EMSP Project 65378 Annual Report

Progress Report

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, Nb, Mo, W and X = Si, P polyhedra are under investigation 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 prospective applications of POAs as *An* complexants in technology of significance to the environmental management of HLW.

Research Progress And Implications

This project summary report provides a synopsis of work performed since the first annual report (15 June 1999) through 30 June 2000. While continuing along previous lines of research with the Wells-Dawson and Preyssler POAs, we have begun to investigate two new avenues of polyoxometalate chemistry. Specifically, the hexaniobate isopolyoxoanion, $[Nb_6O_{19}]^{8-}$, is being investigated because of reports of its stability under highly alkaline conditions. This stability is being exploited for the selective binding and stabilization of *An* ions in basic solution. And, the thermal behavior of *An*-POA complexes is being investigated with regard to their incorporation into borosilicate glass. As an overview of the research progress during this period, selected highlights follow.

Wells-Dawson Heteropolyoxoanion, $[P_2W_{17}O_{61}]^{10-}$. The α-1 and α-2 isomers of the monovacant Wells-Dawson heteropolyoxoanion, $[P_2W_{17}O_{61}]^{10-}$, are complexants of trivalent rare-earth (*RE*) ions, and are known to stabilize otherwise reactive tetravalent lanthanide (*Ln*) and actinide (*An*) ions. In proposed as well as applied practice relating to nuclear waste processing, the α-2 isomer provides *An* valence-control through the formation of stable complexes, $[An(IV)(\alpha\text{-}2\text{-}P_2W_{17}O_{61})_2]^{16-}$, in aqueous solution. This behavior is exploited to facilitate separation of trans-plutonium elements from trivalent *RE* elements. Yet, remarkably, there is a dearth of information about the molecular structure and coordination of *RE* and *An* ions with $\alpha\text{-}2\text{-}[P_2W_{17}O_{61}]^{10-}$. Moreover, no *An* complexes of $\alpha\text{-}1\text{-}[P_2W_{17}O_{61}]^{10-}$ are known. Insights about the structural aspects of *Ln* and *An* coordination with the α-1 and α-2 isomers are what interest us for both fundamental and practical reasons. Issues of *Ln* binding, complexation, and hydration were addressed through use of X-ray crystallography, XAFS (X-ray absorption fine structure), and optical luminescence. We obtained full metrical information about the *Ln*(III) coordination environment and hydration in two types of stoichiometric complexes—$[Ln(\alpha\text{-}1\text{-}P_2W_{17}O_{61})]^{7-}$ and $[Ln(\alpha\text{-}2\text{-}X_2W_{17}O_{61})_2]^{17-}$ (for *Ln* ≡ Sm, Eu, Lu; X ≡ P, As). All the *Ln* ions are 8 coordinate with oxygen atoms in a square antiprism arrangement. For the 1:1 stoichiometric *Ln*:$\alpha\text{-}1\text{-}[P_2W_{17}O_{61}]^{10-}$ complexes, the *Ln* ions are bound to 4 O atoms of the polyoxometalate framework in addition to 4 O atoms from water molecules as $[(H_2O)_4Ln(\alpha\text{-}1\text{-}P_2W_{17}O_{61})]^{7-}$. This structure is the first of its kind for any metal complex of α-1-$[P_2W_{17}O_{61}]^{10-}$, and the XAFS data indicate that the general stoichiometry $[(H_2O)_4Ln(\alpha\text{-}1\text{-}P_2W_{17}O_{61})]^{7-}$ is maintained throughout the lanthanide series. For the 1:2 stoichiometric *Ln*:α-2-$[X_2W_{17}O_{61}]^{10-}$ complexes, no water molecules are in the *Ln*-O_8 coordination sphere. The *Ln* ions are bound to 8 O atoms—four from each of two heteropolyanions—as $[Ln(\alpha\text{-}2\text{-}X_2W_{17}O_{61})_2]^{17-}$. The average *Ln*-O interatomic distances decrease across the lanthanide series, consistent with the decreasing *Ln* ionic radius.

The technological implications for use of POAs, in general, and of $[P_2W_{17}O_{61}]^{10-}$, in particular, in HLW processing operations depend largely upon the strength and stability of *Ln*– and *An*–POA interactions. The high charge-to-size ratio of *Ln* and *An* cations enhances their binding with $[P_2W_{17}O_{61}]^{10-}$ even in the presence of other cations, including transition metals and Na^+, and other anions, including nitrate, which are often present in high concentrations in tank waste. The α-2-$[P_2W_{17}O_{61}]^{10-}$ isomer, like many other POAs, is a robust ligand. As testimony to their thermodynamic stability, POAs are presently used in commercial catalytic processes, and the technology for bulk-quantity, high-yield syntheses is available today. For the most part, POAs are prepared by self-assembly, protonation and condensation reactions, and are relatively inexpensive.

