Complexation of Calcium and Magnesium with Glutarimidedioxime: Implications for the Extraction of Uranium from Seawater

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Abstract

Complexation of calcium and magnesium with glutarimidedioxime, a ligand of importance in the sorption of uranium from seawater by functionalized sorbents, in aqueous solutions was investigated with potentiometry and calorimetry. The stability constants of the complexes and the enthalpies of complexation were determined. Results show that calcium(II) and magnesium(II) form much weaker complexes with glutarimidedioxime than uranium(VI). However, due to the very high concentrations of calcium and magnesium in seawater, small but significant fractions of the sorption sites on the glutarimidedioxime-functionalized sorbent are expected to be occupied by calcium and magnesium. Results also show that the dominant complexation reactions of calcium and magnesium with glutarimidedioxime at seawater pH are endothermic processes, implying that the complexation, as well as the sorption of calcium and magnesium on the glutarimidedioxime-functionalized sorbent, would be enhanced at higher temperatures.

Keywords: amidoxime, uranium extraction, complexation, stability constants, alkaline earths

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1. Introduction

The global supply of uranium derived from conventional terrestrial sources is estimated to be 7.1 million tons, enough to power the world's nuclear reactors for a little over 100 years [1]. However, this estimate does not take into account the increase in demands for uranium due to the expansion of nuclear power in countries such as China and India. In addition to increasing the exploration of new potential mining sites, attempts to meet the growing demand for uranium have involved exploring unconventional sources such as phosphate rocks, black shale, mill tailings, and coal ash. One unconventional source of uranium that could vastly increase the global inventory of uranium is the ocean, which contains 4.5 billion tons of uranium – nearly a thousand times more than the entire known terrestrial supply [2].

Although there is essentially a limitless supply of uranium in the ocean, several factors complicate the efforts to efficiently and economically extract uranium. Firstly, the uranium is present at an extremely low concentration ($3.3 \mu\text{g}\cdot\text{L}^{-1}$) along with a number of other elements that can compete with uranium for an extractant (Table 1) [3]. Secondly, due to the overwhelmingly high concentrations of calcium, magnesium, and carbonate in seawater, uranium exists primarily in the forms of very stable tris(carbonato) species that include the $\text{Ca}_2[\text{UO}_2(\text{CO}_3)_3]^0(\text{aq})$, $\text{Ca}[\text{UO}_2(\text{CO}_3)_3]^{2-}$, $\text{Mg}[\text{UO}_2(\text{CO}_3)_3]^{2-}$, and $\text{UO}_2(\text{CO}_3)_3^{4-}$ species [4]. Lastly, the pH and temperature of seawater can vary by location, ranging from pH 7.5 - 8.5 and 12 - 40 °C, respectively [5,6,7]. Therefore, it is evident that a suitable extraction technique must employ an extractant that can bind uranium very strongly and selectively at slightly alkaline pH and in a relatively wide range of temperatures.

Though many extraction techniques have been investigated over the past five decades, the most advanced technology is the use of polymeric sorbents, particularly those that have been

functionalized with the amidoxime (-C(NH₂)NOH) moiety developed in the 1990s in Japan [8]. The efficacy of poly(acrylamidoxime) sorbents for the extraction of uranium was demonstrated by Japanese scientists in marine tests more than a decade ago, in which the uranium uptake was 1.5 g U/kg adsorbent after 30 days [8]. More recently, another series of marine tests using newly developed amidoxime-based sorbents were conducted in the United States, achieving 3.3g U/kg adsorbent after 8 weeks [9]. Using the current technology, it is roughly estimated that the cost for implementing the amidoxime-based sorption system on a large scale would range from \$610/kg U to \$1000/kg U, still much higher than the cost of recovering uranium terrestrially ($\leq$ \$260/kg U) [1]. To further reduce the cost and make the extraction of uranium from seawater economically viable, research at both the fundamental and practical levels is underway with the objectives of improving the sorption efficiency, selectivity, and recyclability of the sorbents.

