Experimental Thermodynamic Studies for Efficient Extraction of Uranium from Seawater

Fuel Cycle Research & Development

Prepared for
U.S. Department of Energy
Separations and Waste Forms
Christina Leggett and Linfeng Rao
Lawrence Berkeley National Laboratory

September, 2014

FCRD-SWF-2014-000264
LBNL-6728E

DISCLAIMER

This information was prepared as an account of work sponsored by an agency of the U.S. Government. While this document is believed to contain correct information, Neither the U.S. Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, expressed or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness, of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. References herein to any specific commercial product, process, or service by trade name, trade mark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the U.S. Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the U.S. Government or any agency thereof or the Regents of the University of California

Revision 2
12/20/2012

APPENDIX E

FCT DOCUMENT COVER SHEET [1]

Name/Title of Deliverable/Milestone/Revision No.	Experimental Thermodynamic Studies for Efficient Extraction of Uranium from Seawater
Work Package Title and Number	Fuel Resources – LBNL FT-14LB031003
Work Package WBS Number	1.02.03.10
Responsible Work Package Manager	Linfeng Rao (signature on file) (Name/Signature)

Date Submitted 9/10/2014

Quality Rigor Level for Deliverable/Milestone[2]	☒ QRL-3	☐ QRL-2	☐ QRL-1 ☐ Nuclear Data	☐ Lab/Participant QA Program (no additional FCT QA requirements)

This deliverable was prepared in accordance with Lawrence Berkeley National Laboratory
(Participant/National Laboratory Name)

QA program which meets the requirements of
☒ DOE Order 414.1 ☐ NQA-1-2000 ☐ Other

This Deliverable was subjected to:

☒ Technical Review ☐ Peer Review

Technical Review (TR)

Review Documentation Provided

☐ Signed TR Report or,
☐ Signed TR Concurrence Sheet or,
☒ Signature of TR Reviewer(s) below

Peer Review (PR)

Review Documentation Provided

☐ Signed PR Report or,
☐ Signed PR Concurrence Sheet or,
☐ Signature of PR Reviewer(s) below

Name and Signature of Reviewers

Zhicheng Zhang (signature on file)

NOTE 1: *Appendix E should be filled out and submitted with the deliverable. Or, if the PICS:NE system permits, completely enter all applicable information in the PICS:NE Deliverable Form. The requirement is to ensure that all applicable information is entered either in the PICS:NE system or by using the FCT Document Cover Sheet.*

NOTE 2: *In some cases there may be a milestone where an item is being fabricated, maintenance is being performed on a facility, or a document is being issued through a formal document control process where it specifically calls out a formal review of the document. In these cases, documentation (e.g., inspection report, maintenance request, work planning package documentation or the documented review of the issued document through the document control process) of the completion of the activity along with the Document Cover Sheet is sufficient to demonstrate achieving the milestone. If QRL 1, 2, or 3 is not assigned, then the Lab/Participant QA Program (no additional FCT QA requirements box must be checked, and the work is understood to be performed, and any deliverable developed, in conformance with the respective National Laboratory/Participant, DOE- or NNSA-approved QA Program.*

This page is intentionally blank.

SUMMARY

This milestone report summarizes the data obtained in FY14 on three major tasks, including (1) thermodynamic studies of the interaction between Ca(II)/Mg(II) and the triscarbonato uranyl species, with the objective of evaluating the speciation of U(VI) in seawater; (2) Thermodynamic studies of the interactions between Ca(II)/Mg(II) and glutarimidedioxime; and (3) Preliminary investigation of the binding strength of vanadium with glutarimidedioxime and evaluation of the competition between U(VI) and V(V) for binding amidoxime ligands.

The data on the interactions of Ca(II)/Mg(II) with the triscarbonato uranyl species have particular importance, because they show that the dominant U(VI) species under seawater conditions is the neutral complex, $Ca_2UO_2(CO_3)_3(aq)$ (~ 60%), instead of the anionic $Ca_2UO_2(CO_3)_3^{4-}$ species suggested by the previous literature. The results have important implications in the design of effective sorbents to extract uranium from seawater.