Hexaniobate Isopolyoxoanion $[Nb_6O_{19}]^{8-}$. This anion and its tantalum analog, $[Ta_6O_{19}]^{8-}$, are quite possibly the only two POAs that are stable in basic, highly alkaline solutions. Because much of the aqueous tank waste stored at DOE sites is alkaline in nature, the aim of this research was to prepare $[M_6O_{19}]^{8-}$ anions and to determine how they react with actinide ions, particularly neptunium. Alkaline conditions are generally employed to prepare and maintain high oxidation states, like Np(VI) and Np(VII), that are otherwise less stable under neutral and acidic conditions. High-valent Np aquo ions were chosen for initial experimentation for two reasons: (1) their preparation is facilitated in aqueous alkali metal hydroxides by ozonolysis or electrolysis, and (2) they decompose in aqueous hydroxide solutions in the absence of O_3 or controlled electrochemical potentials. We found evidence to suggest that the basic hexaniobate anion reacts with Np to form a coordination complex. Initial indications also suggest that uranium reacts with $[Nb_6O_{19}]^{8-}$. Difficulties in the isolation of solid complexes remain to be understood and resolved. The results from optical spectroscopy and cyclic voltammetry data are inconclusive concerning the stoichiometry and valence of Np and U in the purported complexes with the hexaniobate anion.

Preyssler Heteropolyoxoanion, $[P_5W_{30}O_{110}]^{15-}$, Glass Chemistry. The behavior of *An*-POA complexes under vitrification conditions germane to the formation of borosilicate glass is largely unexplored. We have begun to test the solubility of polyoxoanions in glass. Our initial experiments focused on the immobilization of the Eu-encrypted Preyssler heteropolyoxoanion complex, $[Eu(III)P_5W_{30}O_{110}]^{12-}$. Glasses with 1 and 5 wt. % of $[EuP_5W_{30}O_{110}]^{12-}$ were prepared at 1500 ºC in small Pt crucibles. Depending upon conditions, both blue and colorless glasses were formed. No crystalline phases were observed by powder XRD (X-ray diffraction) in the polyoxoanion-doped glasses. In order to determine if the $[EuP_5W_{30}O_{110}]^{12-}$ cluster dissolved in the glass, we collected SAXS (small angle X-ray scattering) data. The initial results suggested two possibilities: (1) dissolution of the POA without phase segregation; (2) decomposition of the POA and dissolution of its decomposition products (without phase segregation). To sort out this issue, we collected optical and XAFS spectra. Optical fluorescence experiments revealed no evidence for the intact Eu-POA complex. Rather, evidence was obtained for the presence of divalent Eu. XANES (X-ray absorption near edge structure) results confirmed the (minor) occurrence of Eu(II) along with bulk Eu(III). The

Eu XANES and EXAFS (extended X-ray absorption fine structure) did not match those for either $[Eu(II)P_5W_{30}O_{110}]^{13-}$ or $[Eu(III)P_5W_{30}O_{110}]^{12-}$. Moreover, the Eu(III)-O coordination environment—6 O atoms at 2.28 Å—is not consistent with that in $[Eu(III)P_5W_{30}O_{110}]^{12-}$. The combination of results from SAXS, XANES, EXAFS, and optical measurements indicate decomposition of the Eu-POA complex. The decomposition produces a homogeneous distribution of Eu throughout the glass without the formation of discrete phases such as $EuPO_4$. The loading of borosilicate glasses with *An* ions by use of POA precursors represents a new immobilization approach that may offer enhancements concerning *An* solubility and chemical stability.

Planned Activities

We plan to probe the bonding and electrochemical behavior of *An* ions in complexes with Wells-Dawson anion isomers. Synthetic efforts will be targeted to prepare *An* complexes of α-1-$[P_2W_{17}O_{61}]^{10-}$. We aim to resolve the complicating issues regarding the reactions of *An* ions with the hexaniobate anion. Additional synthetic and characterization efforts will be employed to provide insights about solid glass forms, particularly the state of various POA complexes, prepared with *Ln*- and *An*-POA precursor complexes.

Information Access

None.

Optional Additional Information

None.

Optional Proprietary Information

None.