FINAL REPORT
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POLYOXOMETALATES FOR RADIOACTIVE WASTE TREATMENT

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Executive Summary

This research has demonstrated new ways in which polyoxometalate anions (predominantly polytungstates and polyniobates) can be used to address problems of separation and immobilization of radioactive materials (lanthanides, actinides, and technetium).

- The robust polytungstate ("Preyssler") anion , $[P_5W_{30}O_{110}]^{15-}$, is shown to be remarkably selective in removing lanthanide and actinide anions from neutral aqueous solutions of high salt content. The bound cations are easily removed and the polytungstate anion is then available for recycling.
- The first examples of polytungstates incorporating uranyl (UO_2^{2+}) cations have been identified and fully characterized, and the facile (<800EC) thermal conversion of ammonium salts of these complexes to actinide tungsten bronzes, e.g. $U_{0.10}WO_3$, has been demonstrated. Tungsten bronzes are inert materials that should be considered as possible waste forms for immobilization of lanthanide and actinide wastes.
- Hexaniobate and hexatantalate anions are hydrolytically stable in highly basic aqueous solutions and can be used to treat alkaline tank wastes such as those at Hanford. Specific separation of rhenium (used as a surrogate for technetium-99, $t_{½} \sim 10^5$ y) was achieved as the Re(I) complex $[Nb_6O_{19}\{Re(CO)_3\}_2]^{6-}$, by hydrothermal reaction with rhenium carbonyls. The resulting niobate (and tantalate) complexes are remarkably stable towards oxidation and thermal loss of Re (>800EC) and imply that the corresponding Tc complexes could be used as waste forms.

Research Objectives

The research was directed primarily towards the use of polyoxometalate complexes for separation of lanthanide, actinide, and technetium species from aqueous waste solutions, such as the Hanford Tank Wastes. Selective binding of these species responsible for much of the high level waste (HLW) activity, can reduce the volume of material to be subsequently vitrified or otherwise converted for long-term storage. A secondary objective was to explore the direct conversion of the polyoxometalate complexes into possible waste forms, oxide bronzes, thereby avoiding additional handling and energy-intensive vitrification procedures.

Polyoxometalate anions (POMs)[1] form an extensive class of complexes with the general composition $[X_xM_mO_y]^{n-}$ in which the "heteroatoms", X are positive-valent elements (metals or nonmetals) and the "addenda", M, are, in most cases, Mo or W, but can also be V, Nb, or Ta. Insoluble salts of POMs, e.g. $(NH_4)_3[PMo_{12}O_{40}]$, have been employed as ion-exchange materials, or solutions of soluble salts have been used as precipitants, for the separation of Cs-137,[2] and separations of transuranium (TRU) elements[3] have been based on complexes with the polytungstate anion "$_2$-$[P_2W_{17}O_{61}]^{10-}$. Although the advantages of POMs lie in their high thermal and radiolytical stabilities, there has been no attempt to exploit the remarkable variety of these complexes beyond the use of the two anions mentioned above. Our broad knowledge of POM chemistry has allowed us to address and rectify this omission. Related chemistry (see below) is also pursued by Antonio and colleagues at Argonne National Laboratory and by Francesconi at Hunter College.

The innovative aspects of the project are: (a) the *selective* sequestration of lanthanide and actinide cations by a POM system in the presence of excess alkali and transition metal cations; (b) the formation of the first examples of POM complexes of UO_2^{2+} and their extraction into nonaqueous solvents; (c) the thermal conversion of ammonium salts of lanthanide and actinide POM complexes into inert oxide bronzes at relatively low temperatures; (d) the direct formation of highly thermally-robust niobate and tantalate complexes of Re (surrogate for Tc) in highly basic solutions.