CONTENTS

SUMMARY v

FIGURES

Figure 1. A representative Ca^{2+} ion selective electrode potentiometric titration. 1

Figure 2. Spectrophotometric titration of $Mg^{2+}/UO_2(CO_3)_3^{4-}$. 2

Figure 3. Microcalorimetric titrations on the complexation of Ca^{2+} with $UO_2(CO_3)_3^{4-}$ 3

Figure 4. U(VI) speciation under seawater conditions in the absence (upper figure) and presence of 0.01 M Ca(II) and 0.053 M Mg(II) (lower figure) 4

Figure 5. Potentiometric titrations for calcium and magnesium with glutarimidedioxime 5

Figure 6. Calorimetric titration of glutarimidedioxime (denoted as H_2AmidA in the figure) with calcium 6

Figure 7. Representative titration of vanadium with glutarimidedioxime (denoted as H_2AmidA) 7

TABLES

Table 1. Equilibrium constants of Ca/Mg complexation with $UO_2(CO_3)_3^{4-}$. 3

Table 2. Stability constants of calcium, magnesium, and uranium complexes with glutarimidedioxime 5

Table 3. Summary of reaction enthalpies and entropies for calcium-glutarimidedioxime (as H_2L in the table) complexes 6

Table 4. Comparison of the stability constants of V(V) and U(VI) complexes with glutarimidedioxime 7

1. INTRODUCTION

To improve the extraction efficiency and reduce the extraction cost, fundamental understanding of the coordination chemistry of the extraction process is necessary. Therefore, thermodynamic studies need to be conducted to determine the stability constants of the complexes of uranium and other major metal ions in seawater with amidoxime-type ligands, by a combination of techniques including potentiometry and spectrophotometry.

In FY14, three major tasks were taken, including (1) thermodynamic studies of the interaction between Ca(II)/Mg(II) and the triscarbonato uranyl species, with the objective of evaluating the speciation of U(VI) in seawater; (2) Thermodynamic studies of the interactions between Ca(II)/Mg(II) and glutarimidedioxime; and (3) Preliminary determination of the binding strength of vanadium with glutarimidedioxime and evaluation of the competition between U(VI) and V(V) for binding amidoxime-type ligands. This report presents the data obtained for these tasks in FY14.

2. RESULTS

2.1 Interaction between Ca(II)/Mg(II) and $UO_2(CO_3)_3^{4-}$

2.1.1 Stability constants

Figure 1 shows an example of potentiometric titrations carried out to study the formation of the successive complexes of Ca^{2+} with $UO_2(CO_3)_3^{4-}$. The data were processed with the minimization software *Hyperquad* [1]. The best fit was obtained with a model consistent with the formation of two successive complexes, described by equations (1) and (2) (see Table 1). As shown in Figure 1, the agreement between the experimental and calculated values is excellent.

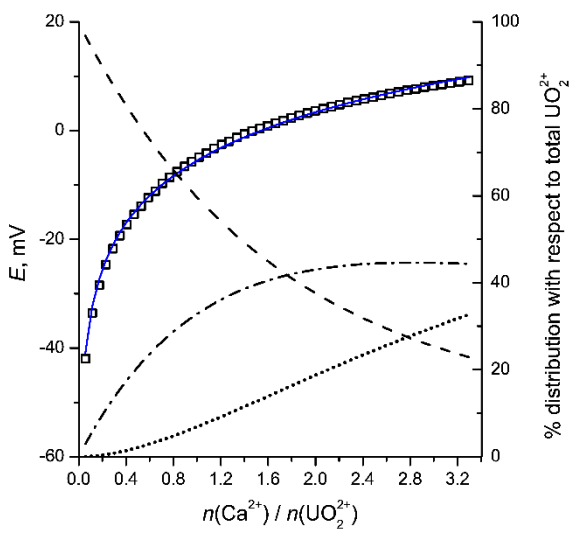

Figure 1. A representative Ca^{2+} ion selective electrode potentiometric titration. $[UO_2^{2+}]_{initial}$ = 0.469 mM; $[CO_3^{2-}]_{initial}$ = 1.85 mM; $[Ca^{2+}]_{titrant}$ = 10.05 mM; pH = 10.3–10.0. Symbols: (left y-axis, *E* in mV) □ observed *E*; solid line - calculated *E*; (right y-axis, percentage of U(VI) species) -- $UO_2(CO_3)_3^{4-}$, -·- $CaUO_2(CO_3)_3^{2-}$, ··· $Ca_2UO_2(CO_3)_3(aq)$.