Table 1 Concentrations of selected elements in seawater [12,13]

Element	Concentration ($\mu\text{g L}^{-1}$)
Na	1.08×10^7
Mg	1.290×10^6
Ca	411,000
U	3.3
Fe	3.4
V	1.6
Cu	0.9
Ni	6.6
Pb	0.03

The efficiency and selectivity of the amidoxime-based sorbents can be assessed by quantifying the binding strength of the amidoxime ligands with uranium and comparing these with the binding strengths with other major competing seawater cations. Recently, in an effort to provide a rigorous thermodynamic explanation for the high uptake of uranium by amidoxime-

based sorbents, we have determined the thermodynamic stability constants for complexes of uranium with a series of amidoxime ligands that could represent the functional groups on the poly(acrylamidoxime) sorbents used for uranium collection from seawater. Among the ligands, a cyclic imidedioxime, glutarimidedioxime (Fig.1, denoted as H₂A in this paper), was found to form strong complexes with uranium at seawater pH [10], and is expected to be responsible for the sorption of uranium from seawater. Building on this work, the thermodynamics of complexation of glutarimidedioxime with a number of other competing cations was studied [11]. Data indicated that the binding strength of glutarimidedioxime with the metal cations in seawater followed the order: Fe³⁺ > UO₂²⁺ ~ Cu²⁺ > Pb²⁺ > Ni²⁺ [11]. The thermodynamic results have helped to predict and interpret the sorption behavior of these cations in the process using the poly(acrylamidoxime) sorbents.

Fig. 1 Glutarimidedioxime (H₂A)

It has been noticed that previous thermodynamic studies do not include the alkali and alkaline earth metals – most notably, Na⁺, Ca²⁺, and Mg²⁺ – that are present in seawater at the highest concentrations (Table 1). Though calcium and magnesium are expected to form weak complexes with glutarimidedioxime, they could still be sorbed on a significant fraction of the binding sites of the poly(acrylamidoxime) sorbents because of their exceedingly high concentrations relative to uranium in seawater. To evaluate the competition of calcium and

magnesium with uranium for sorption, thermodynamic data including stability constants and enthalpies of complexation for the complexes of calcium and magnesium with glutarimidedioxime (H_2A) are needed. Therefore, the present work focused on the determination of thermodynamic parameters ($\log\beta$, ΔH , and ΔS) for the complexation of calcium and magnesium with glutarimidedioxime by potentiometric and calorimetric experiments. Using the thermodynamic data for calcium and magnesium in conjunction with the data for uranium and other cations from previous studies, the competition of all major cations in seawater (except Na) with uranium for sorption can be quantitatively evaluated. The interactions of glutarimidedioxime with Na, which is expected to be much weaker than those of Ca and Mg and could possibly be evaluated using specific ion interaction theory (SIT), is not the focus of this study.

2. Experimental

2.1 Chemicals

Freshly boiled/cooled Millipore water was used to prepare all solutions. Glutarimidedioxime (H_2A) was synthesized according to previous procedures [10] and checked for purity by NMR and potentiometric titrations with a standard sodium hydroxide solution. Sodium chloride (J.T. Baker) was recrystallized from water and was used to adjust the total ionic strengths (I) of all solutions to 0.5 M. This ionic strength was selected because it is similar to the NaCl salinity in seawater. Stock solutions of sodium hydroxide were prepared from a 1.00 N volumetric solution (Metrohm) and standardized against potassium hydrogen phthalate (99.95-100.05%, Sigma Aldrich). Stock solutions of hydrochloric acid were prepared using a 1.00 N volumetric solution (Metrohm) and subsequently standardized against tris(hydroxymethyl)aminomethane (TRIS,

99.9995%, Fluka). Stock solutions of calcium chloride and magnesium chloride were prepared from 1.0 M MgCl₂ and 1.0 M CaCl₂ volumetric solutions (Fluka), respectively, and standardized against ethylenediaminetetraacetic acid (EDTA, 99.995%, Aldrich) at pH 10 using Eriochrome Black T as the indicator according to known methods [14].