Methods and Results

Selective sequestration of lanthanide/actinide cations by the "Preyssler" anion $[P_5W_{30}O_{110}]^{15-}$. The tungstophosphate anion originally reported by Preyssler was shown by us some years ago to adopt a doughnut-shaped structure with an encapsulated Na^+ cation (Figure 1). We had shown that replacement of the central Na^+ (r ~ 1.0 Å) by Ln^{3+} or U^{4+} could be achieved in aqueous solution under hydrothermal conditions. The size requirement for incorporation into the polytungstate structure is so stringent, that other alkali metal cations and other cationic components of tank wastes (Fe^{3+}, Al^{3+}, etc) are excluded. Furthermore, the greater charge of Ln and An cations, allows these to compete effectively with Na^+ (see Table 1).

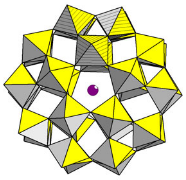


Figure 1

Table 1. Effect of External Sodium Ions on the Exchange of the Na^+ in the Preyssler Anion with Trivalent Lanthanides (Ln^{3+}).[a]

Molar ratio (Na^+ / Ln^{3+})	Yield (%)[b] Nd^{3+}	Eu^{3+}	Tb^{3+}	Tm^{3+}
2	----	----	----	87
5	98	----	----	83
10	95	86	100	78
30	85	----	----	49
50	78	89	100	35
100	67	95	98	21
200	58	----	----	----
300	43	75	96	----
500	15	53	90	----
1000	----	45	55	----

[a] The hydrothermal reactions (170°C for 24 hours) were performed using solutions of 1 : 1 : X molar ratio (POM : Ln^{3+} : Na^+) by varying X from 2 to 1000.

[b] In this and subsequent Tables the yields were calculated from integrals of the peaks in the ^{31}P NMR spectra by normalizing to 100 % for the total.

Tables 2 - 4 summarize the effects of pH, time, and competing cations using the exemplary trivalent lanthanides (6-coordinate radii in parentheses) Nd (1.12), Eu (1.09), Tb (1.06), and Tm (1.02 Å).

Table 2. Effect of pH on the Exchange of the Na^+ in the Preyssler Anion with Trivalent Lanthanides (Ln^{3+}).[a]

		Yield (%)	
pH	Nd^{3+}	Tb^{3+}	Tm^{3+}
2 M HCl	0	22	0
1 M HCl	0	68	0
1	0	99	42
2	62	98	92
3	68	99	94
4	88	100	95
5	98	100	98
6	87	97	99

[a] The hydrothermal reactions for Tb^{3+} were performed at 170°C for 24 hours using solutions where $POM^- : Tb^{3+} : Na^+ = 1 : 1 : 100$. The hydrothermal reactions for Nd^{3+} and Tm^{3+} were carried out in the absence of Na^+.

Table 3. Effect of Heating Time on the Exchange in an Excess Na^+ solutions.[a]

Heating Time (day)	Nd^{3+}	Yield (%) Tb^{3+}	Tm^{3+}
0.5	----	99	----
1	68	98	21
2	78	99	44
3	85	99	52
5	92	99	95
7	95	99	----

[a] The hydrothermal reactions were performed at 170°C using solutions where $POM : Ln^{3+} : Na^+ = 1 : 1 : 100$.

Table 4. Selectivity of the Preyssler anion toward lanthanides in multi-element mixtures[a]

Composition[b]			Yield (%)				
	Nd^{3+}	Eu^{3+}	Tb^{3+}	Tm^{3+}	Na^+	Al^{3+}	Fe^{3+}
A	10	100	100	64	--	--	--
B	40	100	90	0	0	--	--
C	0	100	95	20	--	0	0
D	0	100	90	0	0	0	0

[a] The hydrothermal reactions were performed at 170°C for 7 days; the pH was adjusted to 1.8 in order to prevent precipitation of Fe^{3+}.