$$Ca^{2+} + UO_2(CO_3)_3^{4-} = CaUO_2(CO_3)_3^{2-} \quad (1)$$

$$2\ Ca^{2+} + UO_2(CO_3)_3^{4-} = Ca_2UO_2(CO_3)_3(aq) \quad (2)$$

Figure 2 shows a representative spectrophotometric titration for the complexation of Mg^{2+} with the triscarbonato uranyl species. As $MgCl_2$ was added into the solution of $UO_2(CO_3)_3^{4-}$, subtle changes in the spectra were observed in the wavelength region of 220 – 400 nm (Figure 2, upper left diagram). The data were processed with the minimization software *HypSpec* [1]. Factor analysis of the data indicated that there were two absorbing species, $UO_2(CO_3)_3^{4-}$ and an $Mg^{2+}/UO_2(CO_3)_3^{4-}$ complex. The best fit was obtained with the model consistent with the formation of the 1:1 complex, described by equation (3).

$$Mg^{2+} + UO_2(CO_3)_3^{4-} = MgUO_2(CO_3)_3^{2-} \qquad (3)$$

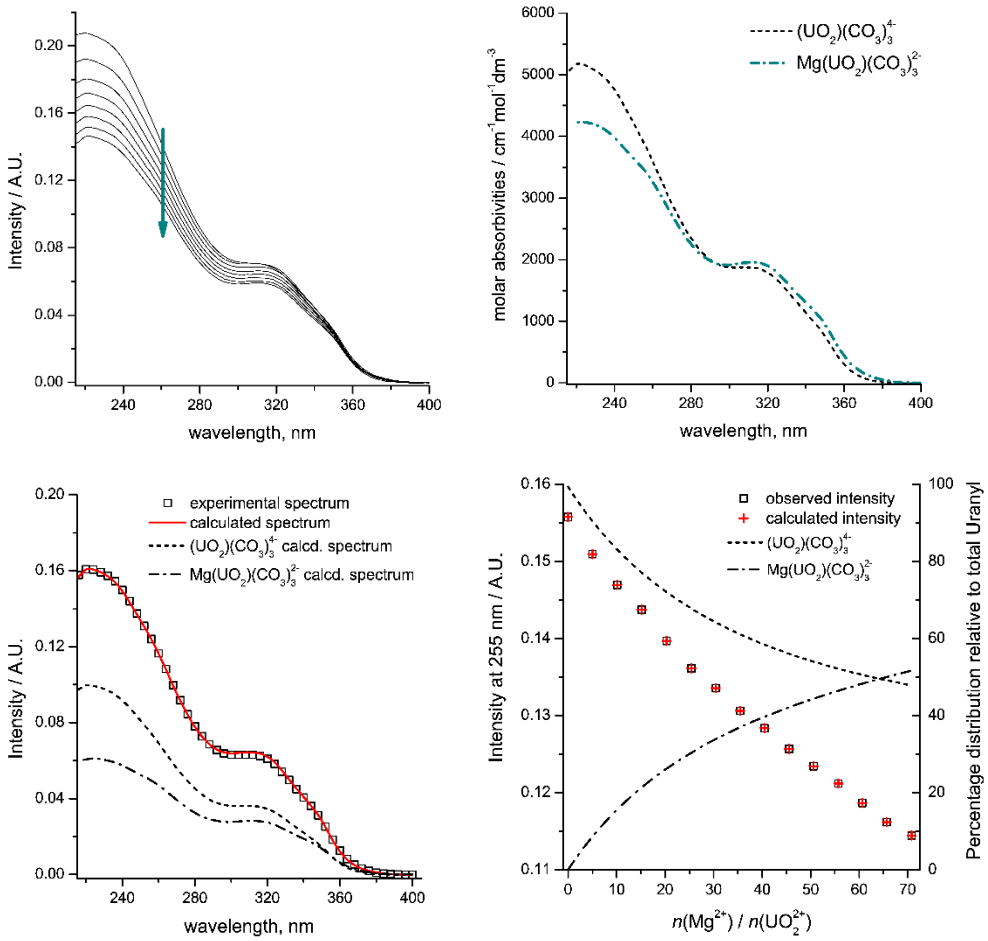

Figure 2. Spectrophotometric titration of $Mg^{2+}/UO_2(CO_3)_3^{4-}$. $[UO_2^{2+}]_{initial}$ = 0.040 mM; $[CO_3^{2-}]_{initial}$ = 0.200 mM; $[Mg^{2+}]_{titrant}$ = 10.22 mM (final $n(Mg)/n(UO_2^{2+})$ = 70.8); pH = 9.75–9.68. Upper left: un-normalized spectra (the number of spectra was reduced for clarity). Upper right: Calculated molar absorptivities of $UO_2(CO_3)_3^{4-}$ and $MgUO_2(CO_3)_3^{2-}$. Lower left: Experimental and calculated spectra at $n(Mg)/n(UO_2^{2+})$ = 45.5 (some experimental points omitted for clarity). Lower right: experimental and calculated absorbance at 255 nm as a function of $n(Mg)/n(UO_2^{2+})$ and the percentage distribution relative to total uranyl on the right axis of the diagram.

