Final Report

Understanding the Chemistry of the Actinides in High Level Waste Tank Systems: The Impact of Temperature on Hydrolysis and Complexation with Organics

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RESEARCH OBJECTIVES

The overall goal of this research plan was to provide a thermodynamic basis for describing actinide speciation over a range of tank-like conditions, including elevated temperature, elevated OH^- concentrations, and the presence of various organic ligands. The project involved three separate groups that received their own independent funding within the overall project: Dr. Sue Clark's group at Washington State University, Dr. Linfeng Rao's group at Lawrence Berkeley Laboratory, and Dr. Scott Wood's group at the University of Idaho. This document reports the results obtained by the University of Idaho (UI) group. The specific goals of the UI group were to determine the solubility of CeO_2 and ThO_2 as a function of pH, ligand concentration (EDTA, oxalate, citrate, siderophores), ionic strength ($NaNO_3$), and temperature. From these solubility measurements, thermodynamic data such as solubility products and stability constants will be derived. The tetravalent Th(IV) and Ce(IV) were being studied as analogues to Pu(IV).

Research Implications

This research program has several important implications on the processing of high-level radioactive waste from tanks at both Hanford and Savannah River. The thermodynamic data generated under this research project can be used by site engineers to develop processing schemes for waste pretreatment prior to vitrification. The impact of temperature on the distribution of actinide solution species in the presence of organic ligands can now be predicted with greater confidence. This information is essential for safe and effective separations of the actinides from the rest of the waste tank matrix.

Research Accomplishments

I. Solubility of CeO_2 in aqueous $NaNO_3$ solutions both with and without organic ligands.

The solubility of CeO_2 in $NaNO_3$ media as a function of pH in the absence of organic ligands and in the presence of EDTA, citrate, oxalate and a siderophore (desferrioxamine B) was determined. A thorough literature review prior to our study revealed almost no quantitative information on the hydrolysis or complexation of Ce(IV), even at standard conditions, so the focus was on determining the solubility of CeO_2 at 25 °C and 1 bar. Studies of the solubility of CeO_2 in the absence of EDTA have been conducted in 0.1, 1.0 and 3.0 M $NaNO_3$ solutions. A classical solubility curve resulted, indicating hydrolysis of the Ce(IV) cation (Fig. 1). Next, the solubility of CeO_2 in 0.1 M $NaNO_3$ solutions was measured as a function of EDTA concentration (100-500 μM) and pH. The presence of EDTA clearly increased the solubility of CeO_2 (Figures 2a-d). We are in the process of deriving equilibrium constants for the Ce(IV)-hydroxide and –EDTA complexes.

