Project No. 11-3256

Innovative Elution Processes for Recovering Uranium from Seawater

Fuel Cycle R&D

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NEUP Nuclear Energy University Programs
U.S. Department of Energy

Innovative Elution Processes for Recovering Uranium from Seawater

DOE-NEUP Project 11-3256

Final Technical Report

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Project Duration: November 2011-December 2013

Report Date: May 28, 2014

Summary

Utilizing amidoxime-based polymer sorbents for extraction of uranium from seawater has attracted considerable interest in recent years. Uranium collected in the sorbent is recovered typically by elution with an acid. One drawback of acid elution is deterioration of the sorbent which is a significant factor that limits the economic competitiveness of the amidoxime-based sorbent systems for sequestering uranium from seawater. Developing innovative elution processes to improve efficiency and to minimize loss of sorbent capacity become essential in order to make this technology economically feasible for large-scale industrial applications. This project has evaluated several elution processes including acid elution, carbonate elution, and supercritical fluid elution for recovering uranium from amidoxime-based polymer sorbents. The elution efficiency, durability and sorbent regeneration for repeated uranium adsorption-desorption cycles in simulated seawater have been studied. Spectroscopic techniques are used to evaluate chemical nature of the sorbent before and after elution.

A sodium carbonate-hydrogen peroxide elution process for effective removal of uranium from amidoxime-based sorbent is developed. The cause of this sodium carbonate and hydrogen peroxide synergistic leaching of uranium from amidoxime-based sorbent is attributed to the formation of an extremely stable uranyl peroxo-carbonato complex. The efficiency of uranium elution by the carbonate-hydrogen peroxide method is comparable to that of the hydrochloric acid elution but damage to the sorbent material is much less for the former. The carbonate-hydrogen peroxide elution also does not need any elaborate step to regenerate the sorbent as those required for hydrochloric acid leaching. Several CO_2-soluble ligands have been tested for extraction of uranium from the sorbent in supercritical fluid carbon dioxide. A mixture of hexafluoroacetylacetone and tri-n-butylphosphate shows the best result but uranium removal from the sorbent reaches only 80% after 10 hours of leaching. Some information regarding coordination of vanadium with amidoxime molecules and elution of vanadium from amidoxime-based sorbents is also given in the report.

Publication and Presentation Derived from the Project

1. Horng-Bin Pan, Weisheng Liao, Chien M. Wai*, Yatsandra Oyola, Christopher J. Janke, Guoxin Tian, Linfeng Rao, "Carbonate-H_2O_2 Leaching for Sequestering Uranium from Seawater", *Dalton Transactions*, 2014, DOI:10.1039/c3dt53404a, first published online March 9, 2014. The paper and a cover page artwork for the issue containing the paper are given in the Appendix.

2. C. M. Wai, W.S. Liao, H.B. Pan, N. Miyamoto, "Uranium Elution from Amidoxime-Based Polymer Sorbents Using Supercritical CO_2", presented at the 244th ACS National Meeting, August 21, 2012, Philadelphia, PA.

Introduction

Developing techniques for extracting uranium from seawater is attracting considerable current interest because land-based uranium sources would be depleted by the end of this century.[1,2] Our ocean contains a very large quantity of uranium (about 1000 times more than terrestrial ores) which is sufficient to support nuclear power production in the next few centuries.[3] Uranium exists in seawater at a low concentration (~3 ppb) and as the very stable uranyl tris-carbonato complex,$UO_2(CO_3)_3^{4-}$.[3] Screening studies conducted in the 1980s with more than 200 functionalized adsorbents showed that sorbent materials with the amidoxime group $RC(NH_2)(NOH)$ were most effective for uranium adsorption from seawater.[4–6] Recent research efforts in Japan and in other countries are focused on using amidoxime-based adsorbents for extracting uranium from seawater.[2] The amidoxime-based fiber can be prepared by a radiation-induced graft polymerization method which involves electron beam irradiation of polyethylene and acrylonitrile (CH_2=CH-CN) grafting onto the polyethylene fabrics. The cyano groups of the grafted polymer are then converted to the amidoxime groups as shown in Figure 1. This type of sorbents show good mechanical strength and high capacity for uranium sorption from seawater in both laboratory and marine experiments. If this uranium extraction technology could be made economically favorable and environmentally sustainable, our ocean would provide virtually an inexhaustible source of uranium for nuclear power production. A recent LBNL report summarizes the international research and development activities in the extraction of uranium from seawater from 1960 to 2010.[2]

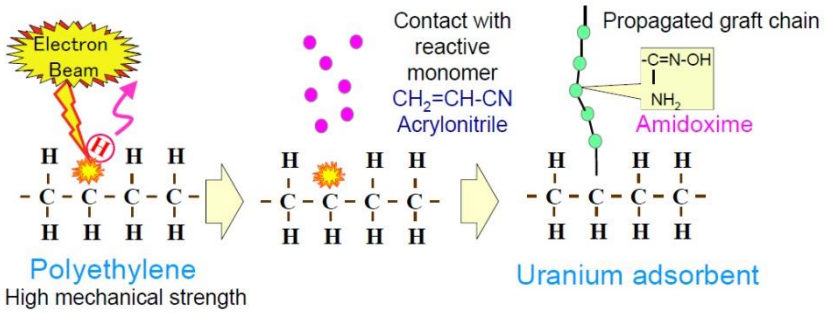


Figure 1. Amidoxime-based sorbents prepared by radiation-induced graft polymerization

The amidoxime groups formed in the polymer sorbent by the synthesis method described above may exist in two different structures as illustrated in Figure 2. Both the cyclic imide dioxime and the open-chain diamidoxime on the sorbent can form strong complexes with uranium.[7,8] Tian et al. recently reported that the open-chain diamidoxime is a weaker competing ligand than the cyclic imide dioxime for complexation with U(VI) under the seawater conditions.[8] The uranium sequestering process may be illustrated by the following reaction:

$$[UO_2(CO_3)_3]^{4-} + 2H_2A \rightarrow UO_2(HA)A^- + 3HCO_3^- \quad (1)$$

where H_2A represents either glutarimidedioxime or glutardiamidoxime shown in Figure 2.

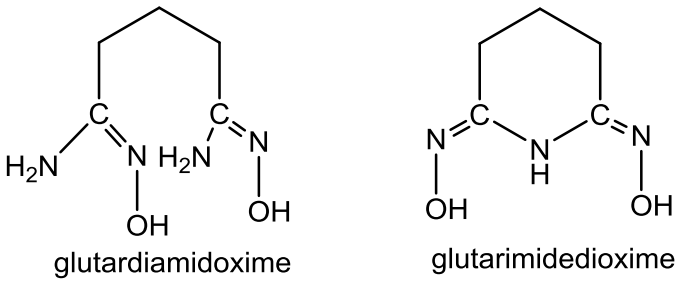


Figure 2. Structures of open chain diamidoxime (left) and cyclic imidedioxime (right).

In addition to uranium, other metals existing in seawater can also be adsorbed by the sorbent. Table 1 show the amounts of uranium and other metals found in an amidoxime-based polymer sorbent fabricated by ORNL (Oak Ridge National Lab) in a field test conducted by scientists at the Pacific Northwest National Lab (PNNL)'s Marine Sciences Lab (MSL) located at Sequim, Washington.[9] The adsorption experiments were conducted using a pump-through system with seawater from Sequim Bay at 20±2 ^{o}C and a flow rate of 250 mL per min.[9] The uranium loading capacity of the sorbent varied from 2.5-3.3 g per kg after 8 weeks of contact with the flowing seawater. High concentrations of transition metals particularly vanadium, iron, and copper are also found in the sorbent as shown in Table 1. The concentration of vanadium is actually higher than that of uranium present in the sorbent. The effects of these transition metals on uranium adsorption onto the sorbent are not known. If they compete with uranium for adsorption sites, it may be necessary to remove them from the sorbent in order to reuse the sorbent for repeated sequestering of uranium from seawater. The coordination chemistry of transition metals with amidoxime molecules, especially vanadium, is virtually unknown.

Table 1. Concentration of uranium and other metals found in the sorbent in a field test using flowing seawater at 20 ^{o}C and a rate of 250 mL per min after 8 weeks (from reference 9)

elem	filtered Sequim Bay seawater [ng/kg]	(a) filtered ambient seawater concn in test syst [ng/kg]	(b) amt of metal uptake [mg of metal/g of adsorbent]	K_d[b] [L/g]
V	1500	1480	5.7	3775
U	2850	2840	2.7	932
Fe	2490	2200	1.9	–
Cu	190	540	1.3	2360
Ni	320	560	0.7	1225
Zn	285	2100	0.7	326
Sr	–	–	0.3	–
Cr	135	180	0.2	1089
Mn	1000	1200	0.1	–
Pb	3	25	0.1	3921
Co	0.02	0.01	0.08	7.8×10^6
Sn	–	–	0.03	–

[a]Density of seawater: 1.02 g/mL. [b]The distribution coefficient, K_d, is determined by the ratio of the corresponding values of columns (b) and (a).

Uranium collected in the sorbent is recovered typically by elution with an acid.[10,11] Hydrochloric acid (1 M) is commonly used to recover adsorbed uranium from the amidoxime-based sorbent systems. Acid leaching is not selective; therefore, other metals in the sorbent are also eluted with uranium. A more serious drawback of the acid elution process is the deterioration of the sorbent which is a significant factor that limits the economic competitiveness of the amidoxime-based sorbent systems for sequestering uranium from seawater.[2] Another problem associated with acid leaching is that the amidoxime-based polymer sorbent requires a regeneration step for its reuse. The reconditioning process involves immersing the sorbent in 2.5% KOH at 80 ^{o}C for 3 hours followed by washing the sorbent with water until the solution pH is neutral.[2,10,11]

Cost analyses of uranium production from seawater using amidoxime-based polymer adsorbents indicate that the production cost depends on several factors including uranium loading capacity, adsorbent degradation rate, number of repeated uses of adsorbent, and mode of uranium elution. A recent cost analysis shows that using an amidoxime-based polymer

adsorbent with a capacity of 6 g uranium per kg of adsorbent and for repeated use of 10 times with 3% loss of capacity per cycle, the production cost is estimated to be $370 per kg of uranium.[9] If offshore elution and polymer anchor rope techniques are applied, for the same sorbent material the production of uranium from seawater can be lowered to $290 per kg. This production cost is comparable to the peak uranium spot-market price observed during the 2007-2009 uranium price boom.

Developing innovative processes to improve the elution efficiency and to minimize loss of sorbent capacity become essential in order to make this technology economically feasible for large-scale industrial applications. This NEUP project has evaluated several elution processes including acid elution, carbonate elution, and supercritical fluid elution for recovering uranium from amidoxime-based polymer sorbents. The elution efficiency, durability and sorbent regeneration for repeated uranium adsorption-desorption cycles in simulated seawater have been studied. Spectroscopic techniques are used to evaluate chemical nature of the sorbent before and after elution. Some information regarding coordination of vanadium with amidoxime molecules and elution of vanadium from amidoxime-based sorbents is also given in this report. A sodium carbonate-hydrogen peroxide elution process for effective removal of uranium from amidoxime-based sorbent is developed. The cause of this sodium carbonate and hydrogen peroxide synergistic leaching of uranium from amidoxime-based sorbent is attributed to the formation of an extremely stable uranyl peroxo-carbonato complex. The efficiency of uranium elution by the carbonate-hydrogen peroxide method is comparable to that of the hydrochloric acid elution but damage to the sorbent material is much less for the former. The carbonate-hydrogen peroxide elution also does not require any elaborate step to recycle the sorbent. Only rinsing with water is sufficient to regenerate the sorbent for reuse. This simple uranium recovery method may lead to a new technique which not only improves sorbent durability but also offers a possibility for offshore elution operation.

Experimental Section

1. Synthesis of Amidoxime-based Sorbent

The polymer sorbent used in this study was prepared by Chris Janke of ORNL, a collaborator of this NEUP project. The amidoxime-based polyethylene adsorbent fibers were prepared by the radiation-induced graft polymerization method, which involves four processing

steps: electron beam irradiation of polyethylene fibers; co-grafting polymerizable monomers containing nitrile groups and hydrophilic groups to form grafted side chains throughout the fiber; conversion of nitrile groups to amidoxime groups; and alkaline conditioning of the grafted fibers as illustrated in the following figure.

