Project ID: **65378**

Project Title: **Complexants for Actinide Element Coordination and Immobiblization**

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Project Title   Complexants for Actinide Element Coordination and Immobilization
DOE Report Number
Publication Date   15 June 1999

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RESEARCH OBJECTIVE

The goal of this project is to develop inorganic metal oxide clusters known as polyoxoanions (POAs) as complexants for the immobilization of actinide (*An*) ions from high-level waste (HLW). A diverse array of rugged isopolyoxoanions, $[M_xO_y]^{z-}$, and heteropolyoxoanions, $[X_aM_bO_c]^{d-}$, comprised of M = V, Mo, W and X = Si, P polyhedra will be investigated for their ability to incarcerate *An* ions. The research combines two objectives—*An*-POA coordination and *An*-POA containment. The first involves the synthesis, isolation, and characterization of POAs that can selectively bind *An* ions to form stable *An*-POA complexes in alkaline and acidic solutions. The second involves investigations of the thermochemistry of the *An*-POA complexes under vitrification conditions germane to the formation of proposed HLW forms, such as borosilicate glass. The approach is envisioned to provide two levels of *An* encapsulation for maximum stability and durability as well as the potential to incorporate higher levels of *An* ions (particularly Pu) in waste forms than now possible. Such versatility bodes well for the potential application of POAs as *An* complexants in technology of significance to the environmental management of HLW.

RESEARCH PROGRESS AND IMPLICATIONS

This report summarizes work performed since the commencement of the project on 1 October 1998. As an overview of the research progress to-date (15 June 1999), the strategic point is that selective binding of *An* ions by POAs depends upon the *An* valence. Actinide reduction-oxidation (redox) chemistry is a pivotal property in the proposed, rational use of POAs as coordinating ligands for *An* ions. Because POAs are oxidants and the transuranium elements are multivalent, the combined redox chemistry is rich and, oftentimes, confusing. The evidence of contrasting and conflicting valence behavior makes it difficult, if not impossible, to make broad generalizations about the collective properties of *An*-POA systems without appropriate experimentation. To illustrate this chemical diversity, we have prepared actinide complexes of two well-known series of heteropolyoxoanions—the Preyssler and Wells-Dawson anions. Research highlights follow below.

Preyssler anion, $[P_5W_{30}O_{110}]^{15-}$. Our previous work has shown that the Preyssler anion exhibits a preference for trivalent *An* and lanthanide (*Ln*) ions. Because we have yet to find a direct route for the preparation of $[An^{3+}P_5W_{30}O_{110}]^{12-}$, the incorporation of actinides into the Preyssler structure is done by exchange of Na^+ in $[NaP_5W_{30}O_{110}]^{14-}$. Based upon structural evidence for $[UP_5W_{30}O_{110}]^{11-}$,[Dickman et al., *J. Cluster Sci.* **1996** 7, 567] the *An* ions are anchored to the internal surface of the tunnel by ten O atoms. Water molecules are also coordinated to *Ln/An* ions.[Soderholm et al., *J. Phys. Chem.* **1995** 99, 9611]

Work Accomplished To-Date. We first examined the reactivity and behavior of Ce because of the stability of the Ce^{3+} and Ce^{4+} aquo ions as a prelude to experiments with U, Np, Am, and Cm. Even under conditions that are well-known to stabilize Ce^{4+}, the reaction of $H_4Ce(SO_4)_4$ with $[NaP_5W_{30}O_{110}]^{14-}$ results in the formation of the Ce^{3+}-exchanged Preyssler anion $[CeP_5W_{30}O_{110}]^{12-}$. Because both Ce^{4+} and $[NaP_5W_{30}O_{110}]^{14-}$ are oxidants, the reduction of Ce^{4+} is remarkable. The reactivity of Ce stands in contrast to that of Np. Under identical conditions, the reaction of Np^{4+} with $[NaP_5W_{30}O_{110}]^{14-}$ does not lead to the encapsulation of either Np^{3+} or Np^{4+} within the molecular confines of $[P_5W_{30}O_{110}]^{15-}$. Instead, Np^{4+} is oxidized to $[NpO_2]^+$, which is not, in turn, encapsulated within the Preyssler tunnel structure. In the Np^{4+}-exchange reaction, the oxidation of Np may be catalyzed by $[NaP_5W_{30}O_{110}]^{14-}$, which is known to act as an oxidation catalyst. Under restricting conditions, the corresponding U^{4+}-exchange reaction with $[NaP_5W_{30}O_{110}]^{14-}$ is possible. Because the formal potentials indicate that Np^{4+} is more stable to oxidation than U^{4+}, we conclude that the Np^{4+}-exchange reaction should be possible. Consistent with this expectation is that, in addition to U^{4+}, Th^{4+} can be encapsulated.[Antonio et al., *J. Alloys Compd*. **1998** 271-273, 846] From our initial

experiments with hydrated actinide aquo ions, $An \cdot nH_2O$, we conclude that actinide redox chemistry, and not ionic size, is the pivotal issue with the use of the Preyssler anion for An^{3+} and An^{4+} complexation.