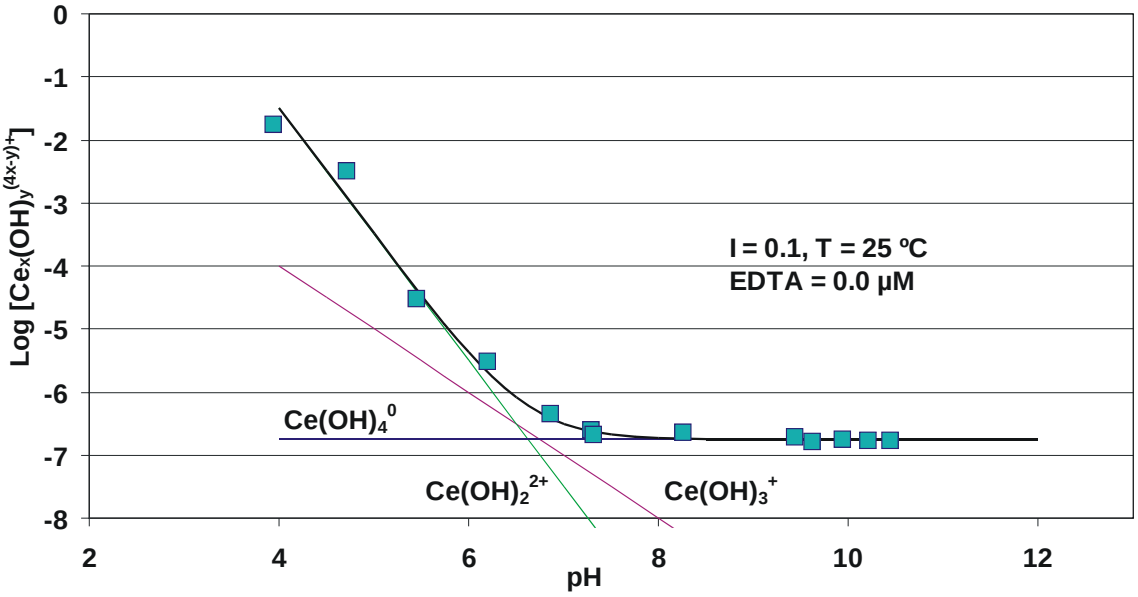
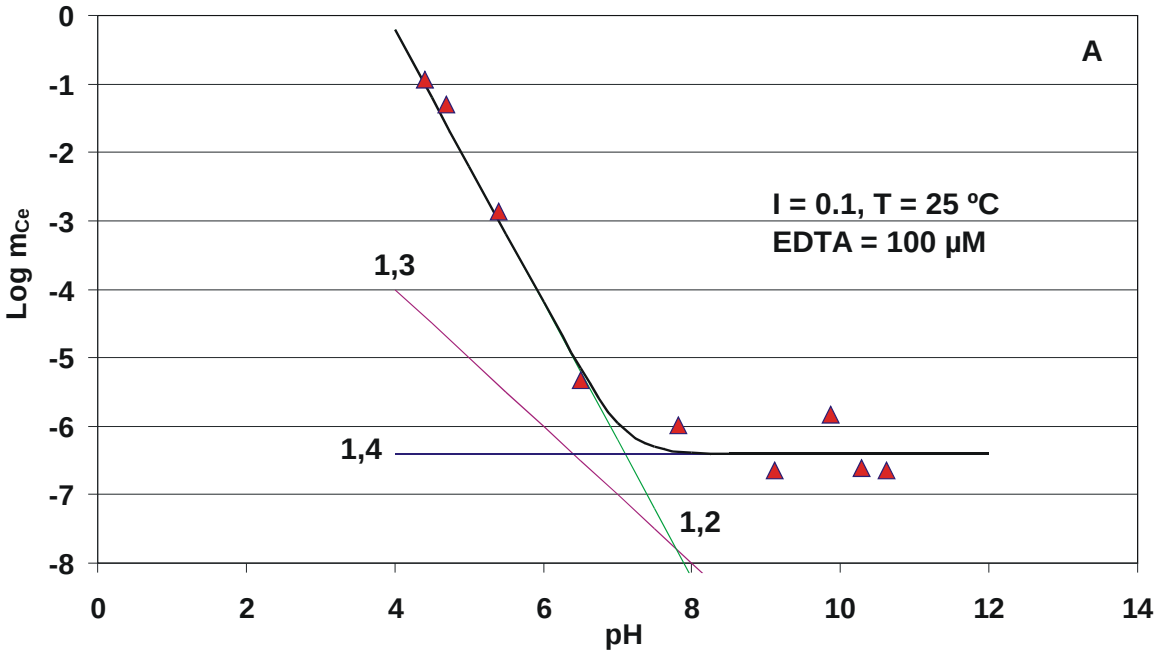