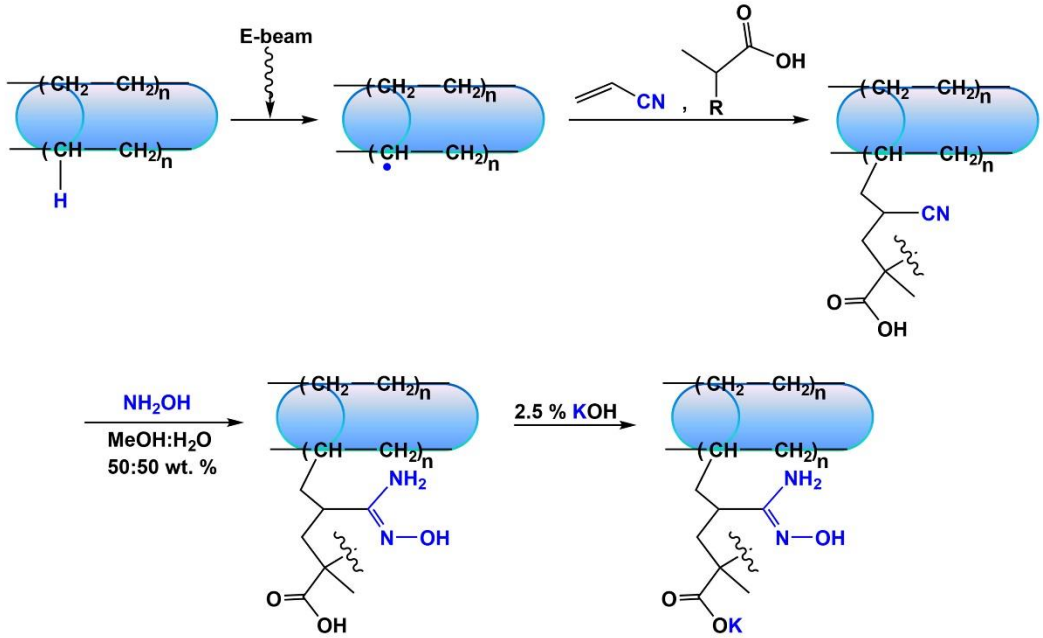


Figure 3. Reaction scheme for preparation of amidoxime-based polyethylene fibers.

Step 1. Irradiation of polyethylene fibers

Prior to irradiation, the polyethylene fibers were placed inside a plastic bag and sealed under nitrogen. The bag was then put inside an insulated container and placed on top of dry ice and irradiated to a dose of 200 kGy using 4.9 MeV electrons and 1 mA current from an electron beam machine.

Step 2. Grafting of polymerizable monomers containing nitrile groups and hydrophilic groups

After irradiation, the fibers were immersed in a flask containing a previously de-gassed solution of acrylonitrile and methacrylic acid in dimethylsulfoxide and placed in an oven at 65 °C for about 18 hours. After the grafting reaction was complete, the fibers were drained from the solution and washed with dimethylformamide (DMF) to remove any monomers or co-polymer by-products. The fibers were then washed with methanol to remove the DMF and dried at 50 °C under vacuum for 72 hours.

Step 3. Conversion of nitrile groups to amidoxime groups

The irradiated and grafted polyethylene fibers were placed in a flask containing 10% hydroxylamine hydrochloride in 50/50 (w/w) water/methanol at 80 °C for 72 hours. The fibers were then washed with deionized water followed by a methanol rinse and allowed to dry at 50 °C under vacuum for 72 hours.

Step 4. Alkaline conditioning of grafted fibers

After the amidoximation reaction the polyethylene fibers were added to a flask containing 2.5 % KOH and heated for 3 hours at 80 °C then washed with deionized water until the pH was neutral.

2. Adsorption of Uranium in Simulated Seawater

Uranium sorption was performed using simulated seawater spiked with 9 ppm of uranium. The simulated seawater contained Na^+ (10,118 ppm), Cl^- (15,573 ppm), and HCO_3^- (140 ppm) at pH=8.0. The uranium sorption experiment was conducted with 20 mg of the amidoxime-based polyethylene fiber suspended in 400 mL of the simulated seawater with stirring for 24 hours. At the end of this period, sorption of uranium was found to reach equilibrium. The evolution plot of the sorption of uranium from simulated seawater is given in Figure 4.

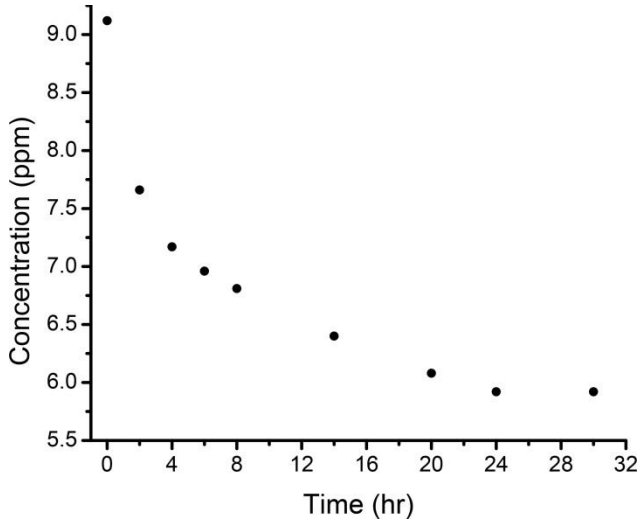


Figure 4. Rate of uranium adsorption to the sorbent at room temperature (21 ^{o}C) measured by decrease in uraniium concentration in the simulated seawater

Uranium in the simulated seawater was analyzed by a spectrophotometric method using Arsenazo III as a complexing agent and the absorbance of the uranyl-arsenazo complex was monitored at 653 nm with a UV-Vis spectrometer.[12,13] The UV-Vis spectra of the urany-

arsenazo complex are shown in Figure 5. According to the literature[13], Arsenazo III reacts with uranium (VI) in acidic media to give a uranyl-arsenazo complex (green-blue complex, λ_{max} = 653 nm) which is very sensitive for determination of U (limit of detection ~ 0.50 μg/L.). The pH value of the solution for spectrophotometric determination of uranium utilizing Arsenazo III was adjusted to one in this study. Under this acidic condition (pH = 1), either $UO_2(CO_3)_3^{4-}$ or $UO_2(O_2)(CO_3)_2^{4-}$ should be converted to $UO_2(H_2O)_5^{2+}$. The linear regression equation for uranium in the concentration range 0–5.38 ppm was Abs = 0.19265 X (R^2 = 0.99966, n = 7) where X is the uranium concentration in ppm (Figure 5, right). The capacity of uranium adsorption on the sorbent under our experimental conditions was about 6 wt %.

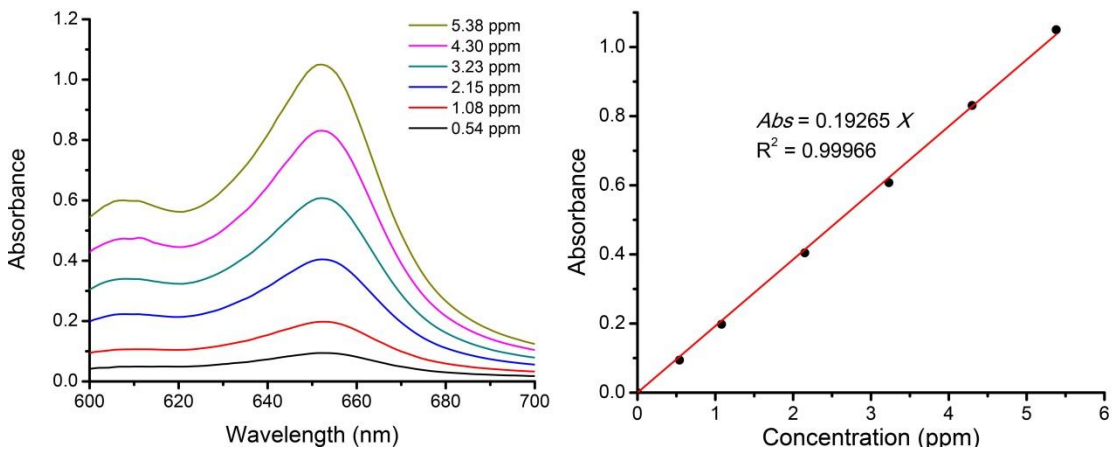


Figure 5. UV-Vis spectra (left) and the calibration curve (right) of the uranyl-arsenazo complex with various concentrations of uranium in acidic medium (pH = 1).

3. Elution with carbonate or carbonate–H_2O_2 solution

Elution of uranium from the sorbent was performed with the uranium loaded fiber immersed in 10 mL of a sodium carbonate solution with or without hydrogen peroxide at room temperature (21 ^oC) with stirring for one hour. Uranium in the leaching solution at appropriate time intervals was measured during the elution process using the same Arsenazo spectrophotometric method. After the elution, uranium remaining in the sorbent was checked by washing the fiber in concentrated HCl followed by analyzing the acid solution. For repeated sorption experiments, the sorbent after the elution was rinsed with de-ionized water several times and then filtered and dried in a chemical fume hood at room temperature. No other treatment is needed for reusing the sorbent.

4. Supercritical Fluid Elution

A typical supercritical carbon dioxide (sc-CO_2) extraction system for uranium elution is shown in the supercritical fluid extraction section (Figure 16). A high-presure syringe pump (ISCO model 260D) is used to deliver liquid CO_2 to the extraction system. The system can stand up to 400 atm of CO_2 pressure and 100 ^oC. Typical sc-CO_2 extraction experiments are performed in the pressure range 100-300 atm and in the temperature range 35-50 ^oC. The system shown in Figure 16 consists of a high-pressure fiber-optic cell connected to a CCD array spectrometer for in situ spectroscopic measurements. Very rapid spectra can be obtained using the CCD array UV-Vis spectrometer which allows measurements of uranium dissolution rates with respect to time. Urany complexes have characteristic absorption peaks in the UV-Vis region which can be used for measuring their solubility and dissolution kinetics in sc-CO_2. Different extractants can be placed in the extraction cell or in a small cell connected upstream of the extraction cell through controlling valves. Uranium dissolved in the sc-CO_2 phase is collected in a trap solution by opening the exit valve of the system. Pressure reduction converts sc-CO_2 to CO_2 gas causing precipitation of the solute dissolved in the supercritical fluid phase.

5. Instrumentation

A CCD array UV-Vis spectrometer (Model 440, Spectral Instruments, Inc., Tucson, AZ) was used to measure the absorption spectra of the uranyl-arsenazo complex. The FT-IR spectra were acquired using a Nicolet Magna 760 FT-IR spectrometer equipped with a DTGS detector. The ^{51}V NMR spectra were obtained by using a Bruker Advance 500 MHz NMR spectrometer at 131.75 MHz. All ^{51}V chemical shifts are referenced to $VOCl_3$ (0.0 ppm) as an external standard.

Results and Discussion

1. Carbonate and Carbonate-Hydrogen Peroxide Elution

Using sodium carbonate (Na_2CO_3) solution for leaching uranium from amidoxime-based sorbent has been reported previously. Das et al.[14] showed that uranium could be recovered over 95% from amidoxime-based membranes by leaching with sodium carbonate at room temperature. A report by Rivas et al.[15] showed that only 67% recovery of uranium from an amidoxime-based sorbent could be achieved and the elution efficiency did not change significantly in the carbonate concentration range 0.5 to 2 M. According to the literature, the solubility of sodium carbonate in water is about 2.59 M at 25 ^oC.[16]

We have recently re-examined the carbonate leaching of uranium from amidoxime-based polymer fiber fabricated by the Oak Ridge National Lab as described in the experimental section. Our carbonate leaching results agree with those reported by Rivas et al. A significant observation in our elution study is that when a small amount of hydrogen peroxide is added to sodium carbonate, the efficiency of uranium elution from the amidoxime-based sorbent is significantly improved to near 100%. The sorbent can be reused after rinse with water without other treatment. The recycled sorbent exhibits a minimal loss (about 3%) of uranium loading capacity per sorption-desorption cycle which is significantly lower than the conventional acid elution process known in the literature.

The results of our sodium carbonate and hydrogen peroxide elution of uranium from the amidoxime-based sorbent are given in Figure 6. Using 1 M sodium carbonate, elution of uranium from the sorbent at room temperature (21 ^{o}C) reaches a near constant value around 77% after one hour. Hydrogen peroxide alone (1 M) is not effective for eluting uranium from the sorbent. When a small amount of hydrogen peroxide is added to 1 M sodium carbonate, there is a significant increase in the efficiency of uranium elution. Even with 0.01 M of H_2O_2 in 1 M sodium carbonate, the uranium elution efficiency is increased from 77% to over 90%. The elution of uranium from the sorbent by 1 M sodium carbonate with 0.1 M of H_2O_2 is near quantitative.

