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Vadim V. Romanovski
Donald W. Whisenhunt, Jr
Alan C. Veeck
Wendy A. Andersen
Darleane C. Hoffman
Xu Jide
David White
Kenneth N. Raymond

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POTENTIAL AGENTS FOR REMOVAL OF ACTINIDES FROM WASTE SOLUTIONS

Vadim V. Romanovski
Donald W. Whisenhunt Jr.
Alan C. Veeck
Wendy A. Andersen
Darleane C. Hoffman
Glenn T. Seaborg Institute for Transactinium Science
Lawrence Livermore National Laboratory
P.O.Box 808, L-231
Livermore, CA 94550
(510)-423-3755

Xu Jide
David White
Kenneth N. Raymond
Department of Chemistry
University of California
Berkeley, CA 94720
(510)-642-7219

ABSTRACT

The uptake of Th(IV) from nitric and hydrochloric acid solutions by chelating ion exchange resins containing catechol, 1,2-hydroxypyridinone (1,2-HOPO) and 3,4-hydroxypyridinone (3,4-HOPO) functional groups, has been investigated. These polystyrene based materials show excellent kinetics for the uptake of Th(IV) and have a high loading capacity. Liquid/liquid extractants have also been synthesized by addition of lipophilic side chains to the chelating groups (1,2-HOPO; 3,4-HOPO; 3,2-HOPO; catecholamide; terephthalamide). The initial evaluation of the extraction properties has been carried out.

I. INTRODUCTION

Safe disposal of radioactive waste streams arising from nuclear power plants, military facilities, medical research and industrial applications is required. The actinides can be among the components of most concern in hazardous waste streams. First, several actinide isotopes have half-lives of many thousands of years and will thus be a concern far into the future. Second, these isotopes decay predominantly by alpha emission which constitutes a special health hazard if ingested. The separation of the actinides is one way to facilitate their disposal, decrease health risks and decrease the cost of waste management. Solvent extraction and ion exchange are the technologies which are most suitable for this purpose.[1-7]

In this study the authors are trying to develop highly selective agents to remove plutonium (IV) (and perhaps other transuranic elements) from acidic and neutral solutions. In nature, bacteria and other microorganisms produce siderophores, low molecular weight multidentate iron chelators, to scavenge ferric ion from their environments. Iron (III) shares many chemical properties with many of actinide elements, especially plutonium (IV).[8] Both Fe(III) and Pu(IV) are "hard" Lewis acid metal cations, carrying a large amount of charge and having a relatively small ionic radius:

$$\text{Fe(III): charge(Z)/radius(A°)} = 3/0.65 = 4.6$$

$$\text{Pu(IV): charge(Z)/radius(A°)} = 4/0.96 = 4.2$$

They also behave similarly in water with very low free metal ion concentrations at near neutral pH:

$$Fe(OH)_{3\,(s)} \rightarrow Fe^{3+} + 3OH^-;\ K_{sp}=10^{-38}$$

$$Pu(OH)_{4\,(s)} \rightarrow Pu^{4+} + 4OH^-;\ K_{sp}=10^{-55}$$

Both Fe(III) and Pu(IV) are bound by basic ligands that can provide electrical charge, such as negatively charged oxygen donors. Because of its larger size and charge, Pu(IV) is eight-coordinate instead of six-coordinate, like Fe(III).

The aim is to develop chelators which are strong Lewis bases and show selectivity for Lewis acidic metal ions in particular Pu(IV) and Th(IV). Differences in charge, preferred coordination number and range of pH stability can be utilized to make the transition from chelators that are specific for Fe(III) to those that are specific for actinide(IV) ions. Choosing the right chelating groups is perhaps the most important aspect of ligand design. The correct choice will give a ligand not only strength to bind a metal ion, but also specificity to bind one metal ion preferentially over another.

In nature siderophores use Lewis basic chelating groups including catechols (e.g., enterobactin) and hydroxamic acids (e.g., desferrioxamine B). These chelating groups are often combined in polydentate ligands to fully bind the metal in a six coordinate complex. Very selective sequestering agents can be synthesized by incorporating these chelating groups into multidentate ligands.[9-14] The chelating groups can also be incorporated into molecules appropriate for use as liquid/liquid extractants or attached onto insoluble polymers for use as solid/liquid extractants.[15]

II. EXPERIMENTAL

Catechol resin, 1,2-hydroxypyridinone (1,2-HOPO) resin and 3,4-hydroxypyridinone (3,4-HOPO) resin were prepared as described elsewhere.[15] The amount of the resin for each experiment was 100 mg, the volume of aqueous phase was 53 mL, the amount of Th was 160 micro mole. The sorption of Th ions by the resins was measured at room temperature (22±1 °C). Distribution ratios, D, were calculated as

