

Innovative Elution Processes for Recovering Uranium and Transition Metals from Amidoxime-based Adsorbents

Fuel Cycle Research and Development

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Summary

Amidoxime-based polymer fibers are considered one of the most promising materials for sequestering uranium from seawater. The high-surface-area polymer fibers containing amidoxime and carboxylate groups synthesized by Oak Ridge National Lab (ORNL-AF1) show very high uranium adsorption capacities known in the literature.¹⁻³ Effective elution of uranium and repeated use of the adsorbent are important factors affecting the cost of producing uranium from seawater using this material. Traditional acid leaching of uranium followed by KOH conditioning of the fiber causes chemical changes and physical damage to the ORNL-AF1 adsorbent. Two alkaline solution leaching methods were developed by this project, one uses a highly concentrated (3 M) potassium bicarbonate solution at pH 8.3 and 40 °C; the other uses a mixture of sodium carbonate and hydrogen peroxide at pH 10.4. Both elution methods do not require KOH conditioning prior to reusing the fiber adsorbent. The conditions of eluting uranium from the amidoxime-based adsorbent using these alkaline solutions are confirmed by thermodynamic calculations. The bicarbonate elution method is selective for uranium recovery compared to other elution methods and causes no chemical change to the fiber material based on FTIR spectroscopy.

Objectives

The main objective of this NEUP project is to develop new elution processes for removing uranium from amidoxime-based polymeric adsorbents with minimal reduction in uranium adsorption capacity for its repeated use. Utilizing spectroscopic techniques to characterize functional groups in the polymer adsorbent is another objective for understanding possible chemical changes caused by the elution. A desirable elution method must demonstrate its effectiveness and selectivity for uranium recovery and allow successful reuse of the adsorbent in real seawater exposure experiments.

Introduction

Developing effective and economic processes for sequestering uranium from seawater is a research area being actively pursued at the present time by scientists in the USA and other countries.⁴ The main drive behind this research is based on the estimate that land-based uranium sources would be depleted by the end of the century and our ocean contains a huge amount of uranium which could provide fuel for nuclear power production for the next few centuries. Uranium exists in seawater at a low concentration (~3 ppb) and as the very stable uranyl tris-carbonato complex. Highly efficient and stable uranium adsorbents are needed in order to economically mine uranium from the ocean.

The amidoxime-based polymer adsorbents, which have been studied by Japanese scientists in the past few decades, appear to be one of the most promising materials for sequestering uranium because of their good mechanical strength and high uranium loading capacities as demonstrated by marine tests. The amidoxime-based fibers are traditionally prepared by a radiation-induced grafting of acrylonitrile ($\text{CH}_2=\text{CH}-\text{CN}$) onto polyethylene fabrics followed by chemical conversion of the $-\text{CN}$ groups with hydroxylamine to the amidoxime groups. To make the polymer adsorbents hydrophilic, carboxylic acid or other weak acid groups are also grafted onto the adsorbents during the synthesis process. After synthesis, the polymer adsorbent is treated with a KOH conditioning process to convert the carboxylic acid groups to carboxylates and to make the material effective for uranium adsorption.

Oak Ridge National Lab (ORNL) has developed a new type of polymer adsorbents which utilizes high-surface-area polyethylene fibers as the backbone material.^{2, 5} With radiation induced grafting and formation of amidoxime and carboxylic acid groups on the surface, the polymer adsorbents show very high uranium adsorption capacities in real seawater experiments. Durability of the sorbent is another factor which must be considered for economic extraction of uranium from seawater. Acid leaching is a traditional method to recover uranium from the sorbent. However, acid leaching causes problems for reusing the ORNL high-surface-area polymer adsorbent (AF-1).

Adsorption capacity and durability for re-use are two key factors determining economic feasibility for commercial extraction of uranium from seawater. After synthesis, the ORNL-AF1 amidoxime-carboxylic acid based polymer adsorbents is typically treated with a strong KOH solution (2.5% KOH) at 80 °C for 1–3 hours. Without the KOH conditioning process, the polymer adsorbent is not effective for uranium adsorption in seawater. After uranium adsorption, hydrochloric acid (0.5–1 M HCl) is traditionally used to elute uranium from the adsorbent. After acid elution, the adsorbent is treated with KOH again to recondition the adsorbent (converting carboxylic acid to carboxylate group again) for its reuse. It is known that under highly acidic or alkaline conditions, single molecules containing amidoxime groups can be converted to carboxylic acid groups.⁶ Fourier transform infrared spectroscopy (FTIR) was used to characterize amidoxime and carboxylate groups attached to the ORNL-AF1 adsorbent before and after acid leaching and KOH conditioning. Two non-acid elution processes which do not