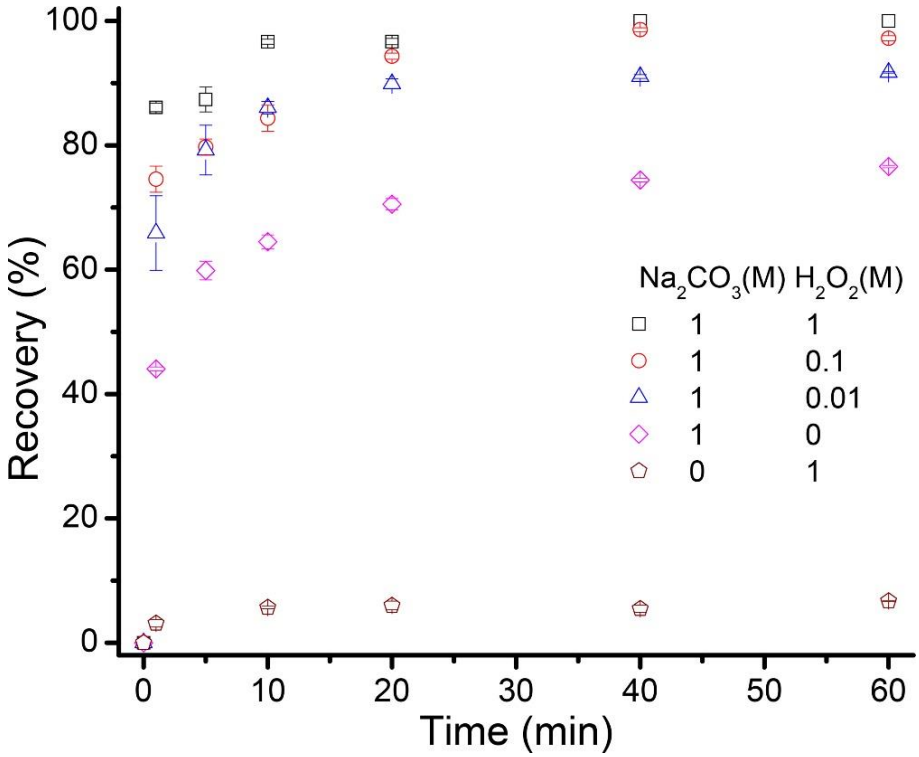


Figure 6. Rates of uranium elution from the sorbent with sodium carbonate and hydrogen peroxide solutions

The carbonate elution of uranium from the amidoxime-based sorbent with 1 M Na_2CO_3 (pH ~ 11.0) may be expressed by the following equation:

$$UO_2A_2^{2-} + 3CO_3^{2-} \rightarrow [UO_2(CO_3)_3]^{4-} + 2A^{2-} \quad (2)$$

At a high carbonate concentration the equilibrium of equation (1) tends to shift to the right favoring formation of the uranyl tris-carbonato species. The synergistic elution of uranium by hydrogen peroxide and sodium carbonate may be attributed to the formation of an extremely stable uranyl-peroxo-carbonato complex as illustrated by equation (3).

$$UO_2A_2^{2-} + 3CO_3^{2-} + H_2O_2 \rightarrow [UO_2(O_2)(CO_3)_2]^{4-} + 2A^{2-} + HCO_3^{-} + H^{+} \quad (3)$$

Figure 7. Structures of $UO_2(CO_3)_3^{4-}$ and $UO_2(O_2)(CO_3)_2^{4-}$. (The structure of $UO_2(CO_3)_3^{4-}$ is from reference 17; the structure of $UO_2(O_2)(CO_3)_2^{4-}$ is built by crystallographic data from reference 18 using molecular modeling software, Spartan.)

A recent report by Goff et al. shows that the uranyl-peroxo-carbonato complex is thermodynamically much more stable than the uranyl tri-carbonate complex.[18] The apparent formation constant of $[UO_2(O_2)(CO_3)_2]^{4-}$ from $[UO_2(CO_3)_3]^{4-}$ according to the following equation

$$[UO_2(CO_3)_3]^{4-} + HO_2^- \rightarrow [UO_2(O_2)(CO_3)_2]^{4-} + HCO_3^- \qquad (4)$$

is about 5×10^4.[18] Therefore even with the addition of 0.01–0.1 M hydrogen peroxide, the efficiency of carbonate elution of uranium from the sorbent can be significantly improved. Under the experimental conditions used by Goff et al.[18] and by us, only monoperoxo uranyl complex, $UO_2(O_2)(CO_3)_2^{4-}$, should be formed in the solution according to the DFT calculations reported by Odoh and Schreckenbach.[19] The DFT calculations also indicate that the reaction energies are -59.8 and 6.3 kcal/mol for $UO_2(O_2)(CO_3)_2^{4-}$ and $UO_2(O_2)_2(CO_3)^{4-}$, respectively, which suggests that the diperoxo uranyl complex, $UO_2(O_2)_2(CO_3)^{4-}$ should not be formed in the solution. In fact, Zanonato et al. reported that no diperoxo uranyl complex, $UO_2(O_2)_2(CO_3)^{4-}$, was found even at a high concentration of H_2O_2.[20]

The reusability of the amidoxime-based polymer sorbent after the sodium carbonate-hydrogen peroxide elution of uranium is illustrated in Figure 8. Reduction of uranium loading capacity of the recycled sorbent depends on the concentration of the hydrogen peroxide used in the carbonate-peroxide elution process. For uranium elution with 0.1 M H_2O_2 in 1 M Na_2CO_3, the decrease in loading capacity was about 3% for each cycle after 3 consecutive cycles. Elution with 1 M H_2O_2 and 1 M Na_2CO_3 resulted in about 10% decrease in uranium loading capacity after each sorption-desorption cycle. We also tested uranium elution from the sorbent with hydrochloric acid. Using 0.5 M hydrochloric acid, elution of uranium from the sorbent at room temperature (21 ^oC) reaches a near constant value around 94% after 20 minutes. The rate of uranium elution from the sorbent with 0.5 M HCl is given in Figure 9. After the acid elution, the sorbent was regenerated in 2.5% KOH at 80 ^oC for 3 hours followed by rinsing with water and drying. The recycled sorbent after the acid elution showed a reduction in uranium sorption capacity by about 20% per cycle based on our experiments (Figure 8).

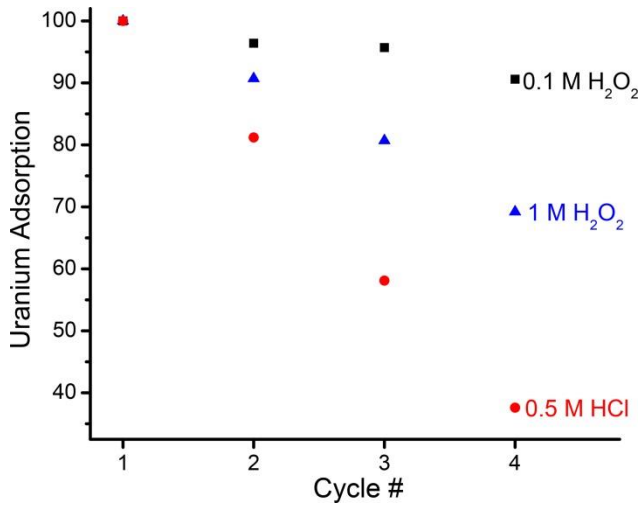


Figure 8. Uranium loading capacity of the amidoxime-based polymer sorbent after each cycle of sodium carbonate-H_2O_2 and 0.5 M HCl leaching. (Note: For 0.5 M HCl leaching, the sorbent required a KOH reconditioning process after each cycle according to the literature.[9, 10])

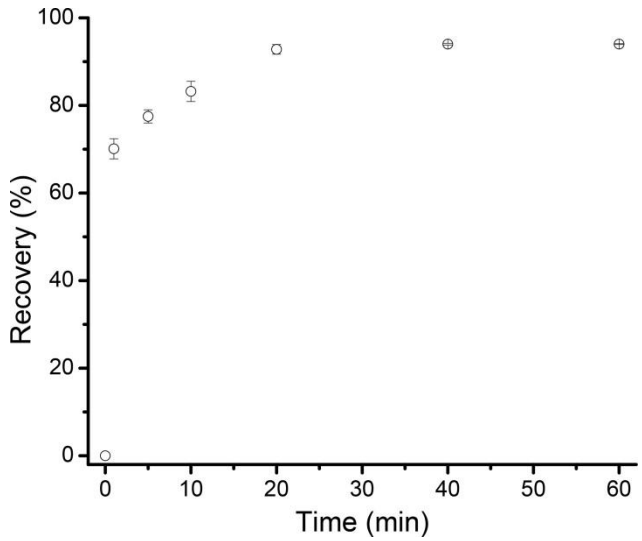


Figure 9. Rate of uranium elution from the sorbent with 0.5 M HCl at room temperature (21 ^{o}C).

The oxime group –C=N–OH on the amidoxime-based fiber is suggested to form a chelate complex with UO_2^{2+} via the η^2 binding with N–O bond (open-chain)[21] or by the two oxime oxygen atom and the imide nitrogen atom of the delocalized –O–N=C–N–C=N–O− group (the cyclic form)[7]. The oxime group containing carbon–nitrogen double bonds (C=N–OH) may be cleaved by oxidation, reduction, or acid hydrolysis to the corresponding carbonyl group (C=O) which would not complex with UO_2^{2+} in seawater.[22,23] The oxidation power of hydrogen peroxide at high concentrations could cause cleavage of the C=N bond.[24] At low concentrations,

hydrogen peroxide apparently causes little damage to the oxime group allowing formation of the stable uranyl-peroxo-carbonato complex and leading to enhanced elution of uranium from the sorbent. Lin and co-workers recently reported that maximizing electron density at the binding site of amidoxime-based ligands through resonance of conjugated π orbitals of electron donating groups (e.g. imidazole–oximate) can improve binding strength for uranyl and stability of ligands.[25] On the basis of this concept, future development of amidoxime-based sorbents with conjugated π orbitals of electron donating groups may lead to new sorbent materials with improved stabilities under carbonate-H_2O_2 leaching conditions.

2. Formation of Uranyl-Peroxo-Carbonato Complex in the Ocean

The feasibility of forming stable uranyl-peroxo-carbonato complex in carbonate solutions raises a question about the possibility of formation of this uranium complex in natural seawater because hydrogen peroxide is known to exist in ocean surface. The concentrations of hydrogen peroxide in open ocean surface may vary from several nM to several hundred nM depending on season and time.[26-30] Hydrogen peroxide probably exists in seawater as one of final products of free radical chemistry in the photochemical decomposition processes of dissolved organic matter. Another hypothesis is that a photochemically-initiated formation mechanism may be involved which was used to explain seasonal variation of H_2O_2 concentrations in open ocean sea surface.[27] We have examined the possibility of formation of uranyl-peroxo-carbonato based on the available thermodynamic data of the following equations:

$$UO_2^{2+} + H_2O_{2(aq)} + 2CO_3^{2-} \rightarrow UO_2(O_2)(CO_3)_2^{4-} + 2H^+ \quad (5)$$

$$UO_2(CO_3)_3^{4-} \rightarrow UO_2^{2+} + 3CO_3^{2-} \quad (6)$$

$$UO_2(CO_3)_3^{4-} + H_2O_{2(aq)} \rightarrow UO_2(O_2)(CO_3)_2^{4-} + 2H^+ + CO_3^{2-} \quad (7)$$

According to the literature[20, 31], the equilibrium constants of reactions (5) and (6) are $10^{4.03}$ and $10^{-21.8}$, respectively. Combination of reactions (5) and (6) results in reaction (7), the most probable dominating reaction that represents the formation of the $UO_2(O_2)(CO_3)_2^{4-}$ species under seawater conditions. The equilibrium constant K of reaction (7) is calculated to be $10^{-17.8}$.

$$K = \frac{[UO_2(O2)(CO_3)_2^{4-}]\,[H^+]^2\,[CO_3^{2-}]}{[UO_2(CO_3)_3^{-4}]\,[H_2O_2]}$$