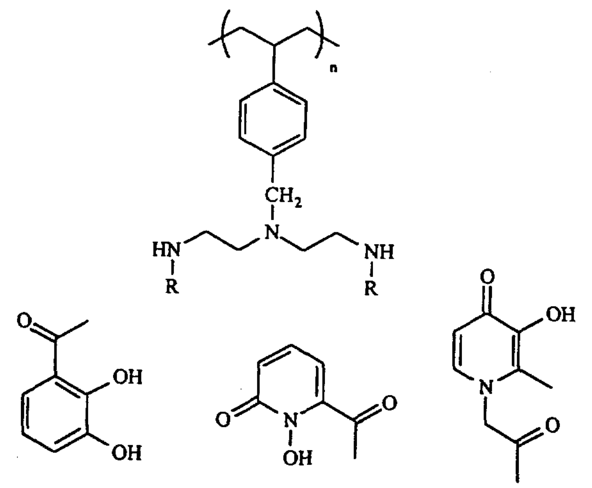
$$D=[(m_0-m_f)/W]/[m_f/V] \qquad (1)$$

where m_0 and m_f are the amount of Th in the aqueous phase (micro mole) before and after equilibration, respectively, W is the weight of resin (g) and V is the volume of the aqueous phase (mL). Th concentrations in aqueous phase were determined by Arsenazo III Method using PC1000 spectrometer following a reported procedure.[16]

Distribution coefficients of Fe(III) for liquid/liquid extraction were determined by spectrophotometery. Spectrophotometric analysis was based on extinction coefficients of Fe(III) complexes with the extractants in dodecane, kerosene, chloroform, 1-octanol and 4-methyl-2-pentanone, which were measured independently.

III. THORIUM UPTAKE BY SULFONATED ION EXCHANGE RESINS

At the present time three polystyrene based chelating ion exchange resins have been synthesized and tested to determine the ability of these materials to remove actinide(IV) ions from solution - Catechol Resin, 1,2-HOPO Resin and 3,4-HOPO Resin (see Fig.1).



Catechol Resin **1,2-HOPO Resin** **3,4-HOPO Resin**

Figure 1. Structure of modified polystyrene resins.

To improve their behavior as extractants these resins have been sulfonated to reduce their hydrophobicity. This improves the uptake properties of the materials but the sulfonate groups introduce some degree of non selective binding (ion exchange). These polystyrene based materials show excellent kinetics for the uptake of Th(IV) and have a high loading capacity. Loading capacities of the resins were determined by three different procedures (Table 1).

Table 1. Summary of estimated loading capacity of sulfonated resins, mmol chelator/g resin.

Chelating group	Citrate Batch	Titration	Elemental Analysis
1,2-HOPO	0.4	0.3	0.1
3,4-HOPO	0.4	0.4	0.5
Catechol	0.8	0.4	0.1

Thorium was chosen for initial test experiments due its lower radiotoxicity and easier handling. It is proposed to study plutonium uptake in future experiments when uptake properties of the resins are better understood.

The kinetics of thorium uptake by Catechol Resin, 1,2-HOPO Resin and 3,4-HOPO Resin have been studied using various aqueous media, in presence of univalent (Na), bivalent (Zn), and trivalent (Fe) metal ions. The goal of these experiments is to investigate the ability of the resins to extract thorium selectively. For uptake from 5 M $NaNO_3$ distribution ratios of Th were ~250 for the Catechol and the 3,4-HOPO Resins, and ~70 for the 1,2-HOPO Resin.

Uptake in the presence of 10-fold excess of Zn is reported in Fig 2. Th distribution ratios are similar for the 1,2-HOPO and 3,4-HOPO Resins and approximately three times greater for the Catechol Resin.