require KOH conditioning were developed for recovering uranium from the ORNL-AF1 adsorbent. One method uses a mixture of sodium carbonate and hydrogen peroxide solution as eluent and the other method uses a potassium bicarbonate solution as eluent. The uranium adsorption, elution and sorbent reuse tests were performed using a recirculating seawater flume system available at the PNNL Marine Sciences Laboratory located at Sequim, Washington. The results of different elution processes for uranium recovery and reuse of the ORNL adsorbent obtained from the seawater flume study are summarized in this report.

Summary of Accomplishments

1. Acid Leaching and KOH Conditioning

Hydrochloric acid is typically used to remove uranium from amidoxime-based adsorbents. The elution of uranium and transition metals from a typical ORNL high-surface-area amidoxime-based polymer adsorbent with different concentrations of hydrochloric acid solution is shown in Figure 1. About 95% of the adsorbed uranium can be eluted from the adsorbent using 0.5 M hydrochloric acid. The elution is fast, taking about 90 min but not specific for uranium. Transition metals with the exception of iron and vanadium are all eluted with uranium using 0.5 M HCl. About 70% of iron could be eluted under this condition. Vanadium (V) can only be partially stripped from the adsorbent with elevated HCl concentration (>3 M) and temperature (e.g. 60°C). However, under such severe acid treatment, the adsorbent is virtually destroyed. We thus employed 0.5 M HCl and 90 min elution at room temperature as the elution condition for this adsorbent recycling study.

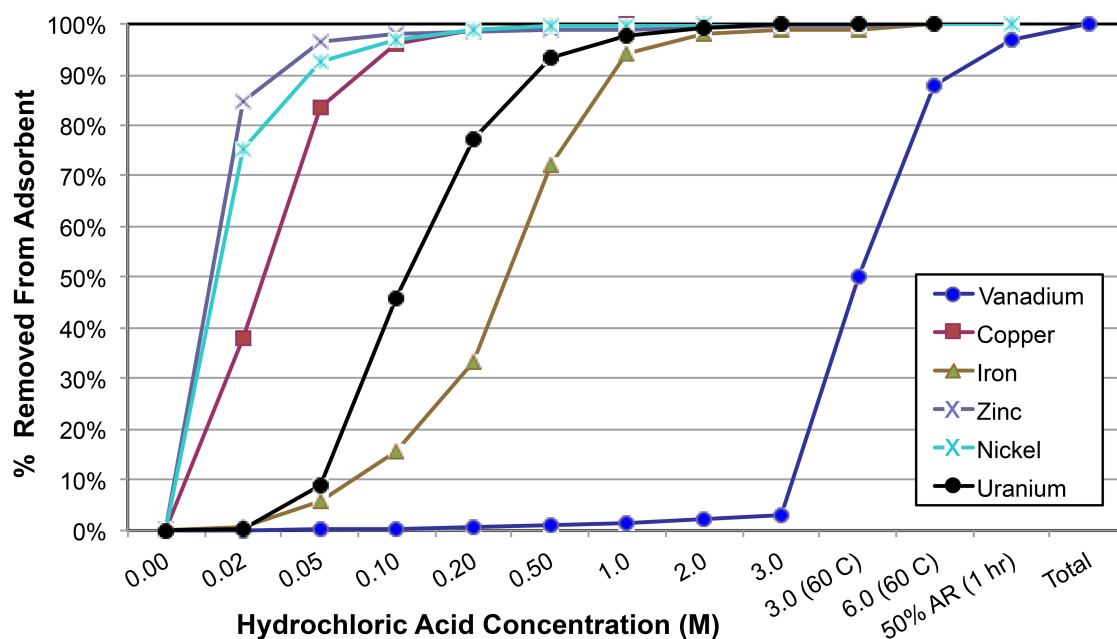


Figure 1. Elution of uranium and transition metals from the ORNL-AF1 adsorbent after seawater exposure using HCl with different concentrations at room temperature (21°C) for 90 minutes.

