

Project ID: **54595**

**f-Element Ion Chelation in Highly Basic Media**

**Lead Principal Investigator:**

Dr. Robert T. Paine  
Professor  
Department of Chemistry  
University of New Mexico  
Clark Hall  
Albuquerque, New Mexico 87131  
Telephone: 505-277-1661  
e-mail: [rtpaine@unm.edu](mailto:rtpaine@unm.edu)

## **f-Element Ion Chelation in Highly Basic Media**

Robert T. Paine, University of New Mexico

### **Research Objective**

High-level radioactive waste (HLW) generated in the DOE complex is stored in tanks at several sites, but predominantly it is found at the Hanford reservation. Much of the material has been exposed to high pHs, consequently the waste exists in a complex, poorly understood mixture of solids, gels and solutions. The final waste remediation plan may involve chemical separation of fractions and a suitable, well developed molecular chemistry basis for performing these separations is not available. Indeed, the fundamental chemical behavior of most radioactive nuclides in basic media is not known.

The goal of this project is to undertake fundamental studies of the coordination chemistry of f-element species in basic aqueous solutions containing common waste treatment ions (e.g.,  $\text{NO}_3^-$ ,  $\text{CO}_3^{2-}$ , organic carboxylates, and EDTA), as well as new waste scrubbing chelators produced in this study. The experimental agenda includes:

1. Studies of the speciation of Sr and Ln ions in basic solutions with and without common counterions;
2. Preparations of new multifunctional ligands that may act as strong, ion-specific chelators for Sr and/or Ln ions in basic media; and
3. Studies of the coordination and dissolution behavior of oxide-hydroxide species, as well as in insoluble sols, gels, and precipitates in combination with new chelating ligands.

It is anticipated that this coordination chemistry will facilitate the design of advanced separation schemes required for handling the complex waste matrices found at the Hanford HLW facility.

### **Research Progress and Implications**

As of 6/1/99 the following advances have been realized.

#### **1. Hydrolysis Chemistry**

We have continued our study of the pH dependence of the hydrolysis of Sr(II), Y(III), La(III), Nd(III), and Er(III) by use of pH titrations and nephelometry. Particular attention was given to determining the pH for the onset of hydrolysis as well as the kinetics of particle growth at onset. The pH values for hydrolysis onset generally agree with related data in the literature. The pH shifts in hydrolysis onset as a function of counterion have also been studied as a function of ions typically present in waste media (e.g.,  $\text{NO}_3^-$ ,  $\text{Cl}^-$ , acetate, oxalate), as well as known chelating anions. As expected, many of these ions cause significant shifts in the pH for hydrolysis onset

due to competing association equilibria. The hydrolysis onset shifts caused by phosphonic acid chelators have also been surveyed. Dramatic shifts are encountered in some cases comparable to those observed with EDTA. For example, for La(III) the pH shifts are typically 6 pH units. Some attention was also given this year to studies of solutions containing several metal ions. This work was undertaken to assess the influence of a “matrix” of metal ions on the hydrolysis of a single ion. The studies completed to date are qualitative in nature and the results are being used to design more quantitative studies in the future. The future studies will assess the cross-behavior of ions in “simulant” waste compositions suggested by Task Focus area personnel.

In related work, we continued studies of the dissolution properties of lanthanide oxide-hydroxide precipitates with complexing anions. It is found that several new phosphonic acids are very active at precipitate dissolution. In support of this work, we have structurally analyzed the precipitates and the dissolution complexes by use of solution and solid-state NMR and we have isolated a number of complexes in the solid state and determined their molecular structures.

## 2. New Complexant Development

Considerable effort has been given to this activity in the last year. First of all the coordination chemistry of ligands 1 – 5 reported last year was explored in support of understanding how these ligands bind to lanthanide ions as they are dissolved from basic sludges. The molecular structures of  $\text{Er}(\underline{1})_3$  (1) was determined and 1 was found to coordinate both in its mono anionic form and as a neutral ligand. The nature of the bonding is consistent with complete replacement of oxo and hydroxo groups from the metal center. A derivative ligand (1') of 1 in which another methylene group is added between the phosphonic acid group and the pyridine ring was prepared. This ligand forms 3:1 complexes with Nd(III) in which each ligand is bound to a metal ion in a bidentate fashion and also bridge bonds to a second metal center. The result is a polymeric structure. The functional analog of ligand 2 has been prepared and the coordination chemistry has been studied. In each case the date, molecular structure determinations show the molecule binds in a tridentate fashion to one metal center and then bridge bonds to two more metal centers giving rise to a polymeric structure.

The implications of these coordination chemistry studies are several. First, they shed light on the powerful dissolution properties of the ligands. Clearly, the strong ligand-metal interactions drive the metals out of their otherwise stable oxide-hydroxide structures. The solid state structures reveal new chelation designs that would be worth pursuing and they point to directions for fruitful decontamination activities.

## **Planned Activities**

We have requested and have been granted a no-cost, one year extension to this grant. During this last year we will pursue additional efforts in chelator design for dissolution agents and we will test the effectiveness of the new ligands in simulant insoluble waste systems.