Table 1 Equilibrium constants of Ca/Mg complexation with $UO_2(CO_3)_3^{4-}$.

Reaction	$\log\beta \pm \sigma$		
	I = 0 M	I = 0.1 M NaCl	I = 0.5 M NaCl
$Ca^{2+} + UO_2(CO_3)_3^{4-} = CaUO_2(CO_3)_3^{2-}$	5.15 ± 0.06	3.42 ± 0.06	2.43 ± 0.10
$2Ca^{2+} + UO_2(CO_3)_3^{4-} = Ca_2UO_2(CO_3)_3(aq)$	9.00 ± 0.06	6.42 ± 0.06	4.96 ± 0.10
$Mg^{2+} + UO_2(CO_3)_3^{4-} = MgUO_2(CO_3)_3^{2-}$	4.41 ± 0.06	2.69 ± 0.06	1.77 ± 0.10

2.1.2 Enthalpy of Ca(II) complexation with $UO_2(CO_3)_3^{4-}$

Figure 3 shows the thermogram of a representative calorimetric titration (heat rate *vs* time, left diagram), and the experimental/fitted heat as a function of the titrant volume (right diagram). As the thermogram shows, small positive heat was observed as Ca(II) was added into the solution containing $UO_2(CO_3)_3^{4-}$, indicating that the formation of the calcium complexes is slightly exothermic. The reaction heat, in conjunction with the stability constants of $CaUO_2(CO_3)_3^{2-}$ and $Ca_2UO_2(CO_3)_3(aq)$ obtained by potentiometry, was fitted with the minimization software *HypDeltaH* [1] to calculate the enthalpies of complexation for the two complexes. As shown in Figure 3 (right diagram), the fitting of the data is reasonably good considering the very small amounts of reaction heat developed during the titrations (50 - 200 μJ/addition). The calculated enthalpies of complexation for reactions (1) and (2) are -(8 ± 6) kJ·mol^{-1}, and -(8 ± 7) kJ·mol^{-1}, respectively.