The ORNL-AF1 adsorbent used for this study had a uranium adsorption capacity of about 3.7 g U/kg adsorbent after 42 days of exposure to seawater in the PNNL-MSL flume system at 20 °C (Figure 2). After the acid elution (0.5 M HCl) and the KOH conditioning process, the uranium adsorption capacity of the recycled adsorbent dropped drastically to about 0.5 g U/ kg adsorbent after 42 days in the seawater flume test. The exact reason of this large drop in uranium adsorption capacity is not known, probably due to a combination of factors during the elution and reconditioning process causing physical and chemical changes to the material.

Spectroscopic techniques (FTIR and SEM) were used to characterize the initial and the recycled adsorbent. The results of FTIR and SEM study support the contention of chemical/physical changes to the adsorbent. About a 20% decrease in amidoxime groups was observed after HCl elution and KOH reconditioning of the adsorbent based on the decrease in the intensity of the -NO stretching peak at 928 cm^{-1} (Figure 3). An increase in the intensity of the carboxylate stretching (-COO^-) at 1559 cm^{-1} was also observed. Conversion of single amidoxime molecules to carboxylic acid molecules in highly acidic or alkaline solutions is known in the literature.⁶ Our study on the effect of KOH conditioning on ORNL-AF1 high-surface-area fiber adsorbent has revealed that KOH conditioning can convert the amidoxime groups to carboxylate groups attached to the fiber and the conversion increases with the conditioning time (Figure 4).

Physical damage to the fiber structure was also observed from SEM images obtained from the KOH conditioned adsorbent fibers. The KOH conditioning study was published in a paper entitled “Towards Understanding KOH Conditioning of Amidoxime-based Polymer Adsorbents for Sequestering Uranium from Seawater” in 2015, listed at the end of the report.

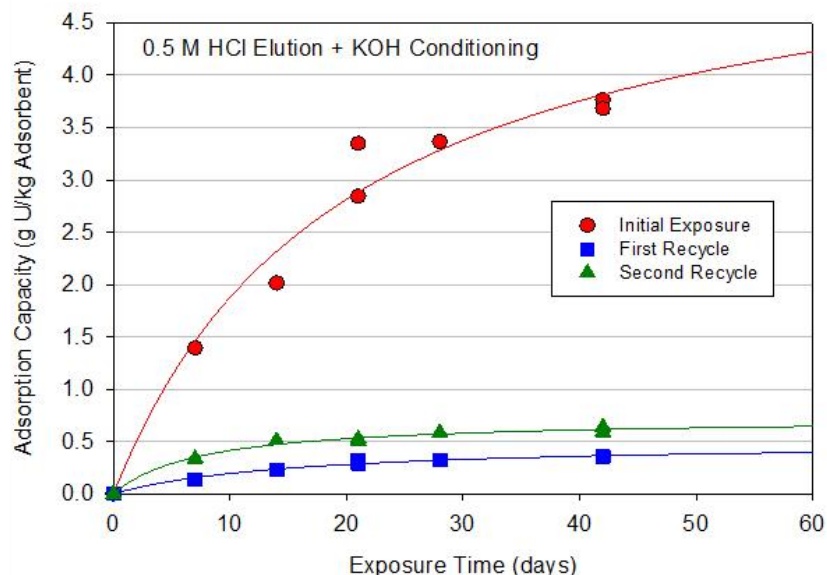


Figure 2. Time-dependent uranium adsorption capacity of initial ORNL-AF1 braid adsorbent and the recycled adsorbent using 0.5 M HCl leaching followed by KOH reconditioning. All data are normalized to a salinity of 35 psu.