2.2 Potentiometry

Potentiometric titrations were carried out using an automated titration system that consists of a thermostated glass cell, Metrohm model 713 pH meter, and a Metrohm model 765 Dosimat. The temperature was maintained at 25 ± 0.01 °C using a circulating water bath and the solutions were blanketed with a gentle stream of argon to minimize the ingress of CO₂. A Metrohm Unitrode pH electrode was used to measure the electrode potentials in the titrations. The electrode potentials can be described using equations (1) and (2) for the acidic and basic regions, respectively:

$$E = E^0 + 2.303 \times (RT/F) \log[H^+] + \gamma_H[H^+] \quad (1)$$

$$E = E^0 + 2.303 \times (RT/F) \log(Q_w/[OH^-]) + \gamma_{OH}[OH^-] \quad (2)$$

where E^0 is the standard electrode potential, $Q_w = [H^+][OH^-]$, $2.303 \times RT/F = 59.16$ mV for the hydrogen ion at 25 °C, and the terms $\gamma_H[H^+]$ and $\gamma_{OH}[OH^-]$ are the electrode junction potential corrections in the acidic and basic regions, respectively. Prior to each protonation or complexation titration, the parameters Q_w , E^0 , γ_H , and γ_{OH} were determined from the electrode potentials by titrating a standard HCl solution with a standard NaOH solution. These values were then used to convert the measured potentials in the subsequent titration to the concentrations of H⁺ for data analysis.

Multiple titrations were performed to determine the protonation constants of glutarimidedioxime and the stability constants of its complexes with Ca²⁺ and Mg²⁺ at a constant

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4 ionic strength ($I = 0.5 \text{ M NaCl}$). For a typical protonation titration, twenty milliliters of a
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6 glutarimidedioxime solution ($0.01 - 0.02 \text{ M}$ glutarimidedioxime and 0.06 M NaOH) was titrated
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8 with 0.0994 M HCl . For the complexation titrations, the stability constants for Ca^{2+} and Mg^{2+}
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10 complexes with glutarimidedioxime were determined from several titrations using different
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12 concentrations of the metal cation (C_M), ligand (C_A), and total protons (C_H). Usually a basic
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14 solution containing the metal cation (Ca or Mg) and glutarimidedioxime was titrated with HCl
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16 and 40 – 60 data points were collected. Details of the potentiometric titration conditions are
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18 provided in Table S1 in the Supplementary Information. The non-linear regression program
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20 Hyperquad 2008 [15] was used to calculate the protonation constants of glutarimidedioxime as
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22 well as the stability constants of the calcium and magnesium complexes with
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24 glutarimidedioxime.
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33 *2.3 Isothermal Titration Calorimetry*

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35 The enthalpies of complexation for the calcium and magnesium complexes with
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37 glutarimidedioxime were determined with a microcalorimeter (TA instruments, TAM III). The
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39 titration assembly consists of two matching stainless steel vessels (1 mL total volume) as the
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41 reference and sample cells, a stainless steel stirrer, and gas-tight syringes (0.250 mL total
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43 volume) equipped with either gold or stainless steel needles for titrant injections. During a given
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45 titration, the heat flow from the sample cell is measured (and compared to that of the reference
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47 cell) as the titrant solution is injected into the cell. A dynamic electrical calibration of the
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49 calorimeter was performed prior to each experiment to determine the gain, offset, and time
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51 constants τ_1 and τ_2 for the calorimeter to calibrate the measured heat flow during titrations. For
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53 the complexation titration, the reference cell contained 0.750 mL 0.50 M NaCl and the sample
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cell contained 0.750 mL solution of glutarimidedioxime ($C_A \sim 0.010 - 0.013$ M). The titrant was 0.050 M CaCl_2 or MgCl_2 ($I = 0.5$ M NaCl). Prior to carrying out the complexation titrations, dilution experiments were conducted to determine the heat of dilution, Q_{dil} , associated with the addition of 0.050 M CaCl_2 or MgCl_2 to 0.75 mL 0.5 M NaCl. Q_{dil} was then used to correct the observed reaction heats in subsequent titrations. Details of the calorimetric titration conditions are provided in Table S2 in the Supplementary Information.