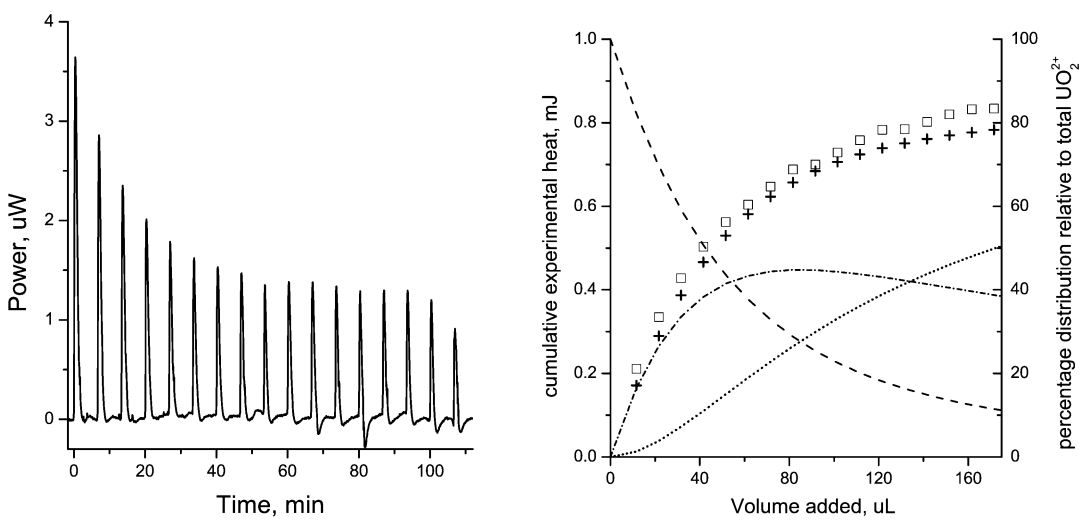

Figure 3. Microcalorimetric titrations on the complexation of Ca^{2+} with $UO_2(CO_3)_3^{4-}$ (0.1 M NaCl, 25.0°C). $[UO_2^{2+}]_{initial}$ = 0.20 mM; $[CO_3^{2-}]_{initial}$ = 0.80 mM; $[Ca^{2+}]_{titrant}$ = 10.05 mM; pH=10.3–10.0. Left: thermogram (Power, μW *vs* time, min). Each peak corresponds to an addition of titrant. Right: cumulative experimental and calculated heats (mJ) on the left axis, percentage distribution of the complexes with respect to total uranyl on the right axis. Symbols: -- $UO_2(CO_3)_3^{4-}$; -·-$CaUO_2(CO_3)_3^{2-}$; ··· $Ca_2UO_2(CO_3)_3(aq)$; □ experimental cumulative heat (mJ); + Calculated cumulative heat (mJ).

2.1.3 Speciation of U(VI) under seawater conditions

Though the complexation between Ca/Mg and $UO_2(CO_3)_3^{4-}$ is fairly weak, the speciation of U(VI) in seawater could be affected due to the high concentrations of Ca and Mg relative to U(VI) in seawater ([Ca(II)] = 0.01 M, [Mg(II)] = 0.053 M, and [U(VI)] = 1.4×10^{-8} M). Consequently, neglecting the formation of Ca/Mg complexes with $UO_2(CO_3)_3^{4-}$ could probably lead to erroneous speciation of U(VI) under seawater conditions. As shown in the lower diagram of Figure 4, when pH is above 6, the aqueous chemistry of U(VI) in the presence of Ca(II) (0.01 M) and Mg(II) (0.053 M) is dominated by the formation of the $M_nUO_2(CO_3)_3^{2(2-n)-}$ (M = Ca or Mg, and n = 1 or 2) complexes. In particular, at the seawater pH (8.2), $Ca_2UO_2(CO_3)_3$(aq) accounts for 58% of the total uranium in solution, $CaUO_2(CO_3)_3^{2-}$ and $MgUO_2(CO_3)_3^{2-}$ 18% each, and $UO_2(CO_3)_3^{4-}$ only 6%. In contrast, more than 97% of U(VI) would exist as $UO_2(CO_3)_3^{4-}$ if the formation of Ca/Mg complexes with $UO_2(CO_3)_3^{4-}$ was neglected, as shown in the upper speciation diagram of Figure 4.

Understanding the speciation of U(VI) under seawater conditions is of great significance in the development of strategies for the extraction of uranium from seawater. Since the dominant species of U(VI) is the neutral complex, $Ca_2UO_2(CO_3)_3$(aq), instead of the highly negatively charged $UO_2(CO_3)_3^{4-}$ as previously believed, the sorbents must be able to interact with $Ca_2UO_2(CO_3)_3$(aq) effectively to achieve efficient collection [2].

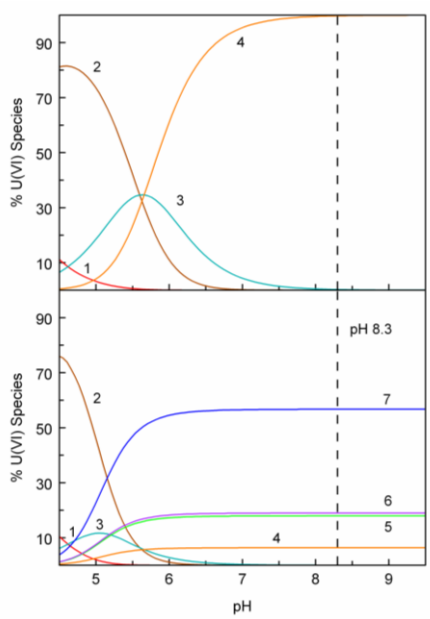

Figure 4. U(VI) speciation under seawater conditions in the absence (upper figure) and presence of 0.01 M Ca(II) and 0.053 M Mg(II) (lower figure). $C_U = 1.4 \times 10^{-8}$ M, $C_{carbonate}$ = 0.0023 M. 1 – UO_2^{2+}, 2 - $UO_2(CO_3)$(aq), 3 - $UO_2(CO_3)_2^{2-}$, 4 - $UO_2(CO_3)_3^{4-}$, 5 - $CaUO_2(CO_3)_3^{2-}$, 6 - $MgUO_2(CO_3)_3^{2-}$, 7 – $Ca_2UO_2(CO_3)_3$(aq).

