Project ID: 54716
Title: POLYOXOMETALATES FOR RADIOACTIVE WASTE TREATMENT
Date: 14 February 2000
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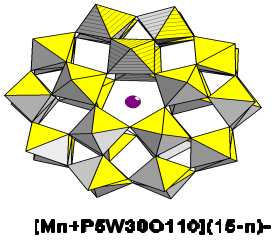
Number of Graduate Students involved: 2

Research Objective: The research project has two major goals: (1) the selective sequestration of lanthanide (Ln) and actinide (An) cations, and technetium species, from tank waste solutions, using radiation-resistant and thermally-stable polyoxometalate anions as complexants, and (2) the conversion of complexed Ln/An/Tc to reduced oxide bronzes (e.g. M_xWO_3) under relatively mild conditions, and evaluation of the use of such bronzes as waste forms.

Research Progress and Implications: This report summarizes progress as of 31 January 2000, after 3.5 years of a 3-year project; i.e during a no-funds extension.

1. Selective sequestration of Ln^{3+}/An^{4+} by $[NaP_5W_{30}O_{110}]^{14-}$ (**I**). The sodium cation that occupies the central cavity of this doughnut-shaped polyoxotungstate can be replaced only by cations of the same size, i.e. Ln^{3+}, An^{4+}(U 6Cm), Ca^{2+}. *Other cations are excluded.* In aqueous solution (neutral or mildly acidic) at 160E, Nd^{3+} for example is incorporated in the presence of the major components of tank wastes, i.e. a 200-fold molar excess of Na^+, and in presence of Fe^{3+} and Al^{3+}. The encrypted metal cations are released by hydrothermal treatment under strongly acidic conditions. [Ref. 1, 3, 7]



2. New polytungstate complexes of Ln^{3+} and An^{4+}. The conditions of formation, structures, and stabilities of several new polytungstates as possible precursors to thermal conversion to tungsten bronzes (see below) have been determined. These include 1:1 and 1:2 complexes of the lacunary anion ligands $[P_2W_{17}O_{61}]^{10-}$ (**II**), and some very large assemblies incorporating multiple Ln cations. [Ref. 2, 5]

3. Polytungstate complexation of UO_2^{2+}. Uranyl (and other actinyl) cations are stable in aqueous solution under normal atmospheric conditions. The first examples of polytungstate complexes of UO_2^{2+} have been synthesized and structurally characterized. Examples include $[Na_2(UO_2)_2(PW_9O_{34})_2]^{12-}$ (**III**) and $[(UO_2)_3(H_2O)_6As_3W_{30}O_{105}]^{15-}$ (**IV**). Anion **III** is formed in solutions of high $[Na^+]$ and is extractable into organic solvents. [Ref. 6 and in preparation]

4. Conversion of tungstolanthanide and -actinide salts into tungsten bronzes. Under relatively mild conditions (N_2 or H_2 atmosphere, 500-700EC) ammonium salts of anions such as **IV** are cleanly converted into the cubic bronzes $(Ln/An)_xWO_3$. This method of synthesis represents a major improvement over conventional methods (ground mixtures of oxides and tungsten powder, $1000EC) and is the subject of a patent application. The chemical stability of the bronzes as candidates for potential waste forms is currently under

investigation. [Ref. 8]

5. Technetium recovery and storage. Initial investigations are being carried out with rhenium as a Tc-surrogate. Tungstorhenates incorporating Re(V) and Re(IV) have been characterized but polyniobates and niobotungstates offer the advantages of stability in alkaline solutions which constitute the majority of tank wastes. The first example of a nioborhenate(IV) complex, $[Re(Nb_6O_{19})_2]^{12-}$, has been isolated from alkaline solution but has proved difficult to crystallize for structural confirmation. Furthermore Re is slowly oxidized and released from this material. A much more promising strategy has recently been discovered. Alkaline (pH ~12) aqueous solutions of $Nb_6O_{19}^{8B}$ react with Re(I) carbonyl complexes under hydrothermal conditions to form $[Nb_6O_{19}Re(CO)_3]^{7B}$ (**V**) and $[Nb_6O_{19}\{Re(CO)_3\}_2]^{6B}$ (*syn* and *anti* isomers, **VI**). The new complexes have been characterized by ^{17}O NMR spectroscopy and single crystal X-ray structural analysis. The solid salts are thermally stable to 400EC (loss of CO, not Re) and are inert to oxidation. Known synthetic routes to M(I) precursor species such as $M(CO)_3^+$ from $Re(Tc)O_4^{B}$, and the variety of nucleophilic polyoxometalate anions available, suggest that complexes such as **V** and **VI** will prove to be excellent vehicles for separation and storage of Tc wastes.

Planned Activities

A renewal proposal describing the development of the recently-discovered Re/Tc polyoxoanion chemistry (see above) is to be submitted for a September 2000 start date.

Information Access

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