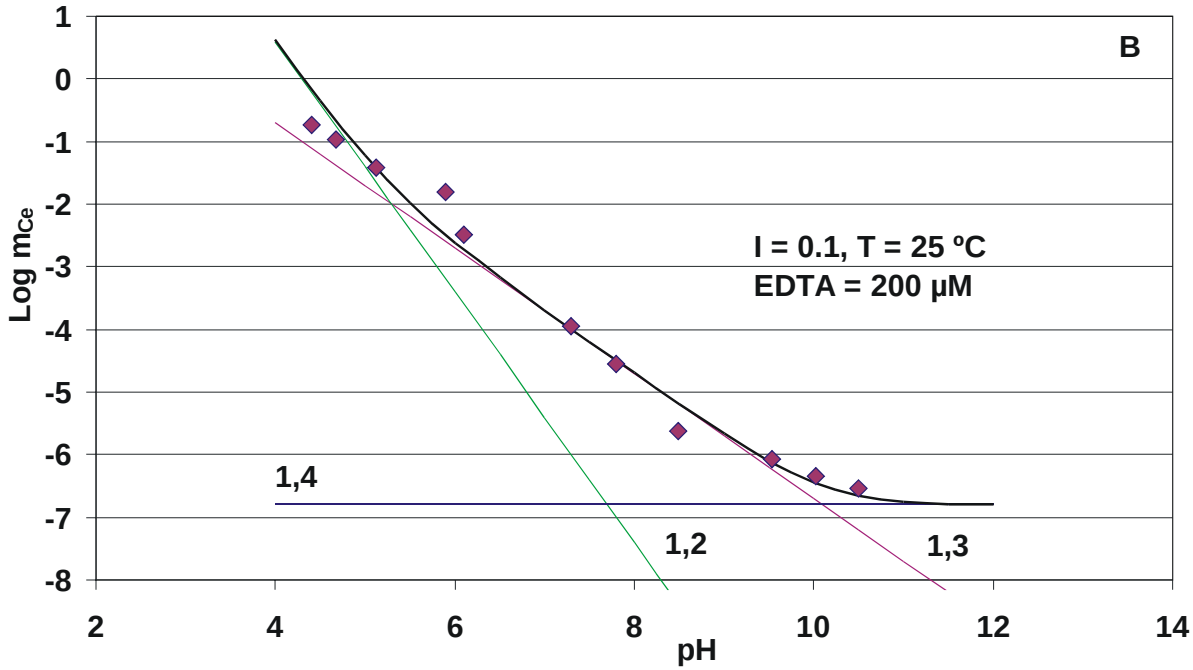
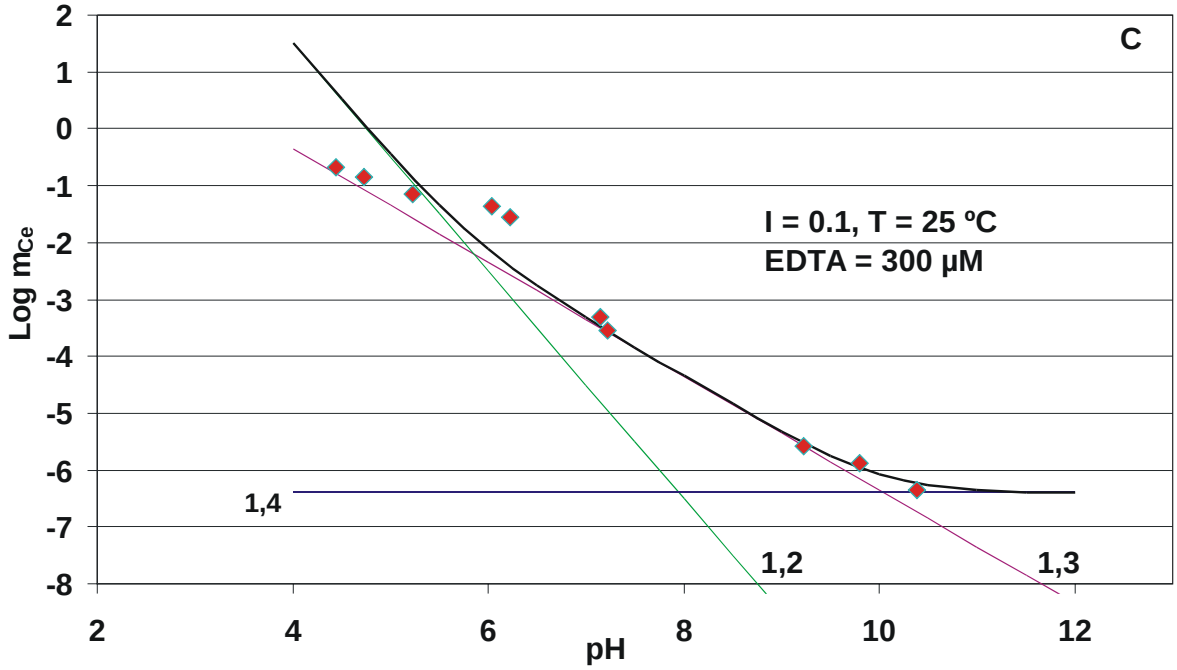