2.2 Complexation of Ca(II)/Mg(II) with glutarimidedioxime

2.2.1 Stability constants

Potentiometric titrations (Figure 5) titrations were performed to determine the stability constants of Ca(II) and Mg(II)/complexes with glutarimidedioxime. The HypQuad program was used to calculate the stability constants (Table 2). It was found that the complexation of Ca(II) and Mg(II) with glutarimidedioxime is significantly weaker than those of U(VI).

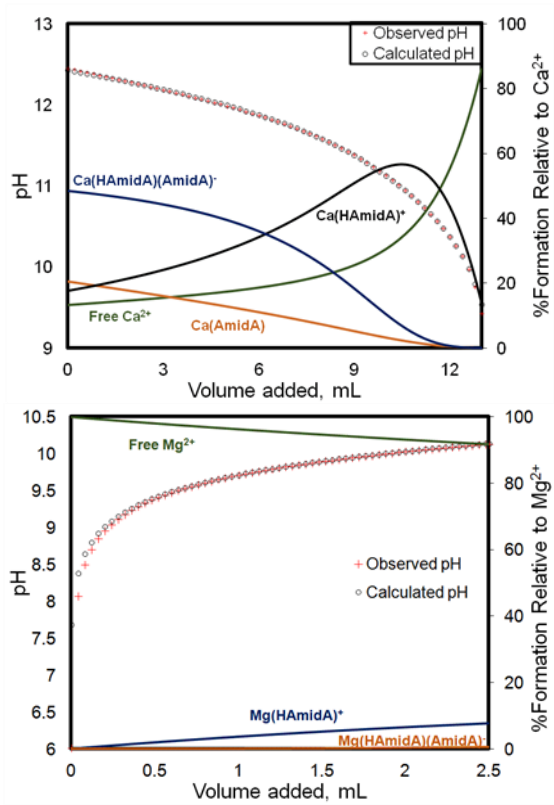

Figure 5. Potentiometric titrations for calcium and magnesium with glutarimidedioxime (denoted as H_2AmidA in the figure). Top: V_o = 15.5 mL, $[Ca]_{TOT}$ = 7.95 mM, $[H_2AmidA]_{TOT}$ = 19.9 mM, [NaOH]: 0.086 M. Titrant: 0.0994 M HCl. Bottom: V_o = 21.1 mL, $[Mg]_{TOT}$ = 1.87 mM, $[H_2AmidA]_T$ = 4.69 mM. Titrant: 0.0102 M NaOH.

Table 2 Stability constants of calcium, magnesium, and uranium complexes with glutarimidedioxime (denoted as H_2L in the table)

Reaction*	Log β
$Ca^{2+} + L^{2-} \rightarrow Ca(L)$	2.44 ± 0.02
$UO_2^{2+} + L^{2-} \rightarrow UO_2(L)$	17.8 ± 1.1
$Ca^{2+} + H^+ + L^{2-} \rightarrow Ca(HL)^+$	14.56 ± 0.02
$Mg^{2+} + H^+ + L^{2-} \rightarrow Mg(HL)^+$	14.40 ± 0.04
$UO_2^{2+} + H^+ + L^{2-} \rightarrow UO_2(HL)^+$	22.7 ± 1.3
$Ca^{2+} + H^+ + 2L^{2-} \rightarrow Ca(HA)(L)^-$	17.27 ± 0.06
$Mg^{2+} + H^+ + 2L^{2-} \rightarrow Mg(HA)(L)^-$	18.56 ± 0.15
$UO_2^{2+} + H^+ + 2L^{2-} \rightarrow UO_2(HA)(L)^-$	36.8 ± 2.1

2.2.2 Enthalpy of complexation

The enthalpy of complexation between Ca(II) and glutarimidedioxime was determined by microcalorimetry (Figure 6). The HypDH program was used to calculate the enthalpy of complexation (Table 3).