Usually, fifty injections of 0.005 mL each were performed with five minutes between injections to determine the reaction heat, Q_r . The net reaction heat, obtained by the difference of ($Q_r - Q_{\text{dil}}$), was used to calculate the enthalpy of complexation with the program HypDeltaH [16]. In the calculation, the protonation constants for glutarimidedioxime and the Ca/Mg-glutarimidedioxime stability constants that were determined in this work, along with the enthalpies of glutarimidedioxime protonation from the previous work [10], were used.

3. Results and Discussion

3.1 Stability constants of calcium and magnesium complexes with glutarimidedioxime

Prior to the determination of the stability constants of the Ca/Mg complexes with glutarimidedioxime at $I = 0.5$ M NaCl, the protonation constants of glutarimidedioxime were measured at this ionic strength in this work because the values in the literature [10] were not obtained at a constant ionic strength. The values from this work (Table 2), which are in fairly good agreement with those in a previous study [10], were used in the calculation of the stability constants of the Ca/Mg complexes with glutarimidedioxime.

Fig. 2 shows representative potentiometric titrations for the complexation of Ca^{2+} and Mg^{2+} with glutarimidedioxime. The model that best fits the potentiometric data is represented by the reaction

where M^{2+} stands for Ca^{2+} or Mg^{2+} . Three calcium complexes, $\text{CaA}^0(\text{aq})$, CaHA^+ , and CaHA_2^- , were identified, while only two magnesium complexes, MgHA^+ and MgHA_2^- , were identified from potentiometric titrations. The calculated stability constants of these complexes are listed in Table 2 and compared with the stability constants of the corresponding uranium complexes.

Table 2. Protonation constants of glutarimidedioxime and stability constants of calcium, magnesium, and uranium complexes with glutarimidedioxime at 25°C and $I = 0.5 \text{ M NaCl}$ (the uncertainties of the values from the present work represent $\pm 3\sigma$).

Reaction	$\log \beta$	Reference
$\text{H}^+ + \text{A}^{2-} \leftrightarrow \text{HA}^-$	12.27 ± 0.03	p.w.
$2\text{H}^+ + \text{A}^{2-} \leftrightarrow \text{H}_2\text{A}$	23.15 ± 0.12	p.w.
$3\text{H}^+ + \text{A}^{2-} \leftrightarrow \text{H}_3\text{A}^+$	25.67 ± 0.12	p.w.
$\text{Ca}^{2+} + \text{A}^{2-} \leftrightarrow \text{CaA}^0$	2.28 ± 0.26	p.w.
$\text{UO}_2^{2+} + \text{A}^{2-} \leftrightarrow \text{UO}_2\text{A}$	17.8 ± 1.1	[10]
$\text{Ca}^{2+} + \text{H}^+ + \text{A}^{2-} \leftrightarrow \text{CaHA}^+$	14.55 ± 0.08	p.w.
$\text{Mg}^{2+} + \text{H}^+ + \text{A}^{2-} \leftrightarrow \text{MgHA}^+$	14.43 ± 0.12	p.w.
$\text{UO}_2^{2+} + \text{H}^+ + \text{A}^{2-} \leftrightarrow \text{UO}_2\text{HA}^+$	22.7 ± 1.3	[10]
$\text{Ca}^{2+} + \text{H}^+ + 2\text{A}^{2-} \leftrightarrow \text{CaHA}_2^-$	17.27 ± 0.16	p.w.
$\text{Mg}^{2+} + \text{H}^+ + 2\text{A}^{2-} \leftrightarrow \text{MgHA}_2^-$	18.5 ± 1.0	p.w.
$\text{UO}_2^{2+} + \text{H}^+ + 2\text{A}^{2-} \leftrightarrow \text{UO}_2\text{HA}_2^-$	36.8 ± 2.1	[10]

Fig. 2. Potentiometric titrations for the complexation of calcium and magnesium with glutarimidedioxime at 25°C and $I = 0.5\ M$ (NaCl). Symbols: (+) observed pC_H ; (○) calculated pC_H (left y-axis); Lines: speciation of calcium or magnesium in the titration (right y-axis). Top: $V_o = 15.5\ mL$, $C_{Ca} = 7.95\ mM$, $C_A = 19.9\ mM$, $C_H = -46.0\ mM$. Titrant: $0.0994\ M\ HCl$. Bottom: $V_o = 21.1\ mL$, $C_{Mg} = 1.87\ mM$, $C_A = 4.69\ mM$, $C_H = 9.38\ mM$. Titrant: $0.0102\ M\ NaOH$. Note: negative values of C_H refer to C_{OH} .