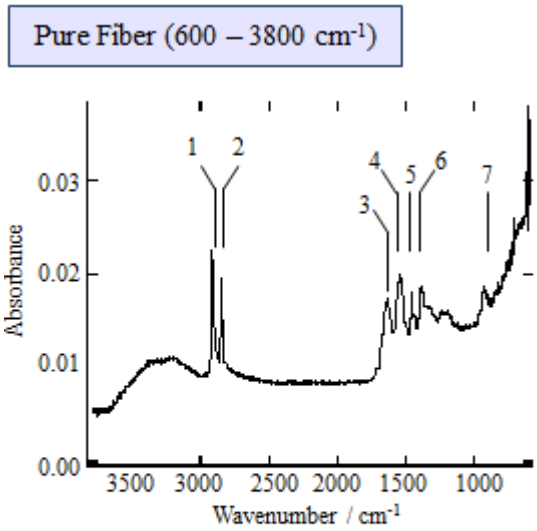
The ratio of $[UO_2(O_2)(CO_3)_2]^{4-}/[UO_2(CO_3)_3]^{4-}$ is determined by equation (8) with the given concentrations of H^+, H_2O_2, CO_3^{2-} and the equilibrium constant of reaction (7),

$$\log\left(\frac{[UO_2(O_2)(CO_3)_2^{4-}]}{[UO_2(CO_3)_3^{4-}]}\right) = -17.8 + \log[H_2O_2] - 2\log[H^+] - \log[CO_3^{2-}] \qquad (7)$$

Using $K=10^{-17.8}$, $[H_2O_2]= 4\times10^{-7}$ M, pH=8.1, $[CO_3^-]=2.4\times10^{-4}$ M[32], and a total uranium of 3.3 ppb, the $[UO_2(O_2)(CO_3)_2]^{4-}/[UO_2(CO_3)_3]^{4-}$ ratio in ocean water should be about 4.2×10^{-5} even as the concentration of H_2O_2 is near the maximum found in seawater ($[H_2O_2]$= 400 nM). According to this simple ideal solution calculation, there could be a trace amount of uranyl-peroxo-carbonato complex present in ocean water with high concentrations of H_2O_2. In real ocean water, the situation may be complicated because the mechanisms of hydrogen peroxide formation are not totally understood yet. It should be noted that there is no report in the literature regarding the existence of the uranyl-peroxo-carbonato complex in ocean water. The very low concentrations of this stable uranyl-peroxo-carbonato complex in ocean water according to our estimate should not affect the sequestering of uranium from seawater using amidoxime-based sorbents.

3. FTIR Study of Amidoxime-based Polymer Sorbent

Infrared spectroscopy may provide information regarding organic functional groups attached to the polymer sorbent. A total reflection Fourier Transform infrared (FT-IR) spectrometer was used to obtain the infrared spectra of the sorbent before and after uranium elution. Figure 10 shows the original FT-IR spectrum of the fresh amidoxime-based polymer sorbent prepared by ORNL before the uranium adsorption experiment. Our assignments of the peaks (wavenumbers and vibrational modes) are given in the table of Figure 10. Figure 11 shows the spectrum of the sorbent after uranium adsorption and carbonate elution. In comparison with the original sorbent spectrum, the general features of the two spectra are basically identical as illustrated in the figure. The IR spectra support our experimental observation that the sorbent after carbonate elution of uranium requires no regeneration for its reuse of uranium adsorption from the simulated seawater.



No.	Wavenumber	Mode
1	2917 cm^{-1}	CH_3 stretching
2	2849 cm^{-1}	CH_2 stretching
3	1647 cm^{-1}	C=N stretching
4	1552 cm^{-1}	N-H bending
5	1472 cm^{-1}	CH_3, CH_3 bending
6	1392 cm^{-1}	C-N stretching
7	934 cm^{-1}	N-O stretching

Figure 10. FT-IR spectrum of the original sorbent and peak assignments

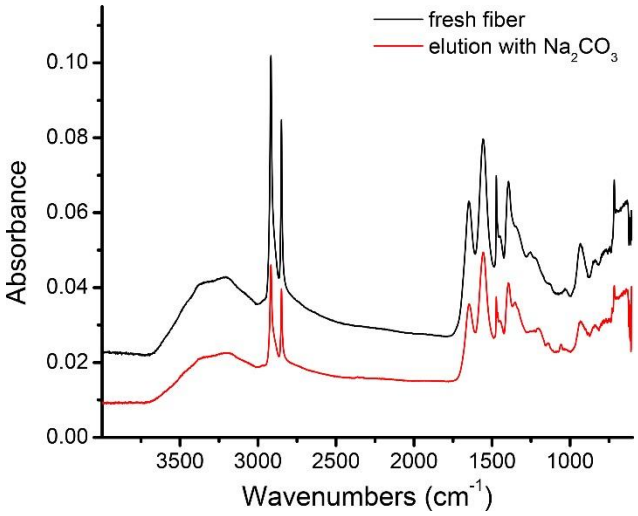


Figure 11. FT-IR spectrum of the sorbent after carbonate elution of uranium (red) in comparison with the original spectrum before uranium adsorption from simulated seawater

Acid leaching results in deterioration of the sorbent loading capacity of uranium as illustrated in Figure 8. A typical FTIR spectrum of the sorbent after elution with 0.5 M HCl is

given in Figure 12. The IR peaks in the region 750-1750 $cm^{-1}$of the acid leached sorbent show noticeable differences from those of the original sorbent. For example, the peaks at 1552 cm^{-1} and at 1392 cm^{-1} are significantly reduced relative to the 1647 cm^{-1} peak. Regeneration of the sorbent in KOH (2.5% KOH at 80 ^{o}C for 3 hours) is recommended in the literature. The FTIR spectrum of the KOH treated sorbent given in Figure 12 indicates reappearance of these peaks but the whole spectrum still shows some differences in detail. For example, the peak at 934 cm^{-1} in the regenerated sorbent appears to be smaller in comparison to the original sorbent spectrum. The FTIR spectra presented in this report provide qualitative information about the chemical groups present in the amidoxime-based sorbent. Further study is needed in order to understand the deterioration mechanisms of the sorbent caused by acid leaching.

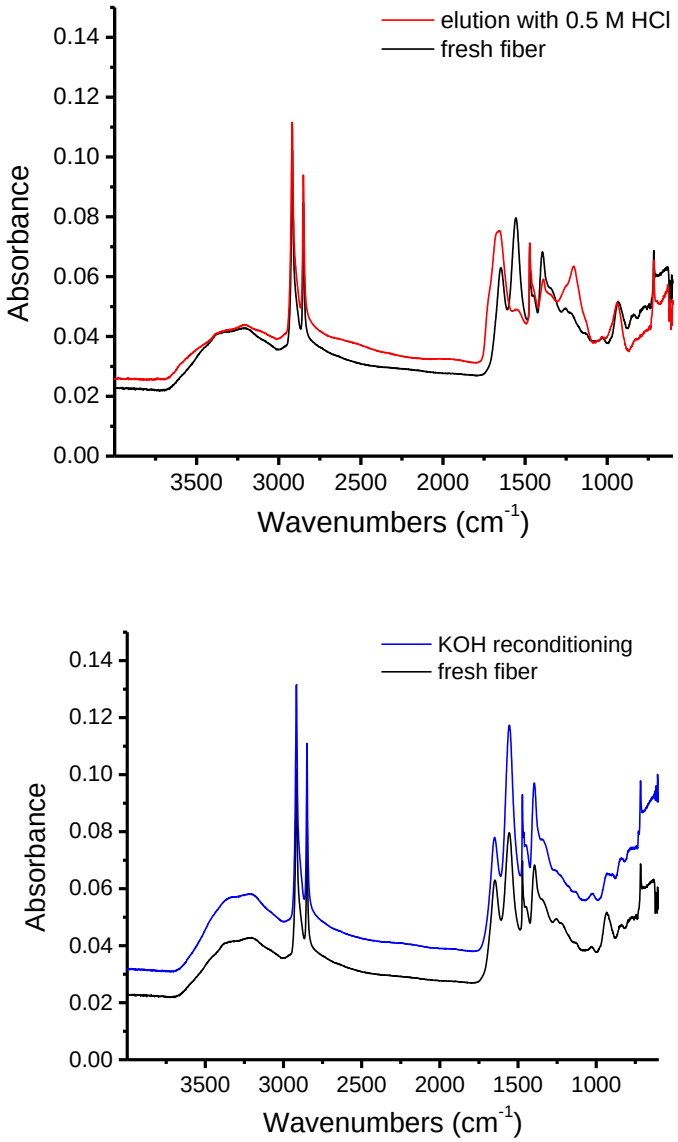


Figure 12. FTIR spectra after 0.5 M HCl leaching (top, red) and after KOH reconditioning with 2.5% KOH at 80 ^{o}C for 3 hours (bottom, blue)

3. Vanadium Complex Formation with Amidoxime Molecules and Elution Study

There is virtually no information available in the literature regarding vanadium coordination with amidoxime molecules. Vanadium should exist in seawater (pH 8-8.3) in the +5 oxidation state as HVO_4^{-3} and $H_2VO_4^{-3}$ according to the literature (Figure 13).[33] We have studied possible reactions of sodium vanadate Na_3VO_4 with single amidoxime molecules including the open chain diamidoxime and the cyclic imidedioxime. These compounds were

synthesized by Guoxin Tian and Linfeng Rao of Lawrence Berkeley National Lab (LBNL) and reported in the literature.[7,8] Sodium vanadate reacts with the cyclic imidedioxime molecule in simulated seawater to form a light yellow complex (Figure 14). Vanadium at the +5 state is NMR active. The ^{51}V NMR spectra of Na_3VO_4 ($2x10^{-4}$ M) and its complex with amidoxime molecules are given in Figure 14. The ^{51}V NMR spectrum of Na_3VO_4 alone in simulated seawater consists of a single peak occurring at about -548 ppm. The ^{51}V NMR peak shifts to -414 ppm when the cyclic imidedioxime molecule ($2x10^{-4}$ M) is added to the Na_3VO_4 solution. This yellow color complex is not found when the open chain diamidoxime is added to the Na_3VO_4 and a ^{51}V NMR peak at -550 ppm is observed suggesting the open chain diamidoxime probably does not react with Na_3VO_4. Our preliminary investigation indicates that vanadium in simulated seawater can react with cyclic amidoxime molecule to form a complex. The structure and chemical nature of the vanadium complex however require further investigation.

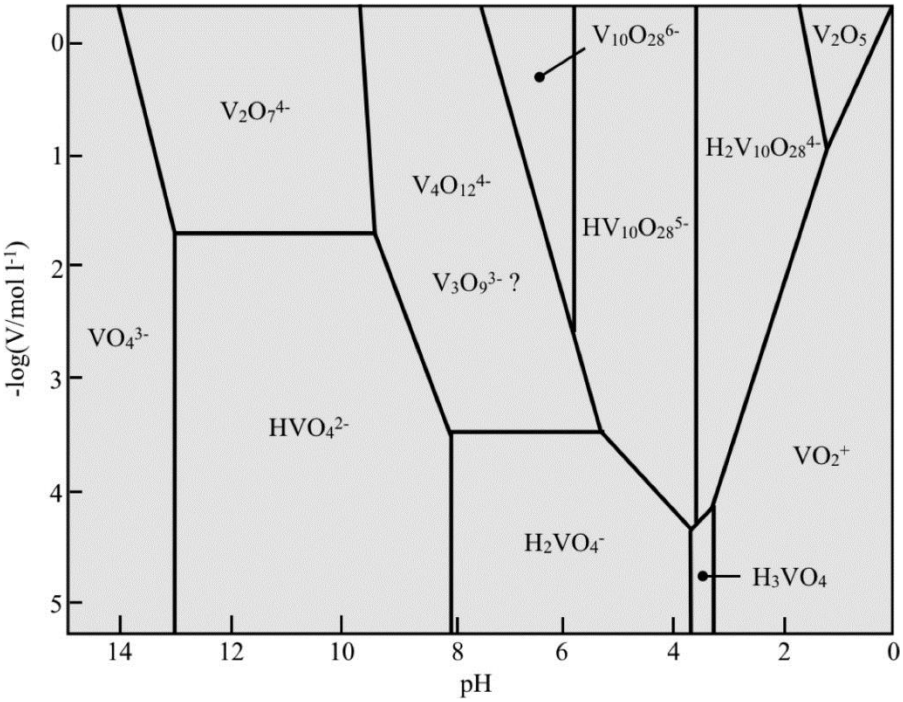


Figure 13. Stability domains of various vanadates and polyvanadates species as a function of pH and vanadium concentration (from reference 33)