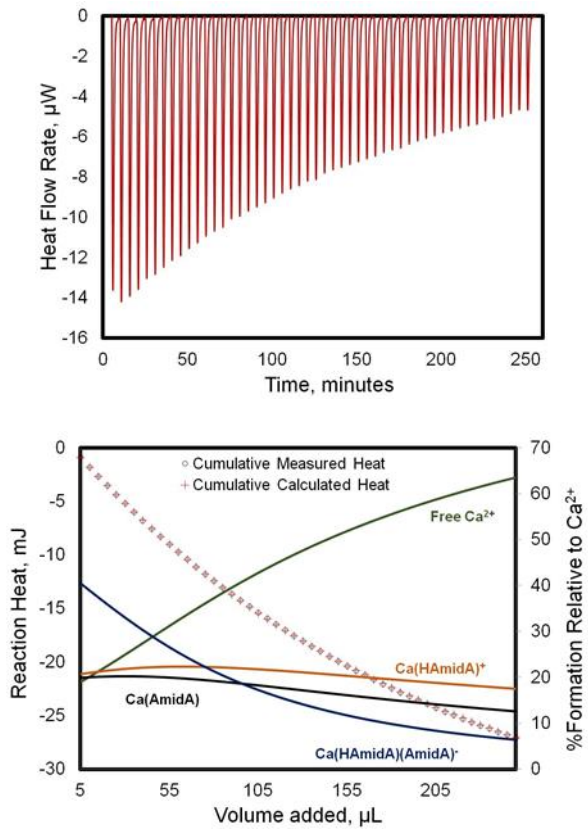

Figure 6. Calorimetric titration of glutarimidedioxime (denoted as H_2AmidA in the figure) with calcium. Top: Thermogram showing reaction heat flow rate as a function of time for a typical calorimetric titration. Bottom: Fit of the data with overlapping speciation. Titration conditions are as follows: cup: V_o = 0.750 mL, $[H_2AmidA]_{TOT}$ = 0.0101 M, $[H^+]_{TOT}$ = -0.020 M. Titrant: 0.05 M $CaCl_2$ (I=0.5 M).

Table 3 Summary of reaction enthalpies and entropies for calcium-glutarimidedioxime (as H_2L in the table) complexes

Reaction	ΔH (kJ mol^{-1})	ΔS (J mol^{-1} K^{-1})
$H^+ + L^{2-} \rightarrow HL^-$	-36.1 ± 0.5	110 ± 2
$2H^+ + L^{2-} \rightarrow H_2L$	-69.7 ± 0.9	202 ± 3
$3H^+ + L^{2-} \rightarrow H_3L^+$	-77 ± 6	218 ± 14
$Ca^{2+} + L^{2-} \rightarrow Ca(L)$	10.5 ± 4	82 ± 13
$Ca^{2+} + H^+ + L^{2-} \rightarrow Ca(HL)^+$	-30.3 ± 4	117 ± 13
$Ca^{2+} + H^+ + 2L^{2-} \rightarrow Ca(HL)(L)^-$	-29.9 ± 0.7	230 ± 3

2.3 Interactions between vanadium(V) and glutarimidedioxime

Potentiometric titrations were performed to evaluate the binding interactions of V(V) with glutarimidedioxime (Figure 7). The tentative stability constants of V(V)/glutarimidedioxime complexes are listed in Table 4, in compassion with those of U(VI).