No precipitation was observed in the calcium titrations even when the total calcium concentration was as high as 0.020 M and the pC_H was 12.5. However, experimental difficulties were encountered in the titrations with magnesium because of the strong tendency of the precipitation of $Mg(OH)_2(s)$. When $C_{Mg} > 5$ mM, $Mg(OH)_2(s)$ was observed at $pC_H \geq 10.5$ even in the presence of excess glutarimidedioxime ligand. Therefore, the titrations with magnesium were carried out using much lower concentrations of magnesium and glutarimidedioxime than those in the titrations with calcium and the maximum pC_H attained was generally ≤ 10.5 . Consequently, the extent of formation of $MgHA_2^-$ was low (the maximum percentage of $MgHA_2^-$ in all titrations was only a few percent) and that of $MgA^0(aq)$ was essentially zero (the corresponding $CaA^0(aq)$ species did not form when $pC_H > 10.5$ as shown in the upper plot of Figure 2). Therefore, no stability constant for $MgA^0(aq)$ was determined and the stability constant for $MgHA_2^-$ in Table 2, though not drastically different from that of $CaHA_2^-$, should be viewed with caution.

The calculated stability constants of the calcium and magnesium complexes with glutarimidedioxime from this work are compared with the corresponding uranyl/glutarimidedioxime complexes in Table 2. The results show that the calcium and magnesium complexes with glutarimidedioxime are much weaker than those for the uranyl complexes by eight to nearly twenty orders of magnitude. The stability constants of the Ca/Mg complexes with glutarimidedioxime are also lower than those of the transition metal complexes [11]. For all metal cations studied for the complexation with glutarimidedioxime [10,11], the stability of the glutarimidedioxime complexes follows the order: $Fe^{3+} > UO_2^{2+} \sim Cu^{2+} > Pb^{2+} > Ni^{2+} > Ca^{2+} \sim Mg^{2+}$. Although the interaction of Na^+ with glutarimidedioxime has not been investigated, as a large monovalent cation, its complexation with glutarimidedioxime is expected

to be even weaker than that of Ca^{2+} or Mg^{2+} . The stronger complexation of the transition metal ions with glutarimidedioxime than that of Ca^{2+} or Mg^{2+} could be attributed to the higher degree of covalent interactions in the former than the latter. The interactions of Ca^{2+} or Mg^{2+} with the ligand are expected to be purely electrostatic. The stronger complexation of UO_2^{2+} with the ligand than Ca^{2+} or Mg^{2+} could be due to, in addition to the possible overlap of the ligand orbitals with the f -orbitals of uranium, the difference in the effective charges. The effective charge on UO_2^{2+} is, in fact, +3.3 as shown in the literature [17], and much higher than that on Ca^{2+} or Mg^{2+} .

3.2 Enthalpies of complexation for calcium- and magnesium-glutarimidedioxime complexes

Fig. 3 shows a representative calorimetric titration to determine the enthalpy of complexation for the calcium/glutarimidedioxime system. Similar titrations for the magnesium/glutarimidedioxime system were also conducted. The enthalpies of complexation were calculated using the dilution-corrected reaction heats in conjunction with the protonation constants determined in this work (Table 2), enthalpies of protonation from the literature [10],[†] and the stability constants of the Ca^{2+} and Mg^{2+} complexes with glutarimidedioxime from this work (Table 2). The calculated enthalpies of complexation are shown in Table 3.

Table 3 Summary of reaction enthalpies and entropies for Ca^{2+} - H_2A and Mg^{2+} - H_2A complexes at 25°C and $I = 0.5$ M (NaCl) (the uncertainties of the values represent $\pm 3\sigma$).