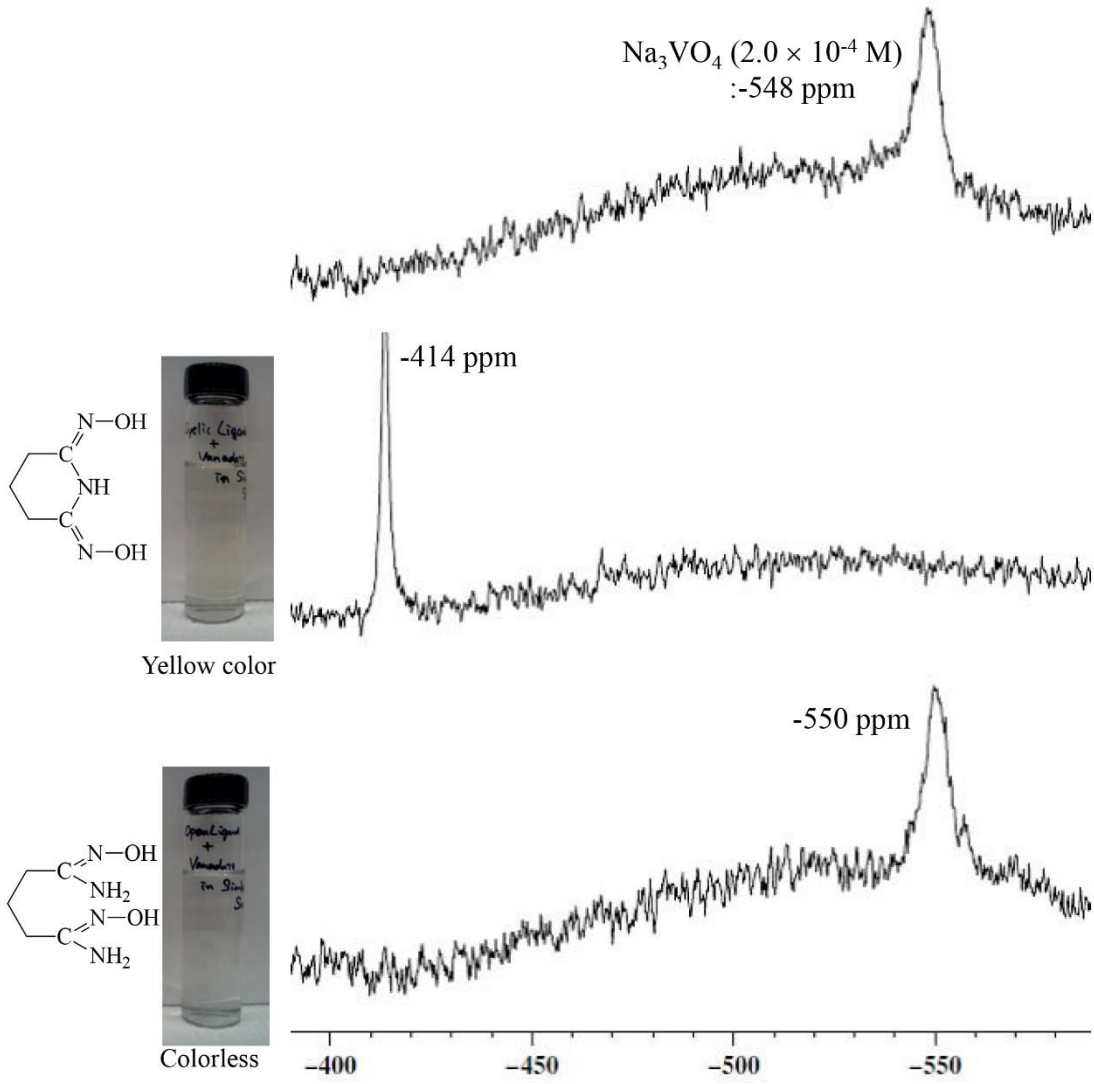


Figure 14. ^{51}V NMR spectra of Na_3VO_4 and its complex with single amidoxime molecules. Top: $2x10^{-4}$ M Na_3VO_4 solution; Middle: $2x10^{-4}$ M Na_3VO_4 + $2x10^{-4}$ M cyclic glutarimidedioxime ; Bottom: $2x10^{-4}$ M Na_3VO_4 + $2x10^{-4}$ M open chain glutardiamidoxime.

Sodium vanadate (Na_3VO_4) in simulated seawater can be adsorbed by the amidoxime-based polymer sorbent as indicated by the color of the sorbent developed in contact with the vanadium containing solution (Figure 15). Leaching the vanadium loaded sorbent with 1 M hydrochloric acid is not able to reduce the color of the sorbent suggesting vanadium cannot be eluted by 1 M HCl. If a solution of 1 M H_2O_2 is used to leach vanadium, the color of the sorbent is reduced from brownish yellow to light yellow and vanadium is detected in the leach solution. Actually, when a solution containing 1 M H_2O_2 and 1 M KOH is used, the color of the sorbent is reduced to very slight yellow close to the color of the original sorbent. This simple color change

test allows us to identify potential reagents which may be used to elute vanadium from the sorbent. However, it does not mean the reagents show positive test results are suitable for removing vanadium from the sorbent for practical purposes. We still have to consider deterioration of the sorbent after treatment with these leaching solutions. Table 2 lists the results of the initial screening test. The reagents cause color change of the vanadium-loaded sorbent are marked with a positive sign (+) and those have no effect on the color of the sorbent are marked with a negative sign (-). According to the results given in Table 2, catechol, hydrogen peroxide, Mercaptosuccinic acid, Nitrilotris(methylene) triphosphonic acid, and oxalic acid are effective for vanadium elution from the amidoxime-based polymer sorbent. Further leaching tests for vanadium removal and durability of the sorbent using these reagents are under investigation in our lab.

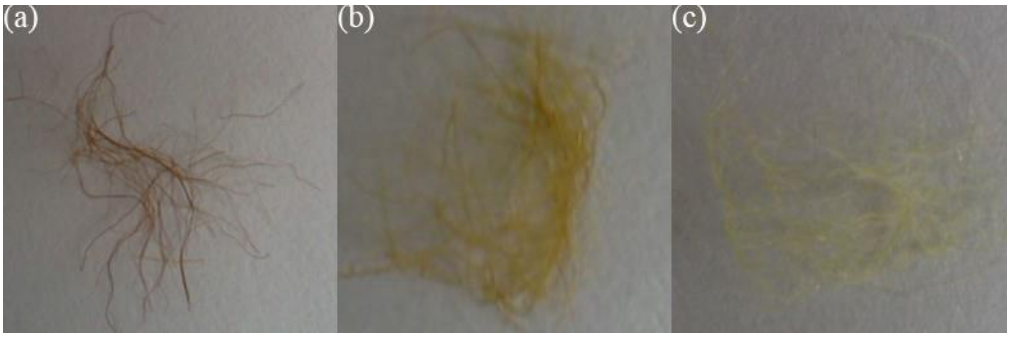


Figure 15. Leaching of vanadium from the sorbent with H_2O_2: (a) vanadium loaded amidoxime polymer sorbent; (b) leaching of the sorbent with 1M H_2O_2 for 3 hours; (c) leaching with 1M H_2O_2+1 M KOH for 3 hours.

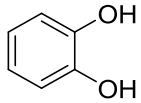
Table 2. Screening test of vanadium desorption from admidoxime-based fiber with different eluting agents at room temperature.

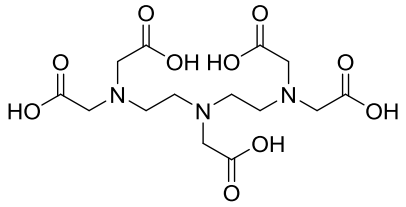
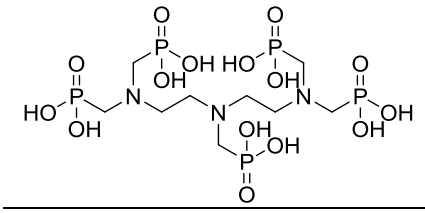
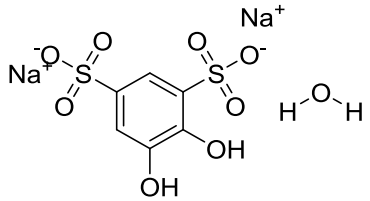
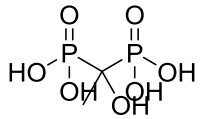
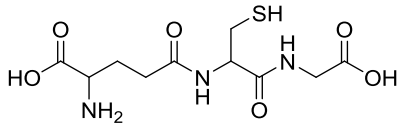
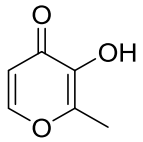
Experimental conditions:

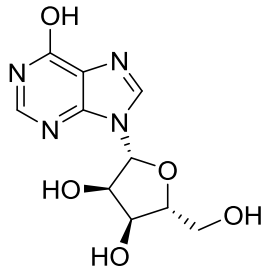
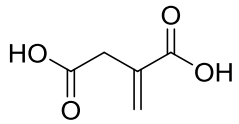
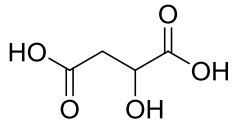
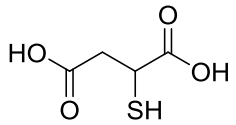
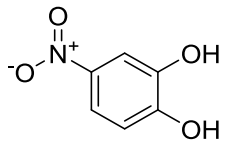
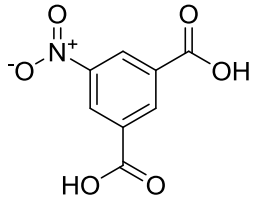
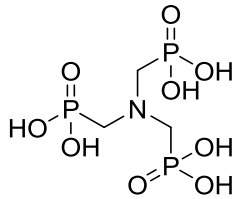
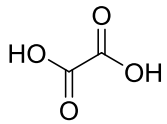
Adsorption - 20 mg sorbent in 400 mL simulated seawater with 10 ppm vanadium, stirring for 24 hours

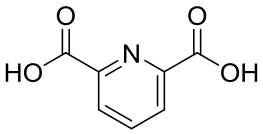
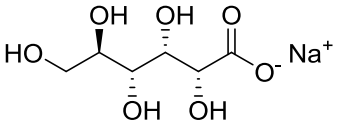
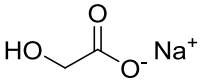
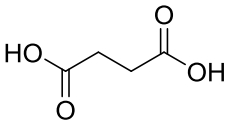
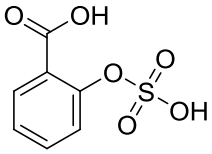
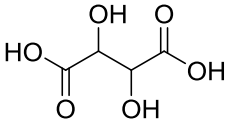
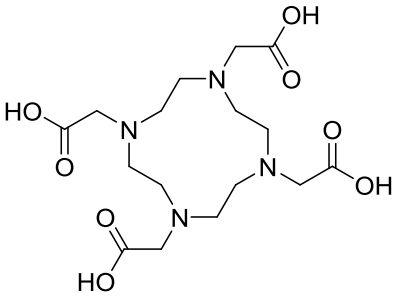
Desorption - 10 mg sorbent in 10 mL leaching solution stirring for 1 hour

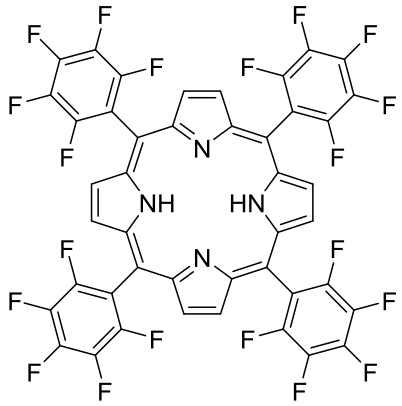
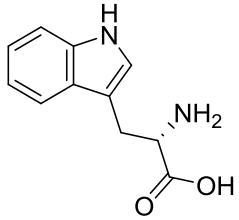
Leaching solution - (1 M aqueous solution at room temperature)

Eluting agent	Positive (+) or Negative (-)
Catechol 	+
Diethylenetriaminepentaacetic acid (0.1 M)	-

	
Diethylenetriaminepentakis (methylphosphonic acid) 	-
4,5-Dihydroxy-1,3-benzenedisulfonic acid disodium salt monohydrate 	+
Etidronic acid 	-
Glutathione 	-
HCl	-
Hydrogen peroxide	+
3-hydroxy-2-methyl-4-pyrone 	-
Inosine	-