Wells-Dawson anion, $[\alpha\text{-2-}P_2W_{17}O_{61}]^{10-}$. A large collection of previous work has shown that this isomer readily accommodates both An^{3+} and An^{4+} ions in sandwich-like structures wherein one An is coordinated between two tetradentate $[\alpha\text{-2-}P_2W_{17}O_{61}]^{10-}$ anions. Although no crystal structures of $[An(\alpha\text{-2-}P_2W_{17}O_{61})_2]^{n-}$ (n=16 for An^{4+}, and n=17 for An^{3+}) anions are available, the An coordination is presumed to be 8-coordinate square antiprimatic. This geometry is exhibited in the crystal structures of the trivalent and tetravalent lanthanide species: $[Lu^{3+}(\alpha\text{-2-}P_2W_{17}O_{61})_2]^{17-}$ by Bartis [Ph.D. Dissertation, Hunter College of CUNY, 1997] and $[Ce^{4+}(\alpha\text{-2-}P_2W_{17}O_{61})_2]^{16-}$ by Molchanov et al.[*Sov. Phys. Crystallogr.* **1979** *24*, 96]

Work Accomplished To-Date. We examined the synthesis and properties of Ce complexes because of the stability of Ce^{3+} and Ce^{4+} ions in aqueous solutions before experimentation with U, Np, and Am. The burgundy-color Ce^{3+} complex $[Ce(\alpha\text{-2-}P_2W_{17}O_{61})_2]^{17-}$ and the yellow Ce^{4+} complex $[Ce(\alpha\text{-2-}P_2W_{17}O_{61})_2]^{16-}$ were prepared for cyclic voltammetry and bulk electrolysis measurements. Solutions of these anions are reversibly interconverted through a one-electron Ce^{3+}/Ce^{4+} redox process. Compared to the formal potential for the Ce^{4+}/Ce^{3+} couple in a noncomplexing electrolyte, the lower potential for the same couple in $[Ce(\alpha\text{-2-}P_2W_{17}O_{61})_2]^{17-/16-}$ indicates stabilization of Ce^{4+}. This stabilizing behavior was found to apply to Np^{4+}, which otherwise is rapidly oxidized by air to $[NpO_2]^+$ in water. Using the conditions employed for the Ce^{4+} studies, the reaction of Np^{4+} with two equivalents of $[\alpha\text{-2-}P_2W_{17}O_{61}]^{10-}$ produced a yellow solution and light-yellow microcrystalline solids. Optical spectroscopy results confirm the presence of Np^{4+}. Even after weeks of storage in air, oxidation of Np^{4+} was not evident. Cyclic voltammetry data revealed three redox waves. Two of these are consistent with the cyclic voltammetry of the uncomplexed $[\alpha\text{-2-}P_2W_{17}O_{61}]^{10-}$ anion. We propose that the third wave is due to the one-electron reduction of Np^{4+} to Np^{3+}, similar to the one-electron reduction of Ce^{4+} to Ce^{3+} in $[Ce(\alpha\text{-2-}P_2W_{17}O_{61})_2]^{16/17-}$. In order to probe the purported redox activity of Np^{4+}/Np^{3+} in $[Np(\alpha\text{-2-}P_2W_{17}O_{61})_2]^{16-/17-}$, optical spectra were obtained (*ex situ*) for the yellow Np^{4+} solution complex and for the deep blue solution resulting from bulk electrolysis at reducing potentials. Although no evidence was found for Np^{3+} in this experiment, we plan to exploit the technique of *in situ* XAFS spectroelectrochemistry to elucidate the Np redox speciation.

Using the conditions established from the Ce^{4+} and Np^{4+} experiments, a violet solution and microcrystalline solids of $[U(\alpha\text{-2-}P_2W_{17}O_{61})_2]^{16-}$ were obtained from the reaction of U^{4+} with two equivalents of $[\alpha\text{-2-}P_2W_{17}O_{61}]^{10-}$. Optical spectroscopy and XAFS results confirm the presence of U^{4+}. Even after months of storage in air, oxidation of U^{4+} was not evident. This indicates that U^{4+} is stabilized by coordination with the Wells-Dawson anion because, otherwise, in noncomplexing aqueous electrolytes U^{4+} is readily oxidized by air. XAFS data reveal that U^{4+} in $[U(\alpha\text{-2-}P_2W_{17}O_{61})_2]^{16-}$ has the same coordination environment in solid and solution. Cyclic voltammetry data obtained under reducing conditions show no evidence for a U^{4+}/U^{3+} redox couple. This is not entirely surprising in view of the very negative formal potential for the reduction of U^{4+}. Compared to Np^{4+}/Np^{3+} couple, U^{4+} is more difficult to reduce than Np^{4+}.

PLANNED ACTIVITIES
We plan to follow up the leads mentioned in the research progress. In addition, we will commence the second objective of the program by testing the solubility of POAs in glasses. Our initial focus will be on the immobilization of Preyssler and Wells-Dawson anion complexes. Phosphorus-31

NMR, luminescence spectroscopy, and XAFS will be employed to characterize the solid glass forms and solution precursor *An*-POA complexes.

INFORMATION ACCESS
None.

OPTIONAL ADDITONAL INFORMATION
None.

OPTIONAL PROPRIETARY INFORMATION
None.