[b] A = POM: Nd^{3+}: Eu^{3+}:Tb^{3+}: Tm^{3+} = 4 : 1 : 1 : 1 : 1
B = POM: Nd^{3+}: Eu^{3+}:Tb^{3+}: Tm^{3+}: Na^+ = 4 : 1 : 1 : 1 : 1 : 83
C = POM: Nd^{3+}: Eu^{3+}:Tb^{3+}: Tm^{3+}: Al^{3+}: Fe^{3+} = 4 :1 : 1 : 1 : 1 : 8 : 0.5
D = POM: Nd^{3+}: Eu^{3+}:Tb^{3+}: Tm^{3+}:Na^+ : Al^{3+} : Fe^{3+} = 4 : 1 : 1 : 1 : 1 : 83 : 8 : 0.5

The data summarized in the above Tables demonstrate the exquisite selectivity of the Preyssler anion for the separation of lanthanide cations. Recently, Antonio has extended our observations with U^{4+} and has shown that the TRU cations Am^{3+} and Cm^{3+} can be also be incorporated.[4] Unlike most polytungstate anions which undergo hydrolytic degradation in mildly basic solution (pH6-8), the Preyssler anion is stable under more basic conditions (pH ~ 10) although these do not approach those found in most of the Hanford waste tanks (pH > 13) and this limits the *direct* use of the anion in such solutions. However, because of its narrow size selectivity, the Preyssler anion can be used to strip lanthanide and actinide cations from neutral aqueous solutions in the presence of virtually any other cation. The resulting complexes can be separated by precipitation or solvent extraction, and the encapsulated cation removed by treatment with acid (Figure 2), whereupon the "empty" Preyssler anion is ready for re-use.

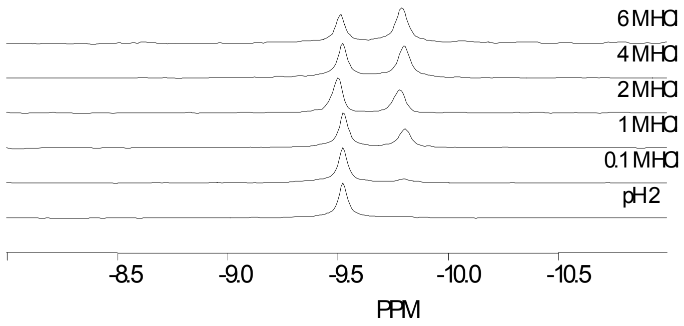
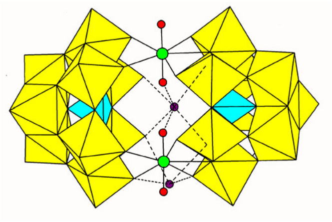


Figure 2. P-NMR of Na-encapsulated Preyssler anion (-9.5 ppm) showing formation of "empty" anion (-9.7 ppm) under acidic conditions

Polytungstate Complexes of the Uranyl Cation. High oxidation states of uranium and early TRU elements are characterized by trans dioxo cations. The uranyl cation UO_2^{2+} is by far the most prevalent species of uranium in aqueous solution under normal oxidizing conditions. No polyoxometalates containing the uranyl moiety were known when this project was initiated. We have since synthesized and fully characterized several such complexes, which can serve as intermediates in the formation of tungsten uranium bronzes (see below). Examples of the new complexes are

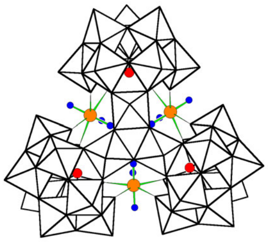
"Sandwich" complexes, $[(UO_2)_2(XW_9O_{34})_2]^{n-}$ (X = P, Si)

Kim 1997

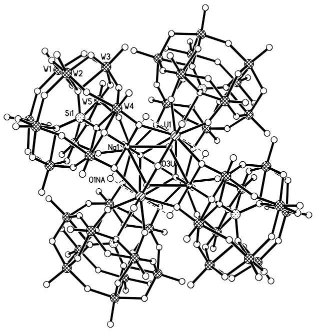


$[(NH_4)_2(UO_2)_2(PW_9O_{34})_2]^{12-}$

"Trimeric" clusters, $[(UO_2)_3(H_2O)_6(W_3O_6)(AsW_9O_{33})_3]^{15-}$



"Tetrameric" clusters, $[(NaOH_2)_4(UO_2)_4(OH)_2((-SiW_{10}O_{36})_4]^{22-}$



With the exception of the last example, which yields a different complex in solution, each of the complexes is formed and isolated in good yield by reaction of the appropriate POM building block with uranyl salts in aqueous solution.

