

Progress Report

Environmental Management Science Program

Project Title: f-Element Ion Chelation in Highly Basic Media

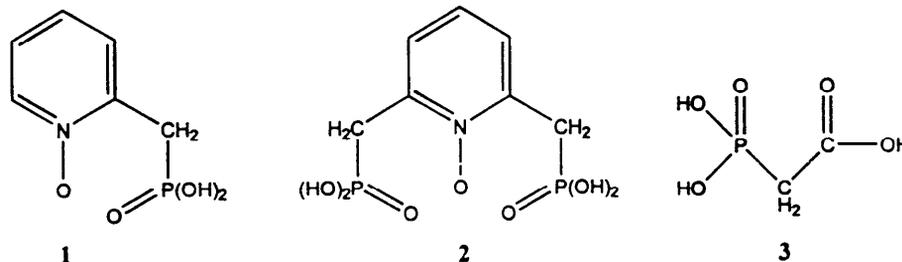
Project P.I.: Robert T. Paine
Department of Chemistry
University of New Mexico
Albuquerque, NM 87131

Project Report Period: 10/1/96 - 7/1/97

Experimental Objectives

The specific fundamental chemical objectives of this project are to:

1. Study the chemical speciation of Sr and Ln ions in basic media formed in aqueous solutions with and without classical chelation agents (e.g., EDTA, polyphosphates, and organic carboxylates);
2. Prepare pyridine N-oxide phosphonate and phosphonoacetate chelators of the types 1-3 and characterize their ionization properties by titrimetric techniques;



3. Study the interactions of 5 - 7 with soluble oxide-hydroxide metallate species and higher molecular weight sols, gels and precipitates containing Sr and Ln ions. As time permits, interactions with oxide-hydroxide metallates of U, Th, Ba, Al and Fe will also be studied.
4. Study the interactions of newly designed phosphonate ligands with oxide-hydroxide metallate species.
5. Transfer the fundamental coordination chemistry revealed here to research groups at LANL and PNNL that will utilize the results to improve tank waste treatment protocols.

Experimental Results

1. Efforts in elucidating the speciation of Sr and lanthanide ions in basic media during these initial months have been focused on chemical synthesis. We have studied various parameters (pH, temperature precipitate drying, anion, organic complexants) and their effect on the qualitative chemical behavior of the resultant oxide-hydroxide precipitation and dissolution. The results of that work will be used in the second year to define the quantitative studies of Sr and lanthanide ion solubility, which will be accomplished by ICP-emission analysis, and speciation, which will be examined by NMR and mass spectrometry analyses. In this regard the ICP emission spectrometer has been purchased, delivered to UNM, and installation will begin next week.
2. The new ligand complexant synthesis effort has received the majority of our attention during this year and considerable progress has been made. The syntheses of ligands 1-3 have been developed, accomplished, and optimized. Samples have been fully characterized by spectroscopic techniques and a paper will soon be prepared describing the results. Titrimetric analyses of 1-3 have likewise been completed. We have also prepared derivatives of the ligands 1 and 2 substituted at the -CH₂ spacer point so that the spacer

arm is now a -C(H)R group. This will likely affect coordination characteristics of the ligands.

3. The studies of the interactions of ligands 1-3 with Sr and Ln oxide-hydroxide precipitates has just begun. That work depends both on the availability of the ligands described in part 2 and on the completion of the qualitative studies described in part 1. What can be concluded at this stage is that Ln oxide hydroxide precipitates can be redissolved under some conditions when 1 and 2 are present in the supernatant solutions. This work will be actively continued as part of the second year project.
4. The characterization of complexes formed between the phosphonic acid ligands and specific oxide hydroxide species has not yet begun and will not likely start until the third year.
5. We have been in regular contact with staff at LANL (J. FitzPatrick) and PNNL (B. Hay and B. Rapko) over various issues pertaining to the eventual application of our results to the very real problems at the Hanford site.