Fig. 1. Solubility of cerium dioxide in 0.1 M $NaNO_3$ solution from oversaturation, and inferred hydrolytic species.




B
I = 0.1, T = 25 ºC
EDTA = 200 µM
1,4
1,2
1,3
Log mCe
pH
1
0
-1
-2
-3
-4
-5
-6
-7
-8
2
4
6
8
10
12
14


C
I = 0.1, T = 25 ºC
EDTA = 300 µM
1,4
1,2
1,3
Log mCe
pH
2
1
0
-1
-2
-3
-4
-5
-6
-7
-8
2
4
6
8
10
12

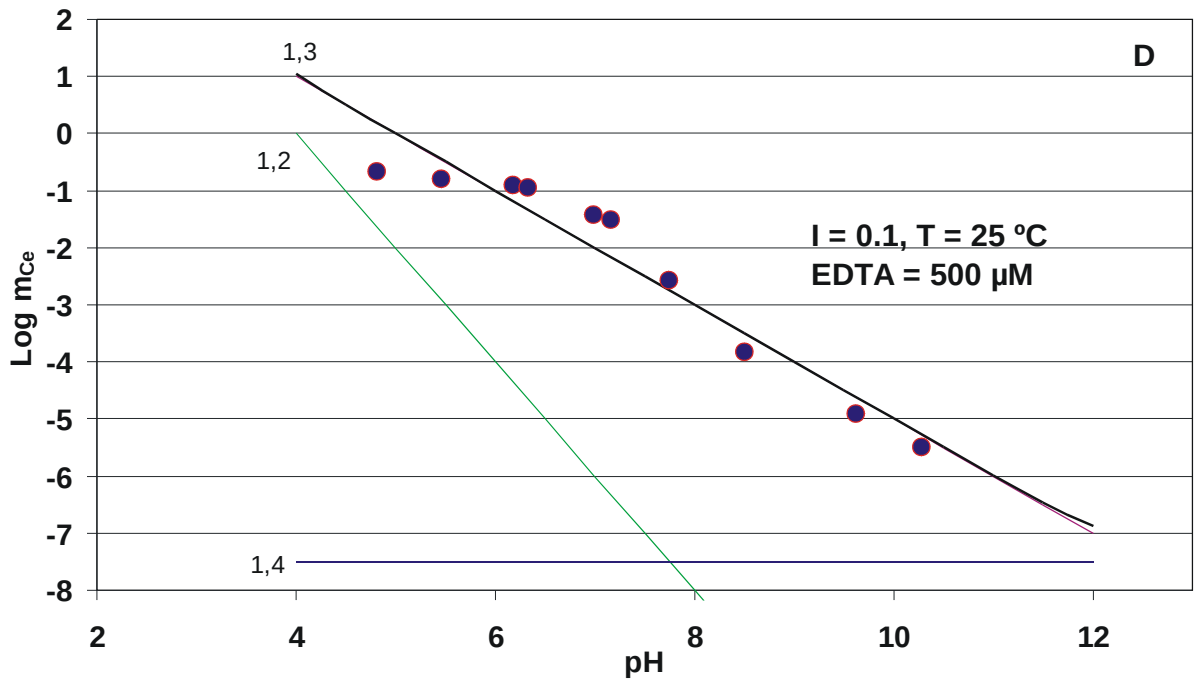


Fig. 2. Dependence of the solubility of cerium dioxide (CeO_2) in 0.1 M $NaNO_3$ solution with various EDTA contents as a function of pH. Note that a Ce(IV) species with 3 hydroxides appears to become increasingly important as a function of EDTA concentration, and the solubility of CeO_2 increases with EDTA concentration.

In another series of experiments the effect of organic ligands (citrate, EDTA and oxalate: 100 to 500 µmol) on the solubility of CeO_2 was investigated at fixed temperature-pH-ionic strength conditions. Experimental solutions were prepared at fixed pH (pH = 2.0, 3.0 or 4.0) and constant ionic strengths of 0.1, 1.0, or 3.0 m. Figure 3 shows solubility data for solutions without any organic ligands, and for 200 µmol kg^{-1} each of citrate, EDTA and oxalate, as a function of pH. The solubility of CeO_2 in the presence of 200 µmol kg^{-1} of oxalate, citrate or EDTA is about an order of magnitude higher than in the organic-free solutions at the same pH and ionic strength. The effects of EDTA and citrate on solubility appear to be very similar, except perhaps at pH 3. Oxalate is slightly less effective at increasing the solubility of CeO_2 than citrate or EDTA. The observed increases in solubility in the presence of organic ligands suggest the formation of aqueous Ce complexes with each of the three organic ligands investigated. Figure 4 demonstrates that at pH 3 the solubility of CeO_2 typically increases with increasing total concentration of organic ligand, further evidence of complex formation. This is also the case at pH 2 (not shown). However, at pH = 4 (not shown) solubility either decreased, or initially decreased and then increased with increasing ligand concentration. Detailed interpretation of these observations is complicated by the facts that the three organic ligands investigated have various states of protonation depending on pH, and the concentrations of Ce in solution are fairly large relative to those of the organic ligands. These issues mean that the free ligand concentrations are likely to be much less than the total ligand concentrations in our experiments, and the free ligand concentrations will be

a sensitive and complicated function of pH (and probably also ionic strength). Thus, detailed interpretation of the species likely to be present in our solutions will be deferred to a subsequent paper. However, the data do indicate the formation of Ce-organic ligand complexes with a relatively low ligand number.