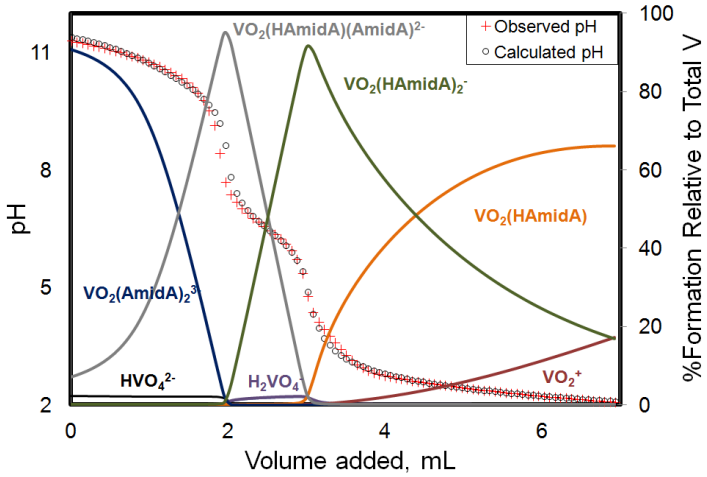

Figure 7. Representative titration of vanadium with glutarimidedioxime (denoted as H_2AmidA). Cup solution: $[V]_{TOT}$ = 5.24 mM, $[H_2AmidA]_{TOT}$ = 10.3 mM, 0.015 M NaOH, 19.9 mL. Titrant: 0.100M HCl.

The stability constants for the vanadium complexes with glutarimidedioxime are at least 8 orders of magnitude stronger than the analogous uranyl complexes as indicated in Table 4. Furthermore, as indicated by the potentiometric data, vanadium forms complexes with glutarimidedioxime over a large range of pH values, which may complicate efforts to remove vanadium from the polymeric fibers that are being developed to sequester uranium.

Table 4 Comparison of the stability constants of V(V) and U(VI) complexes with glutarimidedioxime (denoted as H_2L in the table)

Overall Reaction	Log β_{MLH}
$VO_2^+ + L^{2-} \rightarrow VO_2(L)^-$	(~26-27)
$UO_2^{2+} + L^{2-} \rightarrow UO_2(L)$	17.8 ± 1.1
$VO_2^+ + H^+ + L^{2-} \rightarrow VO_2(HL)$	31.56 ± 0.06
$UO_2^{2+} + H^+ + L^{2-} \rightarrow UO_2(HL)^+$	22.7 ± 1.3
$VO_2^+ + 2H^+ + 2L^{2-} \rightarrow VO_2(HL)_2^-$	54.96 ± 0.04
$UO_2^{2+} + 2H^+ + 2L^{2-} \rightarrow UO_2(HL)_2$	43.0 ± 1.1
$VO_2^+ + H^+ + 2L^{2-} \rightarrow VO_2(HL)(L)^{2-}$	48.52 ± 0.06
$UO_2^{2+} + H^+ + 2L^{2-} \rightarrow UO_2(HL)(L)^-$	36.8 ± 2.1
$VO_2^+ + 2L^{2-} \rightarrow VO_2(L)_2^{3-}$	38.24 ± 0.07
$UO_2^{2+} + 2L^{2-} \rightarrow UO_2(L)_2^{2-}$	36.0 ± 1.1

3. SUMMARY

Though Ca(II) and Mg(II) form weak complexes with triscarbonato uranyl anion, about 60% of U(VI) exists as the neutral $Ca_2UO_2(CO_3)_3$ species under seawater conditions, due to the high concentrations of Ca(II) and Mg(II) in seawater.

The complexes of Ca(II) and Mg(II) with glutarimidedioxime are a number of orders of magnitude lower than those of U(VI) with glutarimidedioxime. They are not expected to have strong competition with U(VI) for the sorption sites of the amidoxime-based sorbents. However, due to their high concentrations in seawater, sorption of Ca(II) and Mg(II) is expected to occur.

Preliminary studies suggest the vanadium(V) interacts with glutarimidedioxime much more strongly than U(VI). Further studies are to be conducted to confirm the binding strength, and gain fundamental understanding of the high binding strength of V(V) by glutarimidedioxime.

4. REFERENCES

1. Gans, P., A. Sabatini, and A. Vacca, *Investigation of equilibria in solution. Determination of equilibrium constants with the HYPERQUAD suite of programs.* Talanta, 1996. **43**(10): p. 1739-1753.
2. Endrizzi, F., and Rao, L. *Formation of Ca^{2+} and Mg^{2+} Complexes with $(UO_2)(CO_3)_3^{4-}$ in Aqueous Solution: Effect on the Speciation of U(VI) and its Extraction from Marine Environments, Chem. Eur. J., in press.*

5. ACKNOWLEGEMENTS

Funding for this work was provided by the Fuel Resources, Fuel Cycle Research and Development Program, Separations and Waste Form Campaign, Office of Nuclear Energy, of the U.S. Department of Energy under Contract Number DE-AC02-05CH11231 with Lawrence Berkeley National Laboratory.