	
Itaconic acid 	-
Malic acid 	-
DL-Mercaptosuccinic acid 	+
4-Nitrocatechol 	-
5-Nitroisophthalic acid 	-
Nitrilotris(methylene) triphosphonic acid 	+
Oxalic acid 	+
Polyvinyl pyrrolidone	-

2,6-Pyridinedicarboxylic acid 	-
Sodium D-gluconate 	-
Sodium glycolate 	-
Succinic acid 	-
Sulfosalicylic acid 	-
Tartaric acid (1 M) 	-
1,4,7,10-Tetraazacyclododecane-1,4,7,10-tetraacetic acid 	-
5,10,15,20-Tetrakis(pentafluorophenyl)porphyrin (0.1 M)	-

	
L-Tryptophan 	-

5. Supercritical Fluid Carbon Dioxide Elution of Uranium from the Sorbent

Using supercritical fluid carbon dioxide (sc-CO_2) as a solvent for extraction of uranium is a well-established technique in the literature.[34] The advantages of supercritical fluid extraction compared with conventional solvent extraction include its great penetration power into porous solid materials, rapid separation of solute from solvent, and minimization of liquid waste generation. The low critical constants of carbon dioxide (T_c=31 ^oC and P_c=73 atm), its chemical inertness, and low cost make sc-CO_2 an attractive solvent for dissolution and extraction of metals from solid materials. Metal oxides and metal ions are not soluble in sc-CO_2 because CO_2 is a linear triatomic molecule with no dipole moment. However, when metal ions are bound to CO_2-soluble organic ligands, the resulting metal chelates often become soluble in sc-CO_2. For example, uranium dioxide or uranyl ions in solid materials can be extracted into sc-CO_2 with CO_2-soluble fluorine-containing and phosphorus-containing ligands.[35] One widely used ligand system for dissolution and extraction of uranium dioxide in sc-CO_2 is tri-n-butylphosphate (TBP). A TBP-nitric acid complex such as $TBP(HNO_3)_{1.8}(H_2O)_{0.6}$ is known to dissolve UO_2 in sc-CO_2 as $UO_2(TBP)_2(NO_3)_2$ which can be identified using UV-Vis spectroscopy (Figure 16).[36,37] A typical supercritical fluid extraction system equipped with a high-pressure fiber-optic cell and a CCD array UV-Vis spectrometer for in situ spectroscopic measurement is shown in Figure 16. This system was used for uranium elution experiments utilizing sc-CO2 as a solvent in this study. Uranium dissolved in the sc-CO_2 phase can also be collected in a trap solution by opening the exit valve of the extraction cell.

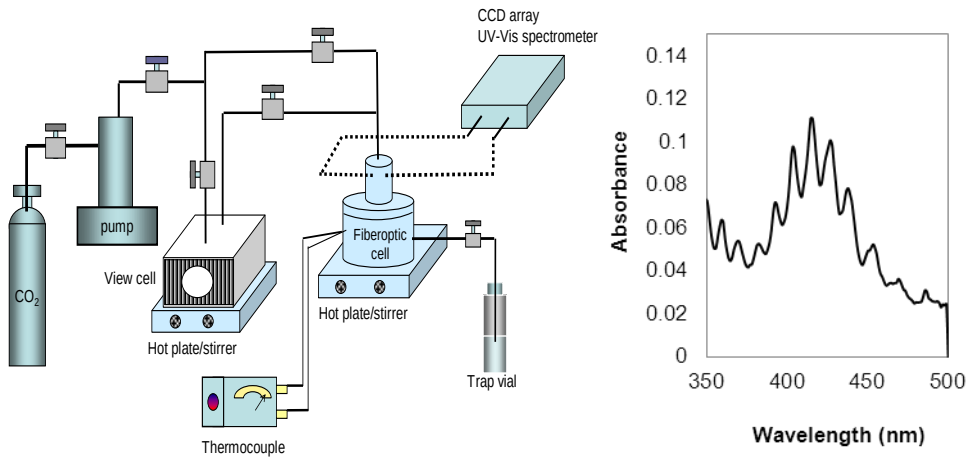
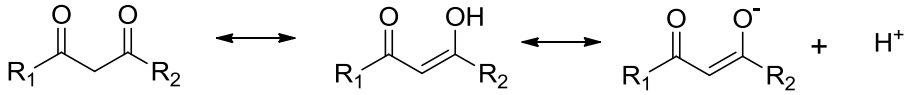


Figure 16. A typical supercritical fluid CO_2 extraction system and UV=Vis spectrum of $UO_2(TBP)_2(NO_3)_2$ obtained by the fiber-optic cell in the CO_2 phase

Using $TBP(HNO_3)_{1.8}(H_2O)_{0.6}$ as extractant, uranium adsorbed on the amidoxime polymer sorbent can be removed but damage to the sorbent material is severe because the extractant contains nitric acid. Acid leaching is known to cause deterioration of the sorbent as shown the data given in Figure 8. Other CO_2-soluble ligands were then tested for uranium elution from the sorbent. For example, acetylacetone and fluorinated acetylacetone are also known to extract uranyl ions in sc-CO_2. These β–diketones can exist in enolate form due to keto-enol equilibrium in sc-CO_2 as illustrated by the following equation.



The enolate form is able to form a neutral chelate with uranyl ion $(UO_2)^{2+}$ (2:1 complex) which is soluble in sc-CO_2. Fluorine substitution in the alkyl group of acac is known to enhance solubility of the ligand in sc-CO_2. Table 3 shows the extraction efficiencies of some fluorinated β–diketones including trifluoroacetylacetone (TFA), hexafluoroacetylacetone (HFA), and thenoyltrifluoroacetylaetone (TTA) for removing uranium from the amidoxime-based polymer sorbent. The extraction efficiency of these β–diketones for uranium increases with increasing fluorine substitution in the ligand. The uranium extraction efficiency is from 31% for acac to 69% for HFA. Other ligands including di-(2-ethylhexyl)phosphoric acid (D2EHPA), trioctylphosphine oxide (TPO), and Cyane 471were also tested for removing uranium from the sorbent. None of them exhibits better uranium extraction efficiency than HFA in sc-CO_2. If a

mixture of HFA and TBP is used, the uranium extraction efficiency can be increased to 79%. Coordination of TBP to $UO_2(hfa)_2$ chelate or the adduct formation apparently can enhance extraction efficiency of uranium from the sorbent, where hfa represents the de-protonated enolate form of HF.

The rate of uranium extraction from the sorbent in sc-CO_2 is rather slow. Figure 17 shows the rate of uranium elution from the sorbent using a mixture of TBP and HFA in sc-CO_2. The amount of uranium dissolved in sc-CO_2 as measured by the absorption of the uranyl-hfa-TBP complex at 356 nm is still increasing after 10 hours of elution of the sorbent. The uranium elution efficiencies given in Table 3 are based on 10 hours of elution for each extractant system. The results suggest that uranium is bonded strongly to amidoxime groups in the sorbent and the CO_2-soluble ligands tested in this study are not strong enough to compete with the amidoxime groups existing in the sorbent. Identifying and developing stronger CO_2-soluble ligands for sc-CO_2 extraction of uranium from amidoxime-based sorbent is necessary in order to improve uranium recovery efficiency using this unconventional solvent. Research along this direction is in progress.

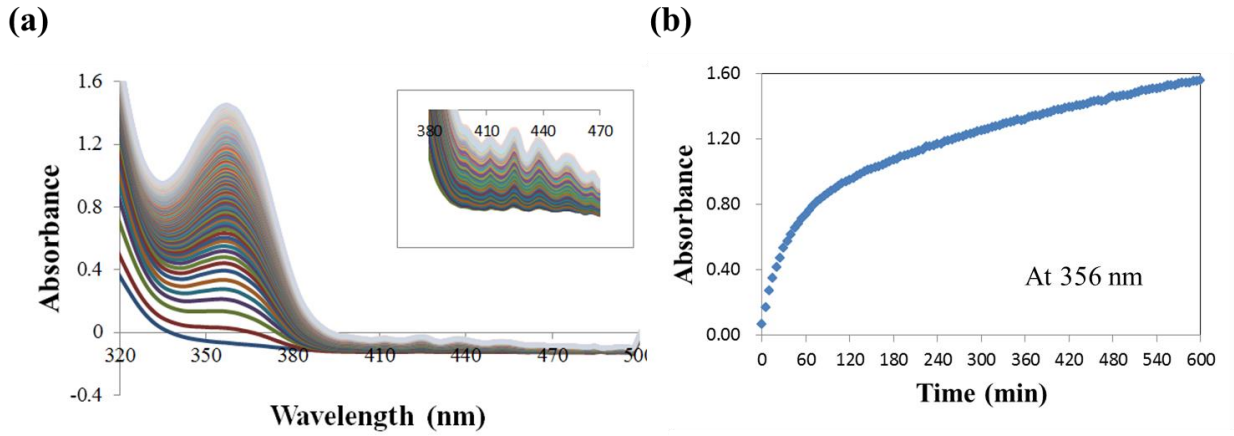


Figure 17. (a) *in situ* UV/Vis spectra in scCO_2 for (HFA + TBP) leaching; (b) monitored at 356 nm. Conditions: 200 µL HFA + 200 µL TBP, 200atm CO_2, 40°C, 5 min interval.

Table 3. Efficiency of uranium elution using supercritical carbon dioxide with different extratants. Conditions: 10 mg uranium loaded sorbent, 200 µL of ligand, 100 µL of DI-H_2O, 200 atm CO_2, 40^oC, 10 hrs.

Entry	Ligand	Recovery (%)
1	Tributyl phosphate (TBP)	10.3
2	Trioctylphosphine oxide (TOPO)	8.7
3	Cyanex 471X	6.3
4	Acetylacetone (acac)	31.0
5	Thenoyltrifluoroacetylacetone (TTA)	43.6
6	Trifluoroacetic acid (TFA)	46.8
7	Di-(2-ethylhexyl)phosphoric acid (D2EHPA)	50.9
8	D2EHPA + TBP	63.2
9	Hexafluoroacetylacetone (HFA)	68.3
10	HFA + TBP	79.2

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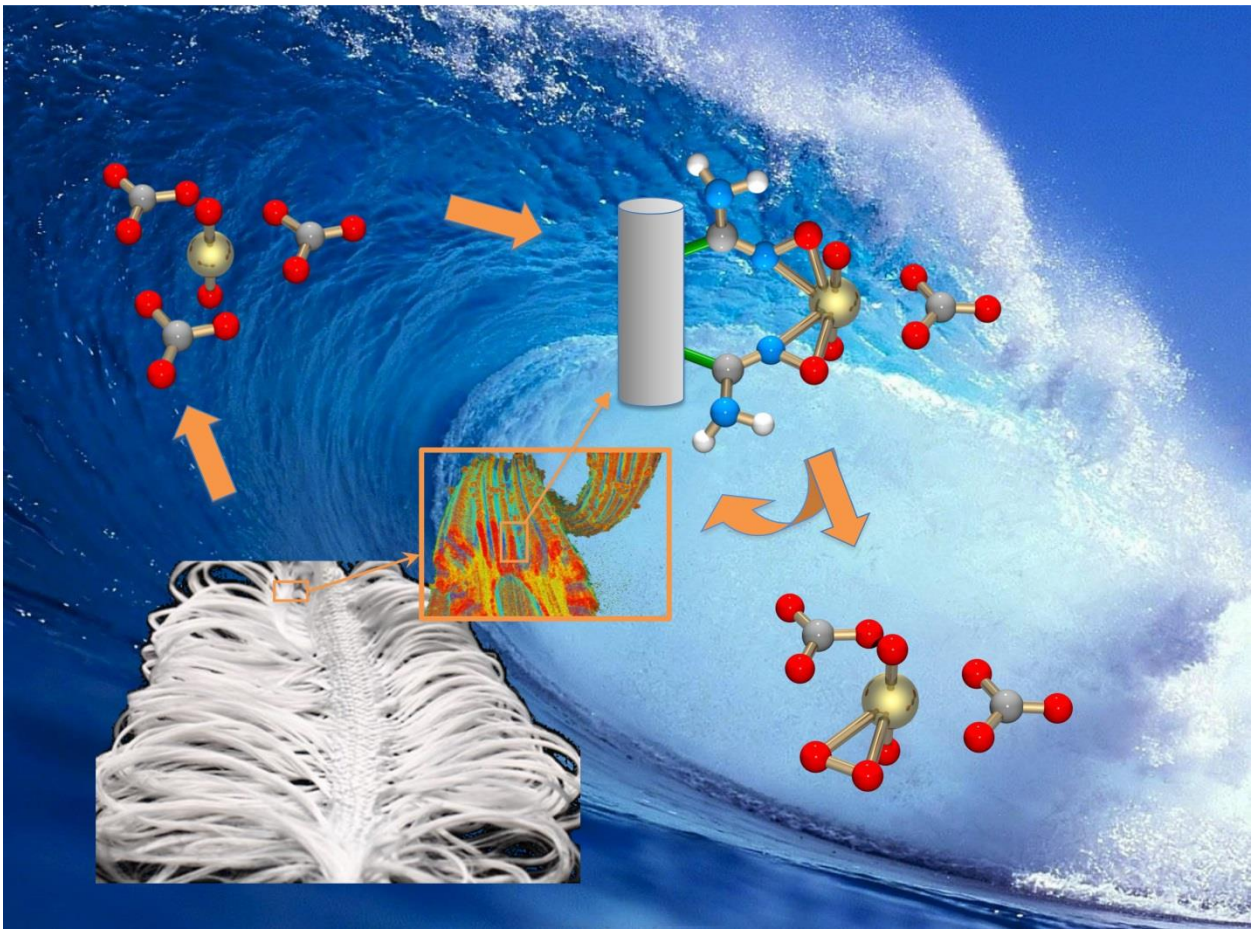
Appendix – A cover page research article entitled "Carbonate-H_2O_2 leaching for sequestering uranium from seawater" is attached. The article was accepted for publication by Dalton Transactions on March 9, 2014, DOI:10.1039/c3dt53404a.