Reaction	ΔH (kJ mol ⁻¹)	ΔS (J mol ⁻¹ K ⁻¹)
$\text{Ca}^{2+} + \text{A}^{2-} \rightarrow \text{CaA}^0$	11.1 ± 4	82 ± 13
$\text{Ca}^{2+} + \text{H}^+ + \text{A}^{2-} \rightarrow \text{CaHA}^+$	-31.8 ± 3	177 ± 13
$\text{Mg}^{2+} + \text{H}^+ + \text{A}^{2-} \rightarrow \text{MgHA}^+$	-30.8 ± 2	173 ± 2
$\text{Ca}^{2+} + \text{H}^+ + 2\text{A}^{2-} \rightarrow \text{CaHA}_2^-$	-30.0 ± 0.6	230 ± 3

[†] The use of the enthalpies of protonation from the previous study is justified because the protonation constants from the present study only slightly differ from those from the previous study, so that the values of enthalpies of protonation remain essentially unchanged even if re-calculated with the protonation constants from the present study.

$$-37.1 \pm 6$$

$$231 \pm 19$$

Fig. 3. Calorimetric titration of glutarimidedioxime with calcium at 25°C and $I = 0.5$ M (NaCl). Titration conditions are as follows: cup: $V_o = 0.750$ mL, $C_A = 0.0101$ M, $C_H = -0.020$ M. Titrant: 0.05 M CaCl_2 . Upper figure: Thermogram showing the reaction heat flow rate as a function of time. Lower figure: (+) observed cumulative heat; (O) calculated cumulative heat (left y-axis); (Lines) speciation of calcium in the titration (right y-axis). Note: negative values of C_H refer to C_{OH} .

With the measured enthalpies of the reactions in Table 3, it is possible to evaluate the enthalpy of the dominant reaction between glutarimidedioxime and calcium or magnesium at seawater pH. The speciation calculations show that the dominant species of calcium, magnesium, and glutarimidedioxime at pH 8 – 8.3 are Ca^{2+} , Mg^{2+} , and H_2A , respectively. In addition, based on the stability constants of the calcium and magnesium complexes with glutarimidedioxime from this work, the dominant complexes in seawater are CaHA^+ and MgHA^+ . Therefore, the dominant reactions involving calcium, magnesium, and glutarimidedioxime at seawater pH can be represented by reaction (4),

where M^{2+} denotes Ca^{2+} or Mg^{2+} . Using the enthalpies of complexation shown in Table 3 and the enthalpies of protonation for H_2A from the literature [10], the enthalpies of reaction (4) are calculated to be $+37.9 \text{ kJ mol}^{-1}$ and $+38.9 \text{ kJ mol}^{-1}$ for calcium and magnesium, respectively. This means that the dominant reactions at seawater pH are endothermic and the complexation of calcium and magnesium with glutarimidedioxime would be enhanced at higher temperatures. This conclusion could have an impact on the sorption of calcium and magnesium by amidoxime-based sorbents at different temperatures.

3.3 Influence of Ca^{2+} and Mg^{2+} complexation with glutarimidedioxime on the extraction of uranium from seawater

Using the thermodynamic data from this work, a speciation diagram (Fig. 4) is drawn for a solution containing calcium and magnesium at their concentrations in seawater (i.e., 0.01 M and

0.053 M, respectively) and 0.01 M glutarimidedioxime.[‡] The speciation diagram shows that the complexation of calcium and magnesium with glutarimidedioxime strongly depends on the pH. At seawater pH (8.3), calcium and magnesium complex about 2 - 3% of the total ligand. This fraction is small, but significant, implying that calcium and magnesium could still compete to some degree with uranium for sorption sites on amidoxime-based sorbents because of their overwhelmingly high concentrations in seawater relative to that of uranium. It is worth noting that the speciation diagram (Fig. 4) also indicates that, because the calcium and magnesium complexes with glutarimidedioxime are most stable at higher pH, desorption of calcium and magnesium from amidoxime-based sorbents could be difficult if eluents of high pH are used.

Fig. 4 Speciation of H₂A as a function of pH (25°C and $I = 0.5$ M). $C_A = 0.01$ M, $C_{Ca} = 0.010$ M, $C_{Mg} = 0.053$ M.