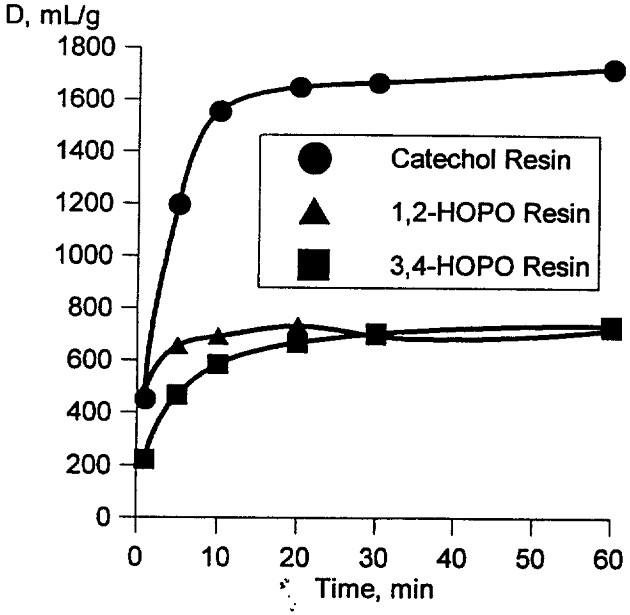


Figure 2. Time dependency of Th uptake in presence of 10-fold excess of zinc nitrate($C_{Zn(NO_3)_2}$= 0.03 M, pH=5.8).

Kinetic experiments of Th uptake by Catechol Resin, 1,2-HOPO Resin and 3,4-HOPO Resin from hydrochloric acid medium had been performed. The results are reported in Fig.3-6.

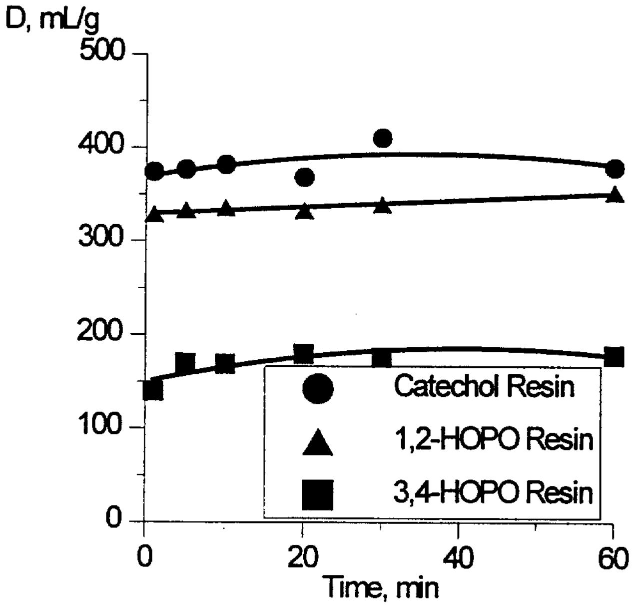


Figure 3. Time dependency of Th uptake in presence of 0.5 M HCl.

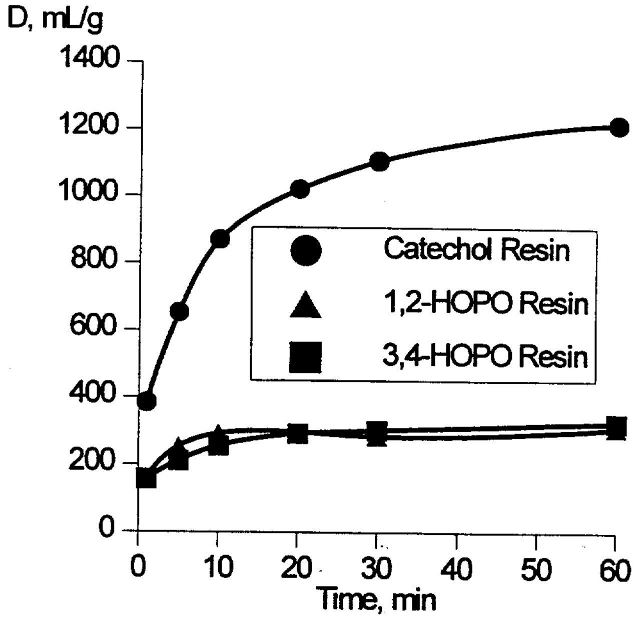


Figure 4. Time dependency of Th uptake in the presence of 1-fold excess of iron chloride (III) (C_{FeCl_3}= 0.003 M, pH=2.8).

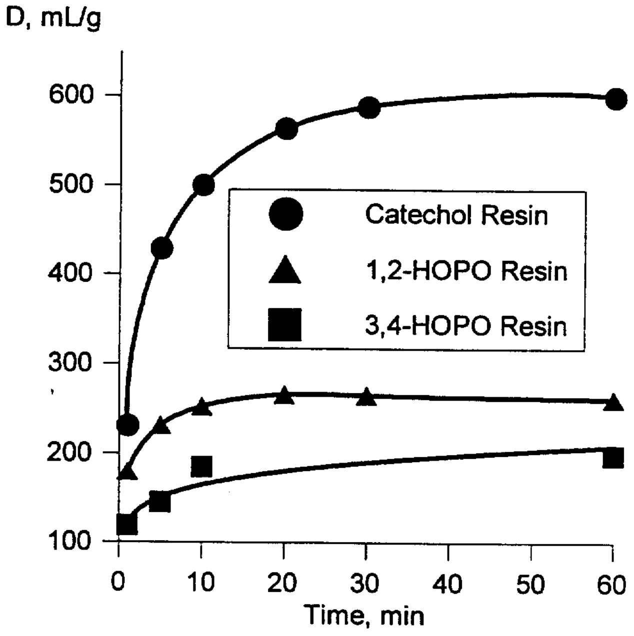


Figure 5. Time dependency of Th uptake in the presence of 10-fold excess of iron chloride (III) (C_{FeCl_3}= 0.03 M, pH=2.3).