The pH-dependence of CeO_2 solubility in the solutions containing organic ligands is similar to that obtained in the absence of organic ligands. This could indicate that the predominant dissolved Ce species in the organic ligand-bearing solutions are bound by several hydroxide ions in addition to an organic ligand. In other words, the species are likely to be highly hydrolyzed, and of the form $Ce(OH)_nL_m^q$, where L is one of the organic ligands and q is the overall charge on the complex.

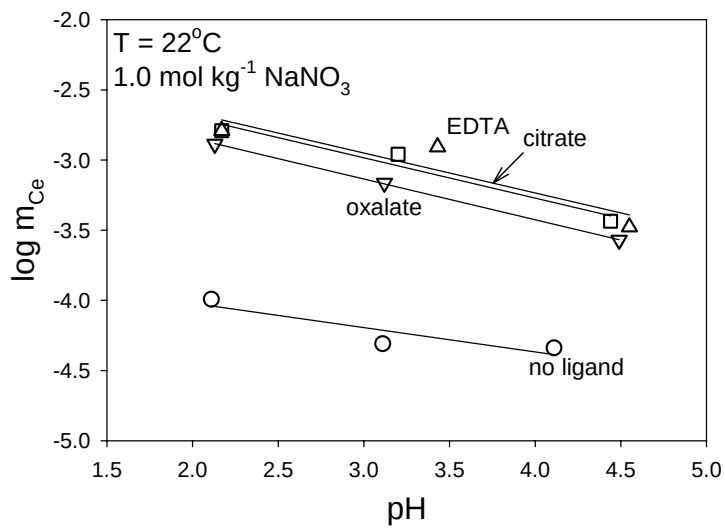


Figure 3: Plot of log m_{Ce} vs. pH for 1.0 mol kg^{-1} $NaNO_3$ solutions in equilibrium with solid CeO_2 at 22 °C. Data are depicted for solutions with no organic ligands, and for those with 200 μmol kg^{-1} of either citrate, EDTA or oxalate. The lines represent least square fits to the data.

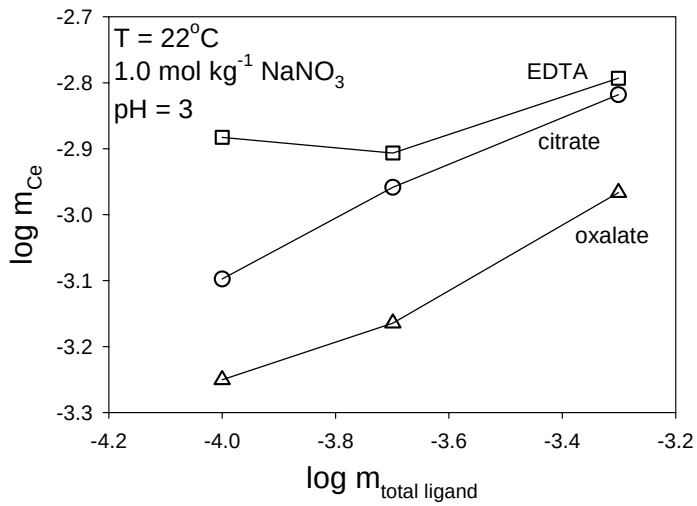
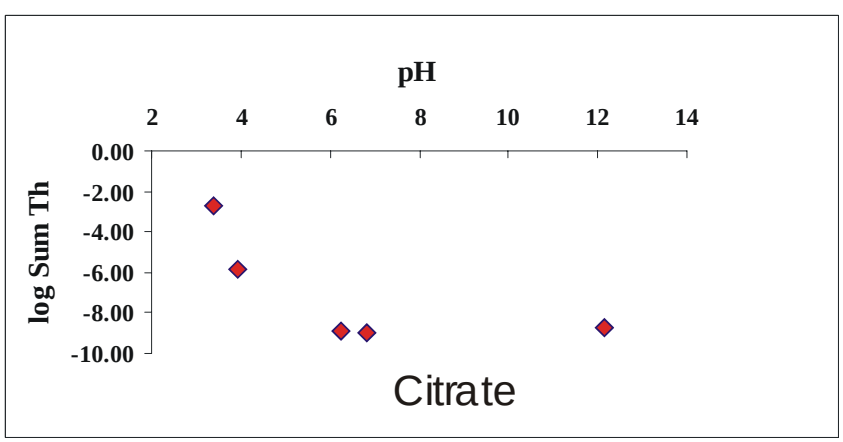