[‡] This concentration is chosen arbitrarily but it is sufficiently high so that the ligand is not “saturated” by Ca(II) and/or Mg(II) in the pH region from 7 to 12. Choosing higher ligand concentrations does not alter the relative distribution of the species.

The speciation discussed above is based on the thermodynamic data for the complexation in aqueous solutions and may not be directly translated into the speciation in the sorption system. However, a qualitative evaluation of the degree of sorption of calcium and magnesium by amidoxime-based sorbents is justifiable. Because the concentrations of calcium and magnesium are six orders of magnitude higher than that of uranium in seawater, a significant number of the sorption sites would still be occupied by calcium and magnesium in a seawater extraction system. For a real seawater extraction system in which the amidoxime-based sorbents are suspended in the ocean, rapid ion exchange occurs between the Ca^{2+} - and Mg^{2+} -rich seawater and the sorbents. It is expected that, as long as there are sufficient sorption sites, a significant fraction of the sites could be occupied by calcium and magnesium. Early and recent marine tests for the extraction of uranium have shown that, indeed, large quantities of calcium and magnesium were sorbed onto amidoxime-functionalized polymers in short time periods [18,19]. In an early study in which micro beads functionalized with a hybrid polyamidoxime/polyhydroxamic acid were packed in glass cloth and immersed in seawater for four months, it was found that calcium and magnesium occupied the highest fraction of sites in the sorbent [18]. In a more recent study in which seawater was pumped through a large-scale column containing amidoxime-based chelating resin for 30 days, more than 6 g calcium and 10 g magnesium were sorbed on one kilogram of the sorbent [19].

Although the high concentrations of calcium and magnesium in seawater could lead to significant sorption of calcium and magnesium on amidoxime-based sorbents, the sorption of uranium by amidoxime-based sorbents may not be affected as long as sufficient sorption sites are available because the stability constants of the U(VI)/glutarimidedioxime complexes are at least eight orders of magnitude higher than the Ca/Mg complexes. However, it should be pointed out

that a most recent study [4] showed that the presence of high concentrations of calcium and magnesium in seawater still affects the extraction of uranium due to the formation of ternary complexes such as $\text{Ca}_2[\text{UO}_2(\text{CO}_3)_3]^0(\text{aq})$, $\text{Ca}[\text{UO}_2(\text{CO}_3)_3]^{2-}$, and $\text{Mg}[\text{UO}_2(\text{CO}_3)_3]^{2-}$. The formation of such ternary complexes, the neutrally charged $\text{Ca}_2[\text{UO}_2(\text{CO}_3)_3]^0(\text{aq})$ species in particular, could alter the sorption mechanism and affect the sorption capacity of uranium on the amidoxime-based sorbents.

4. Conclusion

Thermodynamic studies have revealed that calcium and magnesium form much weaker complexes with glutarimidedioxime than uranium and a few other metal ions. The stability constants decrease in the order: $\text{Fe}^{3+} > \text{UO}_2^{2+} \sim \text{Cu}^{2+} > \text{Pb}^{2+} > \text{Ni}^{2+} > \text{Ca}^{2+} \sim \text{Mg}^{2+}$. Despite the weak complexation, a significant fraction of the sorption sites of the amidoxime-based sorbents is still expected to be occupied by calcium and magnesium due to their overwhelmingly high concentrations in seawater. The dominant reaction between Ca/Mg and glutarimidedioxime at seawater pH was found to be endothermic, suggesting that higher seawater temperatures could lead to higher sorption of calcium and magnesium by amidoxime-based sorbents.

Acknowledgment. This work was supported by the Fuel Resources Program, Fuel Cycle Research and Development Program, Office of Nuclear Energy of the U.S. Department of Energy (DOE) under Contract No. DE-AC02-05CH11231 at Lawrence Berkeley National Laboratory (LBNL).

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Graphical Abstract

Amidoxime-based sorbents are promising extractants for uranium in seawater. Complexes of calcium and magnesium with glutarimidedioxime, a ligand that can be formed during sorbent synthesis, were found to be much weaker than uranyl complexes. However, because of their high seawater concentrations, some sorption is expected and should increase with temperature.