 2 minutes, and this is suitable for use in intensified centrifugal contactors having very short contact/resident times, thereby offering significant advantages over conventional processes. After contact with the Pu^{IV}-loaded organic phase, the aqueous solution becomes dark blue in color, thus indicating that Pu^{IV} might be reduced to Pu^{III} during the stripping. However, similar to the aqueous-soluble reduction/complexation reagents, such as acetohydroxamic acid and formohydroxamic acid reported in previous studies, the stripping efficiency of Pu^{IV} decreases with the acid concentration in the stripping solution, thus suggesting that the fast stripping might go through a complexation mechanism. H_2A as a tridentate ligand and might form hydrophilic complexes with Pu^{IV}, and at higher acid concentration the complexation with Pu^{IV} competes with protonation, thus resulting in a lower stripping efficiency.

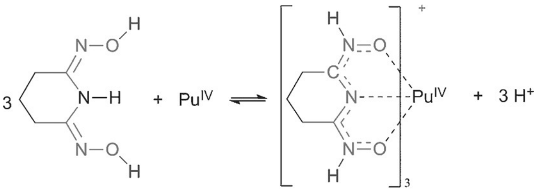
To clarify the mechanism, the complexation-reduction was also investigated in aqueous solution. When 1 mL of 1 mM Pu^{IV} in 1 M HNO_3 was mixed with 1 mL of 0.01 M H_2A in 1 M HNO_3, the mixed solution quickly changed from brown to a dark brown-blue color, and then gradually changed to a light blue color after a few hours. In contrast to this behavior with Pu^{III} as initial oxidation state, mixing 1 mM Pu^{III} in 1 M HNO_3 along with 1 mL of 0.01 M H_2A in 1 M HNO_3 immediately gave a blue-colored solution. There is no apparent difference in the absorption spectra between the two solutions of excessive H_2A mixed with Pu^{IV} and Pu^{III}, and the spectra are typical for Pu^{III} in 1 M HNO_3. However, if the acidic Pu^{III} and Pu^{IV} solutions were mixed with 20 % (v/v) pyridine in water to keep the solutions at pH 9–10 instead of 1 M HNO_3, the solutions changed color to brown, which is the typical color of Pu^{IV} in solution. Therefore, we conclude that the mechanism of the fast stripping of Pu^{IV} with H_2A mainly goes through a complexation combined with a reduction.

To further confirm the complexation-reduction stripping mechanism of Pu^{IV}, single crystals of the Pu^{IV}/A complex were grown from starting materials of the same concentration but different oxidation states of Pu. Adding 0.1 mL of 0.05 M $Pu(ClO_4)_4$ in 0.1 M HNO_3 into 0.25 mL of 20 % (v/v) pyridine in water containing 3 mg of H_2A gave a solution with a brown color, and dark brown crystal blocks formed with slow evaporation. Instead of Pu^{IV}, we started with a Pu^{III} solution, at first the mixed solution was dark blue, but then changed to brown gradually, and same brown crystal blocks formed slowly upon evaporation of the solvent.

The Pu^{IV} complex crystallizes in the $P\bar{1}$ space group with $Z = 2$.[10] The asymmetric unit contains $[Pu(HA)_3]ClO_4{\cdot}6\,H_2O$, in which all water molecules are lattice waters, and the perchlorate anions filling the tunnel along *b*-axis just serve as the counterion to the $[Pu^{IV}(HA)_3]^+$ cations. In the $[Pu^{IV}(HA)_3]^+$ complex ion, the central Pu^{IV} atom is coordinated by six oxygen and three nitrogen atoms from three HA^-, which sits at the center of a slightly distorted tricapped trigonal-prism with six oxime oxygen atoms at the corners and three imide nitrogen atoms capped on the three square faces. The two triangular faces are slightly rotated relative to each other. The Pu^{IV} center and the three capping imide nitrogen atoms are almost coplanar.

In the plutonium complex, there are two unusual and remarkable features are observed. 1) The protons of both oxime groups are rearranged from the oxygen atom to the nitrogen atom and the middle imide group is deprotonated, thus resulting in a −1 charged HA^{-1} ligand coordinating Pu^{IV} in a tridentate mode (through the two oxime oxygen atoms and the imide nitrogen atom). 2) With such an arrangement, a conjugated system is formed by delocalizing the electron density of the HA^- ligand onto the O-N-C-N-C-N-O backbone, which strongly coordinates to Pu^{IV} through two coplanar five-membered rings. The formation of the conjugated system is well illustrated by the change in the structure of the ligand in the complexation (Scheme 2).