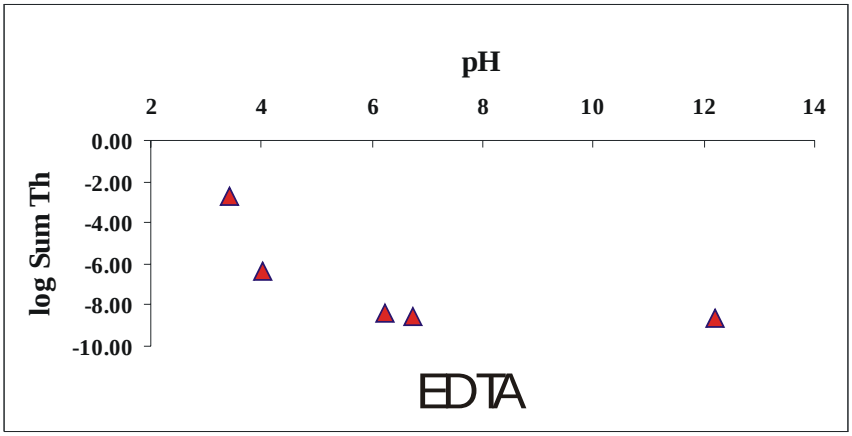
Figure 4: Plot of log m_{Ce} vs. log $m_{\text{total ligand}}$ for 1.0 mol kg^{-1} $NaNO_3$ solutions in equilibrium with solid CeO_2 at 22 °C and pH = 3.

Preliminary results from experiments involving the siderophore desferrioxamine B indicate that such compounds can also increase the solubility of CeO_2. Siderophores are naturally occurring organic compounds that microbes secrete to obtain nutrient iron, but they also complex other metals strongly. Siderophores are common in soils and sediments.

II. Solubility of ThO_2 in in aqueous $NaNO_3$ solutions both with and without organic ligands.

The solubility of a relatively poorly crystalline form of ThO_2 was investigated in the presence and absence of organic ligands under conditions similar to those employed for the CeO_2 solubility studies. We chose not to work with well crystallized ThO_2 because it is known that the solubility is much lower and the kinetics of dissolution are much slower than for the less crystalline form. The conditions of the experiments were: temperature (22±2 ºC), pH (3-12), ionic strength (0.1 M $NaNO_3$). Various concentrations of EDTA, citrate and oxalate were investigated.





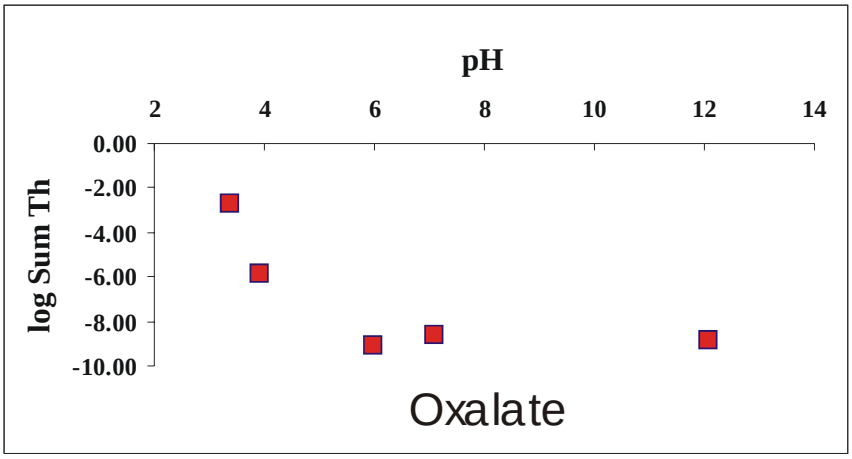


Figure 5: Plot of the solubility of ThO_2 vs. pH for three organic ligands at concentrations of 500 µmolal.