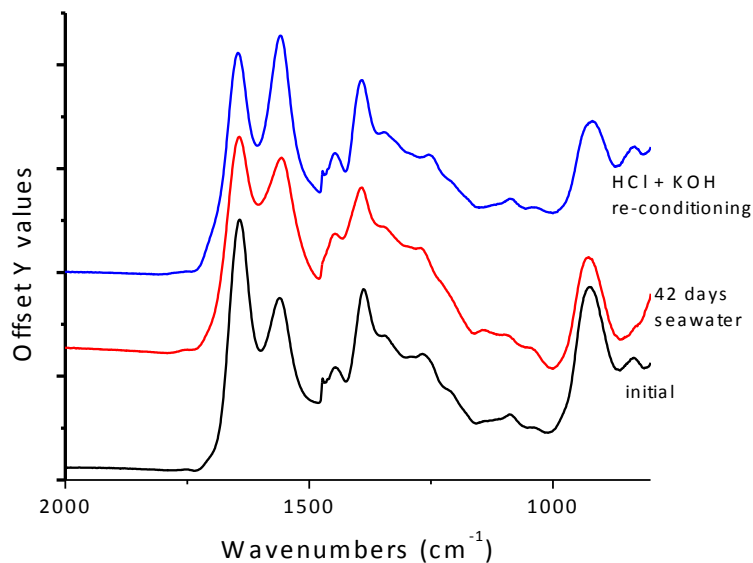


Figure 3. FTIR spectra of the ORNL-AF1 braid adsorbents by HCl elution + KOH reconditioning in the region 800–2000 cm^{-1} . The spectra are normalized to the $-\text{CH}_2-$ asymmetrical stretching peak at 2918 cm^{-1} .

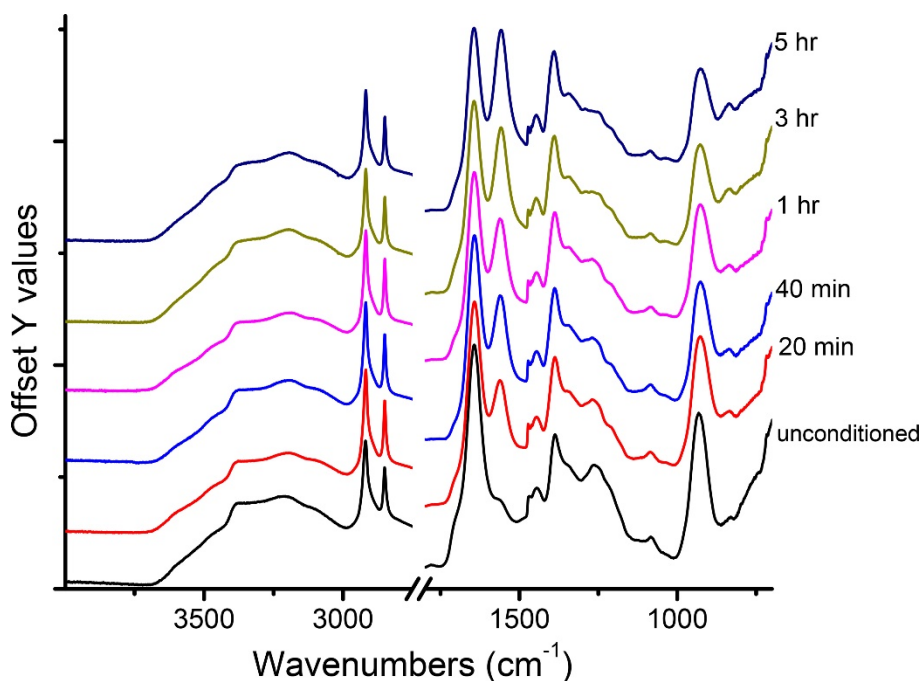


Figure 4. FTIR spectra of the ORNL-AF1 adsorbent before (unconditioned) and after KOH conditioning at 80 °C for different times from 20 minutes to 5 hours. (Note: There is no

characteristic adsorption band between 2750 and 1800 cm^{-1} . The spectra are normalized to the $-\text{CH}_2-$ asymmetrical stretching peak at 2918 cm^{-1} .)

2. Sodium Carbonate-Hydrogen Peroxide Elution

This elution method was developed based on the fact that uranyl forms a very stable uranyl-peroxo-carbonato complex in carbonate solutions containing hydrogen peroxide.⁷ The apparent formation constant of $[\text{UO}_2(\text{O}_2)(\text{CO}_3)_2]^{4-}$ from $[\text{UO}_2(\text{CO}_3)_3]^{4-}$ is about 5×10^4 according to the following equation