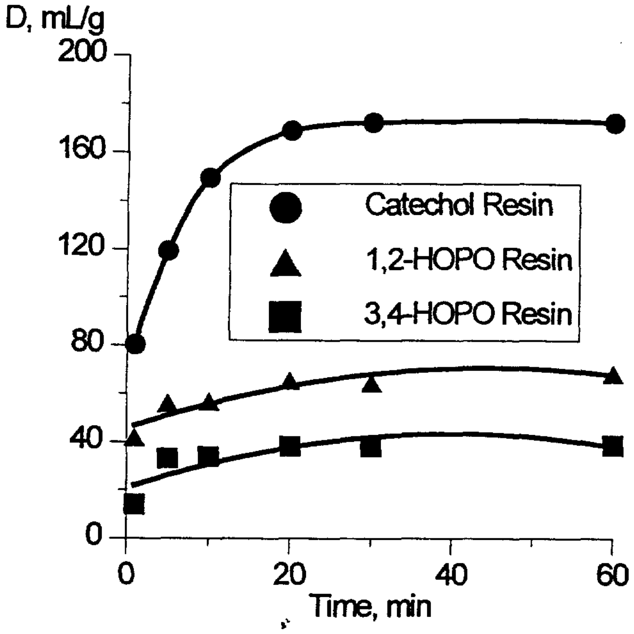


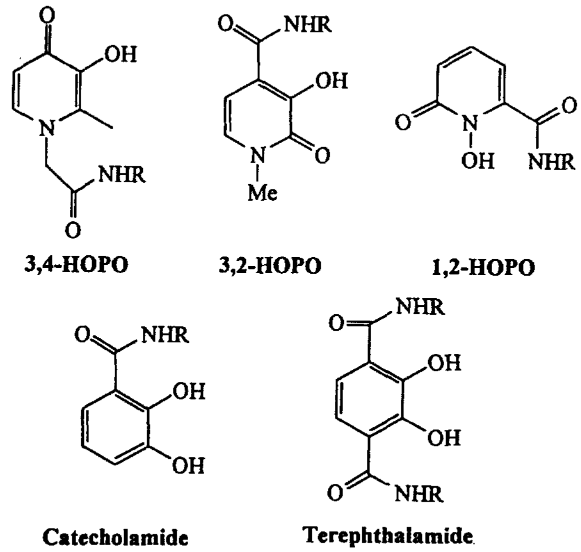
Figure 6. Time dependency of Th uptake in the presence of 100-fold excess of iron chloride (III) (C_{FeCl_3}= 0.3 M, C_{HCl} = 0.05 M).

The Catechol Resin has the highest Th uptake capacity from acid solutions in the presence of univalent, bivalent and trivalent ions.

IV. LIQUID/LIQUID EXTRACTANTS

Liquid/liquid extractants have been synthesized by addition of a lipophilic side chain to chelating groups (Fig.7).

Incorporation of these powerful chelating groups into liquid/liquid extractant systems can produce materials with potential practical application. The liquid/liquid extractants employ simple bidentate chelating groups modified with a wide variety of lipophilic side chains designed to systematically alter their solubility properties. Initial experiments have been performed to determine the distribution coefficients of the extractants between aqueous and a number of common organic phases used in separation technology (dodecane, kerosene, chloroform, 1-octanol, 4-methyl-2-pentanone). Several materials with low water solubility have been tested for their ability to extract Lewis acid metals from aqueous media under varying conditions of pH and ionic strength. Hexyl-1,2-HOPO and octyl-1,2-HOPO sequestering agents seem particularly promising, showing quantitative removal of Fe(III) from acid solutions into organic media.



R = C_6H_{13}, C_8H_{17}, $C_{10}H_{21}$, $C_{12}H_{25}$, $C_{18}H_{37}$, and phenylpropyl

Figure 7. Structure of liquid/liquid extractants synthesized.