From Figure 5 it can be seen that the solubility of ThO_2 drops very steeply with increasing pH from 3 to 6, and then is constant up to pH 12. This is similar to what has been found in other studies of the solubility of ThO_2 in the absence of organic ligands. In fact, the solubility curves in the presence of citrate, EDTA and oxalate are strikingly similar, yielding identical solubilities at each pH, and these solubilities are nearly the same as those in the absence of organic ligands. These data imply that the organic ligands investigated have little effect on the solubility of ThO_2 at the concentrations used. This conclusion is further reinforced by Figure 6, from which it is evident that the solubility of ThO_2 is independent of the concentrations of each of the organic ligands at pH = 3.

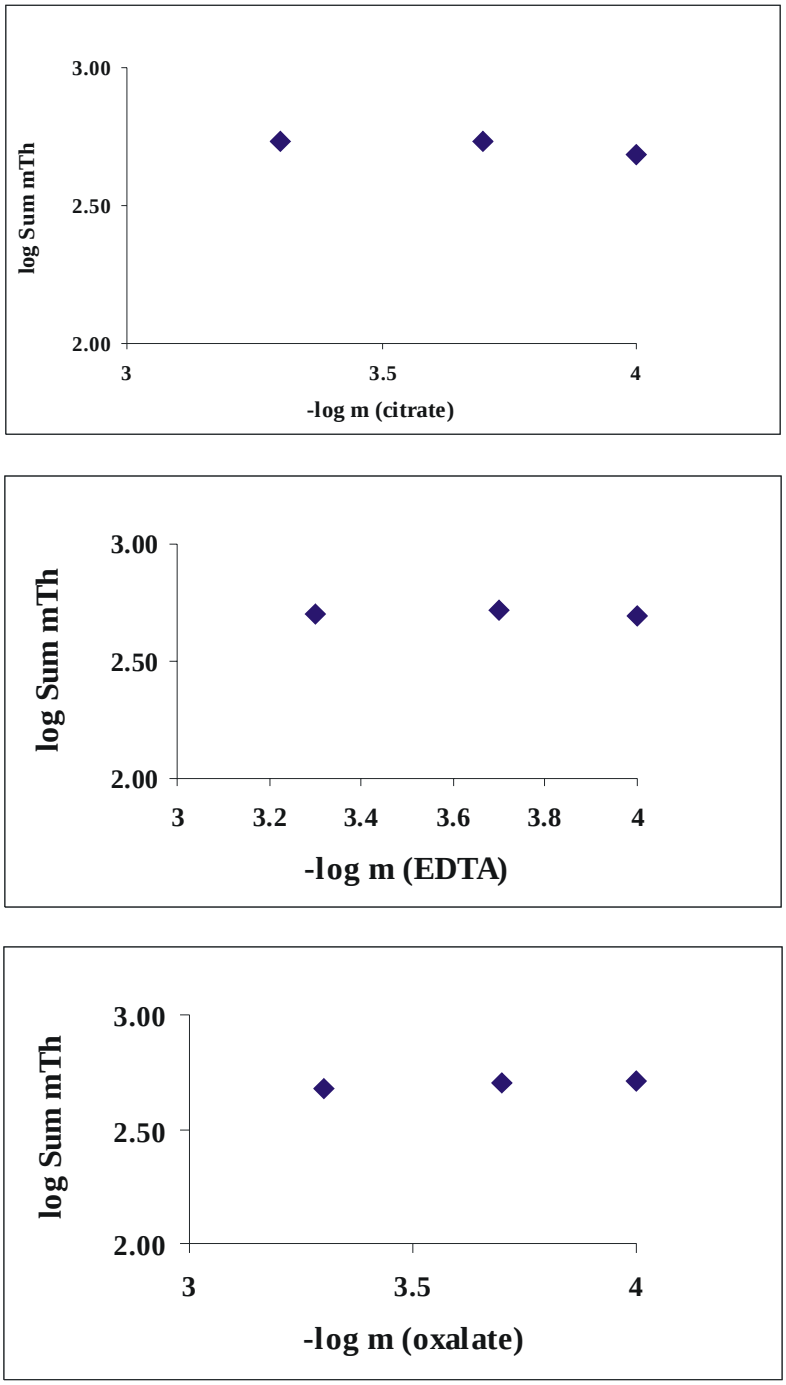


Figure 6: Plots of ThO_2 solubility in the presence of various organic ligands at 100 to 500 μmol kg^{-1} concentrations. The effects of organic ligands on solubility appear to be insignificant at pH 3.