Thermal conversion of polyoxometalate salts to tungsten bronzes. Lanthanide(3+) and actinide(4+) cations are known to form tungsten bronzes, $M_xWO_{3,}$ that are isostructural with the more well-known sodium tungsten bronzes, Na_xWO_3. Such bronzes are typically prepared by high temperature (>1000EC) solid state reactions of the finely-ground components. We investigated the possibility of synthesis of these substances by thermal decomposition of ammonium salts of selected polyoxotungstate complexes under Ar, N_2, or H_2. In every case examined the cubic bronzes were formed in good yield at temperatures between 500 and 850EC. The products were identified by X-ray powder diffraction. For example the ammonium salt of $[(UO_2)_3(H_2O)_6(W_3O_6)(AsW_9O_{33})_3]^{15-}$ gave, at 725EC under N_2, 95% yield of $U_{0.10}WO_3$ (a = 3.797 Å); under similar conditions the ammonium salt of $[Th(W_5O_{18})]^{8-}$ gave $Th_{0.10}WO_3$ (a = 3.837 Å) in 90% yield. [Full details are given in ref.5] This procedure, resulting in the formation of inert solid state materials that can be considered as possible waste forms for radioactive lanthanides and actinides, provides a much more energy efficient process than vitrification.

Technetium immobilization in polyoxometalates. All research carried out at Georgetown University has employed rhenium as a non-radioactive surrogate for technetium. [Promising leads from this research are currently being reexamined using the analogous Tc compounds in collaboration with Prof. Lynn Francesconi at Hunter College.] Most attention has focused on oxidation states 4+ (d^3) and 1+ (d^6), since these are relatively stable towards disproportionation (yielding the volatile $Re(Tc)O_4^-$ anion which is difficult to render immobile).

Although Mn^{4+} readily forms the stable tungstate $[MnW_6O_{24}]^{8-}$ and niobate $[Mn(Nb_6O_{19})_2]^{12-}$ complexes, we were unable to demonstrate the formation of analogous Re^{4+} complexes. The results of numerous and varied synthetic procedures yielded uncharacterizable materials that slowly underwent atmospheric oxidation to yield the perrhenate anion.

The Re(I) compounds $Re(CO)_5Br$ and $[Re(CO)_3(CH_3CN)_3]^+$ (and also $Re_2(CO)_{10}$) react cleanly, under hydrothermal conditions with $[Nb_6O_{19}]^{8-}$ and $[Ta_6O_{19}]^{8-}$, to give 1:1 and 1:2 complexes (Figure 3) in virtually quantitative yields.

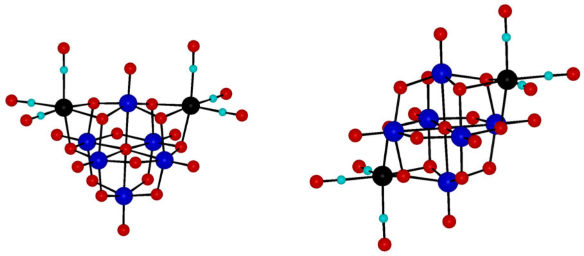


Figure 3. *Cis*- and *trans*- isomers of the 1:2 complexes of $Re(CO)_3^+$ with $[M_6O_{19}]^{8-}$

Since the corresponding Mn(I) complexes are also formed, there is little reason to doubt that Tc will behave analogously. This chemistry is particularly significant for two reasons, (a) the hexametalate anions are stable in extremely basic media (cf. Hanford waste tanks) and the reactions with the metal carbonyls occurs under such conditions; (b) the resulting complexes have high thermal and redox stability. See Figure 4 for thermogravimetric data, which show that Re is not lost until the temperature exceeds 800EC