Dalton Transactions

PAPER

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Cite this: DOI: 10.1039/c3dt53404a

Carbonate–H_2O_2 leaching for sequestering uranium from seawater†

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Received 3rd December 2013,
Accepted 9th March 2014

DOI: 10.1039/c3dt53404a

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Uranium adsorbed on amidoxime-based polyethylene fiber in simulated seawater can be quantitatively eluted at room temperature using 1 M Na_2CO_3 containing 0.1 M H_2O_2. This efficient elution process is probably due to the formation of an extremely stable uranyl-peroxo-carbonato complex in the carbonate solution. After washing with water, the sorbent can be reused with minimal loss of uranium loading capacity. Possible existence of this stable uranyl species in ocean water is also discussed.

Introduction

Developing techniques for extracting uranium from seawater is attracting considerable current interest because land-based uranium sources would be depleted by the end of this century.[1,2] Our ocean contains a very large quantity of uranium (about 1000 times more than terrestrial ores) which is sufficient to support nuclear power production in the next few centuries.[3] Uranium exists in seawater at a low concentration (~3 ppb) and as the very stable uranyl tris-carbonato complex, $UO_2(CO_3)_3^{4-}$.[3] Screening studies conducted in the 1980s with more than 200 functionalized adsorbents showed that sorbent materials with the amidoxime group $RC(NH_2)(NOH)$ were most effective for uranium adsorption from seawater.[4–6] Recent research efforts in Japan and in the USA have focused on using amidoxime-based adsorbents for sequestering uranium from seawater.[4] The amidoxime-based fiber can be prepared by a radiation-induced graft polymerization method which involves grafting of acrylonitrile ($CH_2{=}CH{-}CN$) onto polyethylene fabrics and chemical conversion of the –CN groups with hydroxylamine to the amidoxime groups. This type of sorbents show good mechanical strength and a high capacity for uranium sorption from seawater. If this uranium sequestering technology could be made economically favorable and environmentally sustainable, our ocean would provide virtually an inexhaustible source of uranium for nuclear power production. The amidoxime groups formed in the polymer sorbent by the synthesis method described above may exist in two different structures as illustrated in Fig. 1. Both the cyclic imide dioxime and the open-chain diamidoxime on the sorbent can form strong complexes with uranium.[7,8] Tian *et al.* recently reported that the open-chain diamidoxime is a weaker competing ligand than the cyclic imide dioxime for complexation with U(VI) under the seawater conditions.[8] The uranium sequestering process may be illustrated by the following reaction:

$$[UO_2(CO_3)_3]^{4-} + 2H_2A \rightarrow UO_2(HA)A^- + 3HCO_3^- \quad (1)$$

where H_2A represents either glutarimidedioxime or glutardiamidoxime shown in Fig. 1.

Uranium collected by the amidoxime-based sorbents is recovered typically by elution with an acid such as 1.0 M hydrochloric acid (HCl). After the acid elution, the sorbent requires a KOH reconditioning process, which involves heating the sorbent in 2.5% KOH solution at 80 °C for 3 hours, to regenerate the active functional groups for reuse.[9,10] A serious drawback of the acid elution process is deterioration of the sorbent caused by acid hydrolysis, making its reusability rather limited. Sorbent durability appears to be an important factor determining economic competitiveness of the current amidoxime-based sorbent collection system for sequestering uranium from seawater.[2,4] This paper describes a new desorption method utilizing a mixture of sodium carbonate and hydrogen peroxide as an eluent for recovering uranium from an amidoxime-based polymer sorbent. The high efficiency of this elution

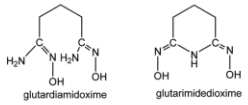

Fig. 1 Structures of open chain diamidoxime (left) and cyclic imide dioxime (right).

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†Electronic supplementary information (ESI) available. See DOI: 10.1039/c3dt53404a

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process is attributed to the formation of an extremely stable uranyl-peroxo-carbonato complex. The carbonate–peroxide desorption process creates little damage to the sorbent and requires only water rinse to regenerate the sorbent for its reuse. This new elution method may provide a simple and benign process for recycling the sorbent for sequestering uranium from seawater. Because hydrogen peroxide is known to exist in the ocean water surface, the possibility of formation of uranyl-peroxo-carbonato complex in seawater is also discussed.

Experimental section

Preparation of amidoxime-based polyethylene fiber

Amidoxime-based polyethylene adsorbent fibers were prepared by the radiation-induced graft polymerization method[11] as illustrated in Scheme 1, which involves four processing steps: electron beam irradiation of polyethylene fibers; co-grafting polymerizable monomers containing nitrile groups and hydrophilic groups to form grafted side chains throughout the fiber; conversion of nitrile groups to amidoxime groups; and alkaline conditioning of the grafted fibers.

Irradiation of polyethylene fibers. Prior to irradiation, the polyethylene fibers were placed in a plastic bag and sealed under nitrogen. The bag was then put inside an insulated container and placed on top of dry ice and irradiated to a dose of 200 kGy using 4.9 MeV electrons and 1 mA current from an electron beam machine.

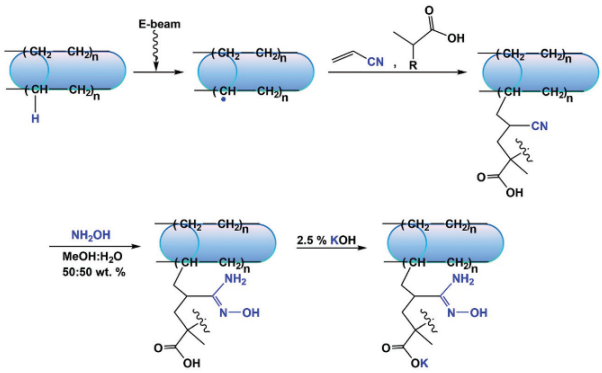
Grafting of polymerizable monomers containing nitrile groups and hydrophilic groups. After irradiation, the fibers were immersed in a flask containing a previously de-gassed solution of acrylonitrile and methacrylic acid in dimethylsulfoxide and placed in an oven at 65 °C for about 18 hours. After the grafting reaction was complete, the fibers were drained from the solution and washed with dimethylformamide (DMF) to remove any monomers or co-polymer by-products. The fibers were then washed with methanol to remove the DMF and dried at 50 °C under vacuum for 72 hours.

Conversion of nitrile groups to amidoxime groups. The irradiated and grafted polyethylene fibers were placed in a flask containing 10% hydroxylamine hydrochloride in 50/50 (w/w) water–methanol at 80 °C for 72 hours. The fibers were then washed with deionized water followed by a methanol rinse and allowed to dry at 50 °C under vacuum for 72 hours.

Alkaline conditioning of grafted fibers. After the amidoximation reaction the polyethylene fibers were added to a flask containing 2.5% KOH and heated for 3 hours at 80 °C, then washed with deionized water until the pH was neutral.

Adsorption of uranium in simulated seawater

Uranium sorption was performed using simulated seawater spiked with 9 ppm of uranium. The simulated seawater contained Na^+ (10 118 ppm), Cl^- (15 573 ppm), and HCO_3^- (140 ppm) at pH = 8.0. The uranium sorption experiment was conducted with 20 mg of the amidoxime-based polyethylene fiber suspended in 400 mL of the simulated seawater with stirring for 24 hours. At the end of this period, sorption of uranium was found to reach equilibrium. The evolution plot of the sorption of uranium from simulated seawater is given in the ESI (Fig. 1S†). Uranium in the simulated seawater was analyzed by a spectrophotometric method using Arsenazo III as a complexing agent and the absorbance of the uranyl–arsenazo complex was monitored at 653 nm with a UV-Vis spectrometer.[12,13] The UV-Vis spectra of the uranyl–arsenazo complex are shown in the ESI (Fig. 2S, left†). According to the literature,[13] Arsenazo III reacts with uranium(VI) in acidic media to give a uranyl–arsenazo complex (green-blue complex, λ_{max} = 653 nm) which is very sensitive for the determination of U (limit of detection ~0.50 μg L^{-1}). The pH value of the solution for spectrophotometric determination of uranium utilizing Arsenazo III was adjusted to one in this study. Under these



Scheme 1 Reaction scheme for the preparation of amidoxime-based polyethylene fibers.

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acidic conditions (pH = 1), either $UO_2(CO_3)_3^{4-}$ or $UO_2(O_2)(CO_3)_2^{4-}$ should be converted to $UO_2(H_2O)_5^{2+}$. The linear regression equation for uranium in the concentration range 0–5.38 ppm was Abs = 0.19265X (R^2 = 0.99966, n = 7) where X is the uranium concentration in ppm (ESI, Fig. 2S, right†). The capacity for uranium adsorption on the sorbent under our experimental conditions was about 6 wt%.

Elution with carbonate or carbonate–H_2O_2 solution

Elution of uranium from the fiber was performed with the uranium loaded fiber immersed in 10 mL of a sodium carbonate solution with or without hydrogen peroxide at room temperature (21 °C) with stirring for one hour. Uranium in the leaching solution at appropriate time intervals was measured during the elution process using the same Arsenazo spectrophotometric method. After the elution, uranium remaining in the sorbent was checked by washing the fiber in concentrated HCl followed by analyzing the acid solution. For repeated sorption experiments, the sorbent after the elution was rinsed with deionized water several times and then filtered and dried in a chemical fume hood at room temperature. No other treatment is needed for reusing the sorbent.

Results and discussion

Using sodium carbonate (Na_2CO_3) solution for leaching uranium from an amidoxime-based sorbent has been reported previously. Das *et al.*[14] showed that uranium could be recovered over 95% from amidoxime-based membranes by leaching with sodium carbonate at room temperature. A report by Rivas *et al.*[15] showed that only 67% recovery of uranium from an amidoxime-based sorbent could be achieved and the elution efficiency did not change significantly in the carbonate concentration range 0.5 to 2 M. According to the literature, the solubility of sodium carbonate in water is about 2.59 M at 25 °C.[16] We have recently re-examined the carbonate leaching of uranium from amidoxime-based polymer fiber fabricated at the Oak Ridge National Laboratory. Our carbonate leaching results agree with those reported by Rivas *et al.* A significant observation in our elution study is that when a small amount of hydrogen peroxide is added to sodium carbonate, the efficiency of uranium elution from the amidoxime-based sorbent is significantly improved to nearly 100%. The sorbent can be reused after rinsing with water without other treatments. The recycled sorbent exhibits a minimal loss (about 3%) of uranium loading capacity per sorption–desorption cycle which is significantly lower than the conventional acid elution process known in the literature.