To conclude, we have reported a new salt-free complexing and reducing reagent, glutarimidedioxime, for recovering Pu in the PUREX process. With an increased phase ratio of organic to aqueous, and possible deployment of the intensified centrifugal contactors resulting from the very fast stripping rate, using H_2A in the PUREX process might



H$_2$A Pu(HA)$_3^+$

Scheme 2. Formation of the $[Pu^{IV}(HA)_3]^+$ complex.

significantly improve the efficiency of operation and reduce the volume of high-level radioactive waste. The crystal structure of the $[Pu(HA)_3]ClO_4{\cdot}6\,H_2O$ complex provides very helpful information from which to investigate the mechanism of stripping Pu^{IV} from 30% TBP and to guide further development of new reagents for advanced fuel cycles through the understanding of chemical bonding.

Experimental Section

Spectrophotometric measurements were performed on a LAMBDA 950 UV/Vis/NIR Spectrophotometer (PerkinElmer) using a 1 cm quartz cuvette.

Stock solutions of 0.14 M Pu^{III} in 1 M $HClO_4$ and 0.14 M Pu^{IV} in 1 M $HClO_4$ were prepared by electrochemical method starting with a solution of 0.14 M Pu^{VI} in 1 M $HClO_4$. The purity of the oxidation states were over 99% confirmed with UV/Vis-NIR spectra after the solutions were diluted 100 times with 1 M $HClO_4$ (see Figure S1 in the Supporting Information). The stock solution of Pu^{IV} in 4 M HNO_3 was prepared by dissolving the precipitate of Pu^{IV} from 1 M $HClO_4$ solution with 2 M NaOH and washed twice with water (see Figure S2).

Initial organic phase solution loaded with Pu^{IV} was prepared by mixing 0.2 mL of 0.18 M Pu^{IV} in 4 M HNO_3 with 10.5 mL of 30% TBP in kerosene pre-contacted with 4 M HNO_3 twice (v/v 1:1). The stripping experiments were conducted by contacting 1 mL of organic phase with various aqueous solutions with a Vortex mixer at fixed rate. The phase separation was enforced by centrifugal immediately after the stripping experiment.

Single crystals of $[Pu(HA)_3]ClO_4{\cdot}6\,H_2O$ were prepared from a mixture of 0.1 mL of 0.05 M $Pu(ClO_4)_4$ or $Pu(ClO_4)_3$ in 0.1 M HNO_3 with 0.25 mL of 20% (v/v) pyridine in water containing 3 mg of H$_2$A by slow evaporation in a fuming-hood. A small crystal (20–50 μm) was immersed in Paratone-N oil, sealed inside a plastic capillary (inner diameter 1.5 mm), and mounted on the goniometer. The crystallographic data collection was conducted at 200 K using a Bruker APEX II CCD diffractometer on the Small-Crystal Crystallographic Beamline 11.3.1 at the Advanced Light Source of Lawrence Berkeley National Laboratory (LBNL).

Acknowledgments

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[10] Crystallographic data for $[Pu(HA)_3]ClO_4{\cdot}6\,H_2O$, $M_r = 875.98$: Brown block, $0.040\times0.040\times0.010\ mm^3$, triclinic, $P\bar{1}$, $Z=2$, $a=10.168(2)$, $b=12.3245(19)$, $c=12.884(2)$ Å, $\alpha=71.390(2)$, $\beta=75.901(2)$, $\gamma=73.625(2)°$, $V=1447.0(4)$ Å^3, $\rho_{calcd}=2.011\ g\,cm^{-1}$ ($T=150(2)$ K), $\lambda=0.7749$ Å, $\mu=3.261\ mm^{-1}$, $\theta=3.024$–33.714°, 20584 reflections collected, 8664 independent reflections ($R_{int}=0.0550$), $-14\leq h\leq14$, $-17\leq k\leq17$, $-18\leq l\leq18$, completeness ($\theta=30°$) = 99.0%, absorption correction was applied with semi-empirical methods using equivalent reflections. The data was refined against F^2, data/restraints/parameters of 8664/3/385, $R1=0.0495$ ($wR2=0.1541$, $I>2\sigma$), $R1=0.0515$, ($wR2=0.1570$, all data), GoF = 1.108, largest difference peak and hole of 2.091 and −1.820 e Å^{-3}. Intensity data were collected within one hour using Bruker Apex 2 software.[11] Intensity data integrations, cell refinement and data reduction were performed using the Bruker SAINT software package.[12] Absorption correction was made with SADABS.[13] Dispersion factors (f′and f″) at 16 keV for C, N, O, and Pu atoms were calculated using XDISP for Windows.[14] The structure was solved with direct methods using SHELXS and refined using SHELXL.[15] Non-hydrogen atoms were refined anisotropically. CCDC 1427881 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.
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