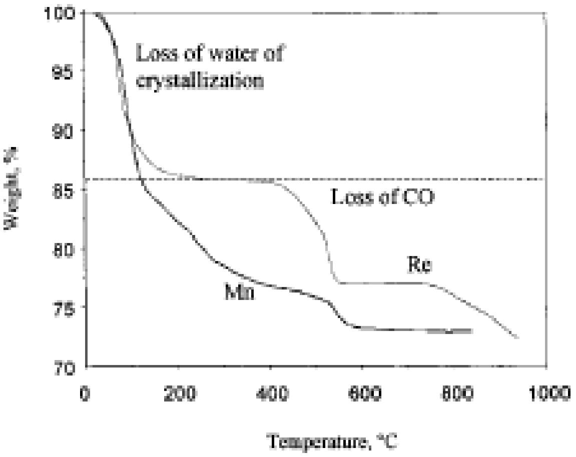


Figure 4. TGA curves for trans-Mn_2Ta_6 (Mn) and trans-Re_2Nb_6 (Re).

Relevance, Impact, and Technology Transfer

The results of this research impact DOE's environmental management problems in three important areas - the *selective* separation of lanthanides and actinides from complex aqueous mixtures of high salt content, potential new energy-efficient waste forms, and the separation and immobilization of technetium. Each of these foci, separations, waste forms, and Tc-immobilization is sufficiently promising that patent applications have been submitted, but each requires further development to determine whether larger scale trials are warranted.

The use of the Preyssler anion as a robust, efficient, selective, and recyclable separations agent ("inorganic crown ether") is limited to aqueous solutions that are acidic, neutral or only slightly alkaline, and it is therefore not appropriate for direct treatment of the Hanford tank wastes. On the other hand, the *extreme selectivity* of this tungstophosphate for Ln and An cations in the presence of sodium and other metal cations is *unprecedented*. Its use in the treatment of low level waste streams of appropriate acidity should be seriously considered.

We have discovered an energy-efficient route to tungsten bronzes containing lanthanide and actinide elements. The sodium tungsten bronzes are known to be inert solid state materials, and if this property carries over into the Ln/An species, these could prove to be alternative waste forms. Future work will determine feasibility; an unknown factor is the effect of oxidation under neutral or slightly alkaline conditions.

Immobilization of Tc is an ever-present problem for which no approach has been fully successful. The crucial difficulty is the tendency of Tc compounds to become oxidized (or to disproportionate under neutral or alkaline conditions) to yield the highly mobile TcO_4^- anion. Our approach has been to use Tc(I), stabilized by CO ligands, bound to the alkali-stable hexaniobate anion. The resulting complexes (at least the analogous ones containing Re) are stable towards oxidation and loss of metal below 800EC. Since $Tc(CO)_3(aq)^+$ can be generated in aqueous solution, we foresee a viable route to the niobate complexes under the solution conditions present in the Hanford tank wastes.

Personnel Supported

Michael T. Pope, Principal Investigator
Knut Wassermann, Postdoctoral
Michael H. Dickman, Postdoctoral
Kee-Chan Kim, Graduate student (Ph.D. 1998)
Alexei Besserguenev, Graduate student (Ph.D. expected 2001)
Angelo Ostuni, Undergraduate/graduate student (M.S. 1998)

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“Chemistry of Large Polyoxometalate Anions Assembled from Lacunary Structures”, Pope, M.T. Invited lecture, Summer School on Coordination Chemistry, Polanica-Zdroz, Poland, June 1999

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Patents

“Preparation of Tungsten Bronze for Nuclear Waste Storage forms and Electronic Materials” Pope, M.T.;Wassermann, K. PCT/US99/16869

“New Polyoxometalates and Process for Immobilization of Technetium Based Thereon” Pope, M.T.; Besserguenev, A. , provisional application filed 02/28/2001

Future Work

See under “Relevance, Impact, and Technology Transfer”. Long-term stabilities of actinide tungsten bronzes; conversion of TcO_4^- to $Tc(CO)_3^+$, and formation of polyniobate complexes inaqueous media. Thermal and redox stabilities of the latter complexes.

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