The results of our sodium carbonate and hydrogen peroxide elution of uranium from the amidoxime-based sorbent are given in Fig. 2. Using 1 M sodium carbonate, elution of uranium from the sorbent at room temperature (21 °C) reaches a nearly constant value around 77% after one hour. Hydrogen peroxide alone (1 M) is not effective for eluting uranium from the sorbent. When a small amount of hydrogen peroxide is added to 1 M sodium carbonate, there is a significant increase in the efficiency of uranium elution. Even with 0.01 M of H_2O_2 in 1 M sodium carbonate, the uranium elution efficiency is increased from 77% to over 90%. The elution of uranium from the sorbent by 1 M sodium carbonate with 0.1 M of H_2O_2 is near-quantitative (Fig. 2).

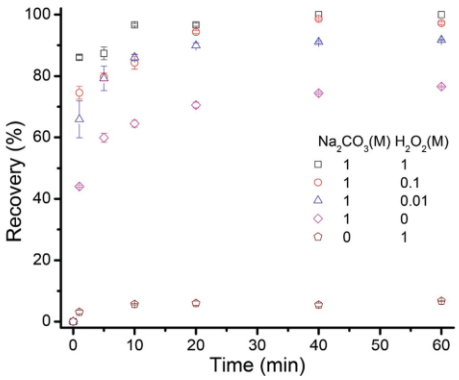

Fig. 2 Rates of uranium elution from the sorbent with sodium carbonate and hydrogen peroxide solutions.

The carbonate elution of uranium from the amidoxime-based sorbent with 1 M Na_2CO_3 (pH ~ 11.0) may be expressed by the following equation:

$$UO_2A_2^{2-} + 3CO_3^{2-} \rightarrow [UO_2(CO_3)_3]^{4-} + 2A^{2-} \quad (2)$$

At a high carbonate concentration the equilibrium of eqn (2) tends to shift to the right favoring the formation of the uranyl tris-carbonato species. The synergistic elution of uranium by hydrogen peroxide and sodium carbonate may be attributed to the formation of an extremely stable uranyl-peroxo-carbonato complex as illustrated by eqn (3) (Fig. 3).

$$UO_2A_2^{2-} + 3CO_3^{2-} + H_2O_2 \rightarrow [UO_2(O_2)(CO_3)_2]^{4-} + 2A^{2-} + HCO_3^- + H^+ \quad (3)$$

A recent report by Goff *et al.* shows that the uranyl-peroxo-carbonato complex is thermodynamically much more stable than the uranyl tricarbonate complex.[18] The apparent for-

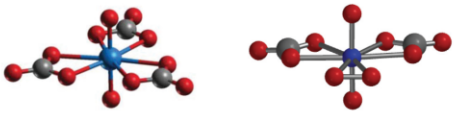

Fig. 3 Structures of $UO_2(CO_3)_3^{4-}$ and $UO_2(O_2)(CO_3)_2^{4-}$. (The structure of $UO_2(CO_3)_3^{4-}$ is from ref. 17; the structure of $UO_2(O_2)(CO_3)_2^{4-}$ is built by crystallographic data from ref. 18 using the molecular modeling software Spartan).

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mation constant of $[UO_2(O_2)(CO_3)_2]^{4-}$ from $[UO_2(CO_3)_3]^{4-}$ according to the following equation

$$[UO_2(CO_3)_3]^{4-} + HO_2^- \rightarrow [UO_2(O_2)(CO_3)_2]^{4-} + HCO_3^-$$

is about 5×10^4.[18] Therefore even with the addition of 0.01–0.1 M hydrogen peroxide, the efficiency of carbonate elution of uranium from the sorbent can be significantly improved. Under the experimental conditions used by Goff *et al.*[18] and by us, only a monoperoxo uranyl complex, $UO_2(O_2)(CO_3)_2^{4-}$, should be formed in the solution according to the DFT calculations reported by Odoh and Schreckenbach.[19] The DFT calculations also indicate that the reaction energies are −59.8 and 6.3 kcal mol^{-1} for $UO_2(O_2)(CO_3)_2^{4-}$ and $UO_2(O_2)_2(CO_3)^{4-}$, respectively, which suggests that the diperoxo uranyl complex, $UO_2(O_2)_2(CO_3)^{4-}$, should not be formed in the solution. In fact, Grenthe *et al.* reported that no diperoxo uranyl complex, $UO_2(O_2)_2(CO_3)^{4-}$, was found even at a high concentration of H_2O_2.[20]

The reusability of the amidoxime-based polymer sorbent after the sodium carbonate–hydrogen peroxide elution of uranium is illustrated in Fig. 4. Reduction of the uranium loading capacity of the recycled sorbent depends on the concentration of the hydrogen peroxide used in the carbonate–peroxide elution process. For uranium elution with 0.1 M H_2O_2 in 1 M Na_2CO_3, the decrease in loading capacity was about 3% for each cycle after 3 consecutive cycles. Elution with 1 M H_2O_2 and 1 M Na_2CO_3 resulted in an about 10% decrease in uranium loading capacity after each sorption–desorption cycle. We also tested uranium elution from the sorbent with hydrochloric acid. Using 0.5 M hydrochloric acid, elution of uranium from the sorbent at room temperature (21 °C) reaches a nearly constant value around 94% after 20 minutes. The rate of uranium elution from the sorbent with 0.5 M HCl is given in the ESI (Fig. 3S†). The sorbent was regenerated in 2.5% KOH at 80 °C for 3 hours followed by rinsing with water and drying. The recycled sorbent after the acid elution showed a reduction in uranium sorption capacity by about 20% per cycle based on our experiments (Fig. 4).

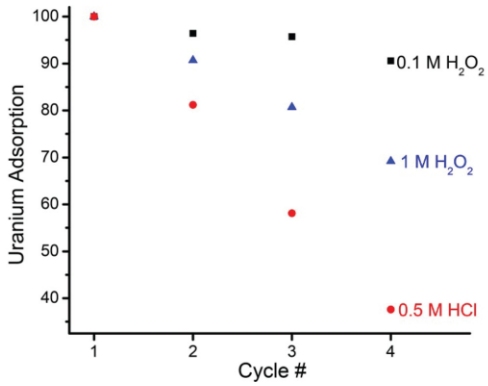

Fig. 4 Uranium loading capacity of the amidoxime-based polymer sorbent after each cycle of sodium carbonate–H_2O_2 and 0.5 M HCl leaching. (Note: for 0.5 M HCl leaching, the sorbent required a KOH reconditioning process after each cycle according to the literature[9,10]).

The oxime group –C=N–OH on the amidoxime-based fiber is suggested to form a chelate complex with UO_2^{2+} *via* η^2 binding with the N–O bond (open-chain)[21] or by the two oxime oxygen atoms and the imide nitrogen atom of the delocalized –O–N=C–N–C=N–O– group (the cyclic form).[7] The oxime group containing carbon–nitrogen double bonds (C=N–OH) may be cleaved by oxidation, reduction, or acid hydrolysis to the corresponding carbonyl group (C=O) which would not complex with UO_2^{2+} in seawater.[22,23] The oxidation power of hydrogen peroxide at high concentrations could cause cleavage of the C=N bond.[24] At low concentrations, hydrogen peroxide apparently causes little damage to the oxime group allowing formation of the stable uranyl-peroxo-carbonato complex and leading to enhanced elution of uranium from the sorbent. Lin and co-workers recently reported that maximizing electron density at the binding site of amidoxime-based ligands through resonance of conjugated π orbitals of electron donating groups (*e.g.* imidazole–oximate) can improve the binding strength for uranyl and stability of ligands.[25] On the basis of this concept, future development of amidoxime-based sorbents with conjugated π orbitals of electron donating groups may lead to new sorbent materials with improved stabilities under carbonate–H_2O_2 leaching conditions.

The feasibility of forming stable uranyl-peroxo-carbonato complex in carbonate solutions raises the question of the possibility of formation of this uranium complex in natural seawater because hydrogen peroxide is known to exist in the ocean surface. The concentrations of hydrogen peroxide in the open ocean surface may vary from several nM to several hundred nM depending on season and time.[26–30] Hydrogen peroxide probably exists in seawater as one of the final products of free radical chemistry in the photochemical decomposition processes of dissolved organic matter. Another hypothesis is that a photochemically-initiated formation mechanism may be involved, which was used to explain the seasonal variation of H_2O_2 concentrations in the open ocean sea surface.[27] We have examined the possibility of formation of uranyl-peroxo-carbonato based on the available thermodynamic data of the following equations:

$$UO_2^{2+} + H_2O_{2(aq)} + 2CO_3^{2-} \rightarrow UO_2(O_2)(CO_3)_2^{4-} + 2H^+ \quad (4)$$

$$UO_2(CO_3)_3^{4-} \rightarrow UO_2^{2+} + 3CO_3^{2-} \quad (5)$$

$$UO_2(CO_3)_3^{4-} + H_2O_{2(aq)} \rightarrow UO_2(O_2)(CO_3)_2^{4-} + 2H^+ + CO_3^{2-} \quad (6)$$

According to the literature,[20,31] the equilibrium constants of reactions (4) and (5) are $10^{4.03}$ and $10^{-21.8}$, respectively. Combination of reactions (4) and (5) results in reaction (6), the most probable dominant reaction that represents the formation of the $UO_2(O_2)(CO_3)_2^{4-}$ species under seawater con-

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ditions. The equilibrium constant K of reaction (6) was calculated to be $10^{-17.8}$.

$$K = \frac{[UO_2(O_2)(CO_3)_2{}^{4-}][H^+]^2[CO_3{}^{2-}]}{[UO_2(CO_3)_3{}^{4-}][H_2O_2]}$$

The ratio of $[UO_2(O_2)(CO_3)_2]^{4-}/[UO_2(CO_3)_3]^{4-}$ was determined using eqn (7) with the given concentrations of H^+, H_2O_2, and $CO_3{}^{2-}$ and the equilibrium constant of reaction (6),

$$\log\left(\frac{[UO_2(O_2)(CO_3)_2{}^{4-}]}{[UO_2(CO_3)_3{}^{4-}]}\right) = -17.8 + \log[H_2O_2] - 2\log[H^+] - \log[CO_3{}^{2-}] \quad (7)$$

Using $K = 10^{-17.8}$, $[H_2O_2] = 4 \times 10^{-7}$ M, pH = 8.1, $[CO_3{}^-] = 2.4 \times 10^{-4}$ M,[32] and a total uranium concentration of 3.3 ppb, the $[UO_2(O_2)(CO_3)_2]^{4-}/[UO_2(CO_3)_3]^{4-}$ ratio in ocean water should be about 4.2×10^{-5} even as the concentration of H_2O_2 is nearly equal to the maximum found in seawater ($[H_2O_2]$ = 400 nM). According to this simple ideal solution calculation, there could be a trace amount of uranyl-peroxo-carbonato complex present in ocean water with high concentrations of H_2O_2. In real ocean water, the situation may be complicated because the mechanisms of hydrogen peroxide formation have not been totally understood yet. It should be noted that there is no report in the literature regarding the existence of the uranyl-peroxo-carbonato complex in ocean water. The very low concentrations of this stable uranyl-peroxo-carbonato complex in ocean water according to our estimate should not affect the sequestering of uranium from seawater using amidoxime-based sorbents.

Conclusion

In summary, the sodium carbonate–H_2O_2 elution process described in this paper offers an efficient new method for recovering uranium from amidoxime-based polymer sorbents for sequestering uranium from seawater. The synergistic effect is attributed to the formation of an extremely stable uranyl-peroxo-carbonato complex known in the literature. The efficiency of uranium elution offered by the carbonate–H_2O_2 method is comparable to that of the hydrochloric acid elution but damage to the sorbent material is much less for the former. The carbonate–H_2O_2 elution also does not require any elaborate step to recycle the sorbent. Rinsing with water is sufficient to regenerate the sorbent for reuse. The acid elution method requires boiling of the leached polymer sorbent in a KOH solution for several hours to regenerate the active functional groups for reuse. The carbonate–H_2O_2 elution appears to offer a new approach for sequestering uranium from seawater by simplifying the recycling procedure and improving the durability of the sorbents. Our thermodynamic calculation indicates that formation of uranyl-peroxo-carbonato complex in ocean water is possible but its concentration is very low even at high concentration of hydrogen peroxide. Its effect on sequestering uranium from seawater using amidoxime-based sorbents appears to be negligible.

Acknowledgements

We acknowledge the financial support by DOE-NEUP Program under contract number 00042246. GT and LR are supported by the Uranium Resources Program, Fuel Cycle Research and Development Program, Office of Nuclear Energy of the U.S. Department of Energy (DOE) under contract number DE-AC02-05CH11231 at Lawrence Berkeley National Laboratory (LBNL).

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