CONCLUSIONS

The results of our study show that organic ligands such as citrate, oxalate, and EDTA can have an important effect on the solubility of CeO_2, but are far less effective at increasing the solubility of ThO_2. The difference may be related to the size of Ce(IV) vs. Th(IV), the latter being somewhat larger than the former. Because Pu(IV) is very similar in size to Ce(IV), we would expect the effect of organic ligands on Pu(IV) to be more similar to that of Ce(IV) than Th(IV).

Products Delivered under our Current and Previous EMSP Funding for the Project on "Understanding the Chemistry of the Actinides in High Level Waste Tank Systems"

Peer-Reviewed Publications:

1. C. H. Gammons, S. A. Wood, and Y. Li (2002). Complexation of the rare earth elements with aqueous chloride at 200°C and 300°C and saturated water vapor pressure. In Hellmann, R. and Wood, S.A., ed., *Water-rock Interaction, Ore Deposits, and Environmental Geochemisty: A tribute to David A. Crerar*. Geochemical Society Special Publication No. 7.
2. Nicholson, K.N. and Wood, S.A. (2002) Aqueous geochemistry of rare earth elements and yttrium. XII: Potentiometric stability constant determination of Bis-Tris complexes with La, Nd, Eu, Gd, Yb, Dy, Er, Lu, and Y. *Jour. Sol. Chem.* 31, 703-717.
3. Nicholson, K.N., Twamley, B. and Wood, S.A. (2001) [Bis(2-hydroxyethyl)amino]-tris(hydroxymethyl)methane (Bis–Tris), an important complexing agent. Acta Cryst. E57, o1133-o1135.
4. Wood, S.A., Wesolowski, D.J. and Palmer, D.A. (2000) The aqueous geochemistry of the rare earth elements. IX. A potentiometric study of Nd^{3+} complexation with acetate in 0.1 molal NaCl solution from 25°C to 225°C. Chemical Geology 167, 231-253.
5. R. Ding and Scott A. Wood (2002) The aqueous geochemistry of the rare earth elements and yttrium. Part X. Potentiometric determination of stability constants of acetate complexes of La^{3+}, Nd^{3+}, Gd^{3+} and Yb^{3+} at 25-70 °C and 1 bar. In Hellmann, R. and Wood, S.A., ed., *Water-rock Interaction, Ore Deposits, and Environmental Geochemisty: A tribute to David A. Crerar*. Geochemical Society Special Publication 7.
6. S. A. Wood, D. A. Palmer, D. J. Wesolowski, and P. Bénézeth (2002) The aqueous geochemistry of the rare earth elements and yttrium. Part XI. The solubility of $Nd(OH)_3$ and hydrolysis of Nd^{3+} from 30 to 290°C at saturated water vapor pressure with *in-situ* pH_m measurement. In Hellmann, R. and Wood, S.A., ed., *Water-rock Interaction, Ore Deposits, and Environmental Geochemistry: A tribute to David A. Crerar*. Geochemical Society Special Publication No. 7.
7. S.A. Wood and Z.S. Cetiner (in review) Solubility of CeO_2 in aqueous solutions as a function of pH and concentration of organic ligands. Jour. Alloys Comp. (submitted May 2005).

Conference Abstracts:

1. Cetiner, Z.S. and Wood, S.A. (2004) Measurements of the solubility of CeO_2 in $NaNO_3$ solutions: Hydrolysis of Ce(IV) and complexation by organic ligands. Geol. Soc. Amer. Prog. w. Abstr. No. 149-1.

2. Cao, H. and Wood, S.A. (2003) The solubility of CeO_2 in $NaNO_3$ medium. Geol. Soc. Amer. Prog. w. Abstr. CD-ROM Abstr. 96-14.
3. Cao, H. and Wood, S.A. (2004) The effect of organic ligands on the solubility of CeO_2 in $NaNO_3$ medium. Geochim. Cosmochim. Acta 69, A427.
4. Wood, S.A. and Cetiner, Z.S. (2004) Experimental measurements of the solubility of ThO_2 in $NaNO_3$ solutions: Hydrolysis of Th(IV) and complexation by organic ligands. Geochim. Cosmochim. Acta 69, A430.

Post-doctoral Associates and Students Trained:

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H. Cao, Post-doctoral Associate, UI

Z.S. Cetiner, Post-doctoral Associate, UI

A. Taunton, Graduate Student, UI

D. Koenig, Undergraduate Student, UI