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REFERENCES

1. E.P. Horwitz, R. Chiarizia, H. Diamond, R.C. Gatrone and others, "Uptake of Metal Ions by A New Chelating Ion-Exchange Resin .1. Acid Dependencies of Actinide Ions," *Solvent Extraction and Ion Exchange*, 11(5), 943-966 (1993).
2. E.P. Horwitz, M.L. Dietz, R. Chiarizia, H. Diamond, and others, "Separation and Preconcentration of Actinides by Extraction Chromatography Using A Supported Liquid Anion Exchanger - Application to the Characterization of High-Level Nuclear Waste Solutions," *Analytica Chimica Acta*, 310(1), 63-78 (1995).
3. Z.K. Karalova, E.A. Lavrinovich, B.F. Myasoedov, L.A. Fedorov, and others, "Extraction of Actinides and Lanthanides by Alkylphenol Sulfides," *Radiochemistry*, 36(5), 441-445 (1994).
4. A.M. Rozen, A.S. Nikiforov, B.S. Zakharkin, Z.I. Nikolotova, and others, "Optimized Extracting Agents for Removing Actinides," *Atomnaya Energiya*, 72(5), 453-459 (1992).

5. N. Condamines, C. Musikas, "The Extraction by N,N-Dialkylamides. 2. Extraction of Actinide Cations," *Solvent Extraction and Ion Exchange*, **10(1)**, 69-100 (1992).

6. J.N. Mathur, M.S. Murali, G.H. Rizvi, R.H. Iyer, and others, "Separation and Recovery of Plutonium from Oxalate Supernatant Using CMPO," *Solvent Extraction and Ion Exchange*, **12 (4)**, 745-763 (1994).

7. T.C. Maiti, J.H. Kaye, A.E. Kozelisky, "Sequential Separation of Pu, Np, U and Am from Highly Radioactive Hanford Waste by Ion Exchange Methods," *Journal of Radioanalytical and Nuclear Chemistry-Articles*, **161(2)**, 533-540 (1992).

8. K.N. Raymond et al. "Specific Sequestering Agents for the Actinides," *Lanthanide and Actinide Chemistry and Spectroscopy,* ACS Symposium Series, 131, American Chemical Society, Washington, DC (1980).

9. W.R. Harris, K.N. Raymond, and F.L. Weitl, "Ferric Ion Sequestering Agents. 6. The Spectrophotometric and Potentiometric Evaluation of Sulfonated Tricatecholate Ligands," *J.Am.Chem.Soc.*, **103**, 2667 (1981).

10. P.E. Riley, K. Abu-Dari, and K.N. Raymond, "Specific Sequestering Agents for the Actinides. 9. Synthesis of Metal Complexes of 1-Hydroxy-2-pyridinone and the Crystal Structure of Tetrakis(1-oxy-2-pyridonato) aquothorium (IV) Dihydrate," *Inorganic Chemistry*, **22**, 3940 (1983).

11. R.C. Scarrow, P.E. Riley, K. Abu-Dari, D.L. White, and K.N. Raymond, "Ferric Ion Sequestering Agents. 13. Synthesis, Structures and Thermodynamics of Complexation of Cobalt(III) and Iron(III) Tris Complexes of Several Chelating Hydroxypyridinones," *Inorganic Chemistry*, **24**, 954 (1985).

12. R.C. Scarrow, P.E. Riley, D.L. White, and K.N. Raymond, "Ferric Ion Sequestering Agents. 14. 1-Hydroxy-2(1H)-pyridinon Complexes: Properties and Structure of a Novel Fe-Fe Dimer," *J.Am.Chem.Soc.*, **107**, 6540 (1985).

13. R.C. Scarrow, and K.N. Raymond, "Synthesis of N-Alkyl-3-hydroxy-2(1H)-pyridinones and Coordination Complexes with Iron(III)," *Inorganic Chemistry*, **27**, 4140 (1988).

14. Z. Hou., D.W. Whisenhunt, Jr., J. Xu, and K.N. Raymond, "Potentiometric, Spectrophotometric, and ^{1}H NMR Study of Four Desferrioxamine B Derivatives and Their Ferric Complexes," *J.Am.Chem.Soc.*, **116**, 840 (1994).

15. D.W. Whisenhunt, Jr., *Synthesis and Evaluation of Chelating Agents and Resins Specific for the Actinides*, Ph.D. Thesis, University of California at Berkeley (1994).

16. H. Onishi, *Photometric determination of tracers of metals*, p.449, John Wiley & Sons, Inc., New York, New York (1978).

Technical Information Department • **Lawrence Livermore National Laboratory**
University of California • Livermore, California 94551