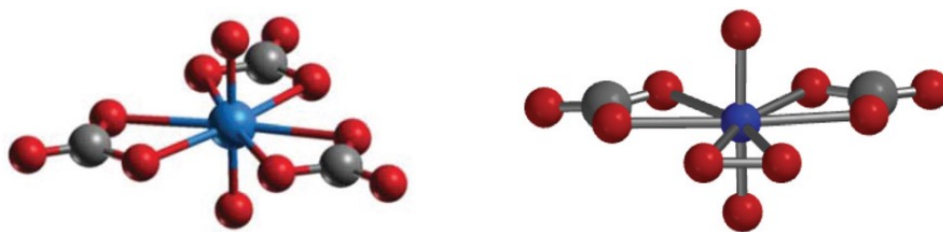


Figure 5. Structures of $[\text{UO}_2(\text{CO}_3)_3]^{4-}$ (left) and $[\text{UO}_2(\text{O}_2)(\text{CO}_3)_2]^{4-}$ (right)

In the process of developing the elution method in the laboratory using a simulated seawater, we observed that >95% of the uranium adsorbed on ORNL-AF1 can be eluted using a 1 M Na_2CO_3 and 0.1 M H_2O_2 solution at room temperature in 30 minutes or less of elution time. The pH of the Na_2CO_3 - H_2O_2 elution under the specified conditions is about 10.4. No KOH reconditioning is necessary for reuse of the adsorbent. The uranium adsorption capacity of the recycled adsorbent decreased by about 3% per cycle after 5 repeated cycles. The carbonate-hydrogen peroxide elution method was published in a paper entitled “Carbonate- H_2O_2 Leaching for Sequestering Uranium from Seawater” in 2014.

In real seawater experiments, elution of uranium from the amidoxime-based adsorbent ORNL-AF1 is much slower relative to the simulated seawater experiments. About 85% of the uranium can be stripped from real-seawater exposed adsorbent using 1 M Na_2CO_3 and 0.1 M H_2O_2 after 4 hours at room temperature. The results given in Figure 6 was obtained from an elution experiment using 1 M Na_2CO_3 and 1 M H_2O_2 for 2 hours at room temperature. About 95% leaching of uranium from the adsorbent can be achieved. Some adsorbed iron (~25%) and vanadium (~38%) are co-eluted with uranium in the Na_2CO_3 - H_2O_2 elution process. Nickel, copper, manganese, and cobalt cannot be eluted by the Na_2CO_3 - H_2O_2 elution method.

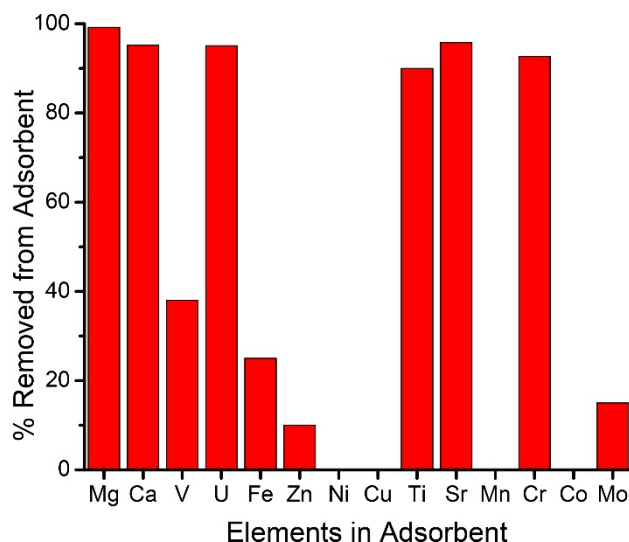


Figure 6. Removal of several elements from the ORNL-AF1 adsorbent using 1 M Na_2CO_3 and 1 M H_2O_2 elution for 2 hours at room temperature.

The adsorbent requires only water rinse for its reuse and no KOH reconditioning is needed. A summary of the time-dependent measurements of uranium sorption on the ORNL-AF1 adsorbent recycled by 1 M Na_2CO_3 and 1 M H_2O_2 leaching is shown in Figure 7. The uranium adsorption capacity of the first re-used and second re-used adsorbent are 62% and 40%, respectively. The reduction in the uranium adsorption capacity of the recycled adsorbent is not well understood.

The FTIR spectra of the initial ORNL-AF1 adsorbent, after its exposure to seawater for 28 days, and after the Na_2CO_3 – H_2O_2 elution are given in Figure 8. A decrease in the intensity of the –NO stretching peak I_{928} is observed after 28 days of seawater exposure. A further decrease in the –NO stretching peak intensity is also observed after the Na_2CO_3 – H_2O_2 elution as shown in Figure 8. The FTIR spectra appears to suggest that just seawater exposure may cause a reduction of the amidoxime groups in the fiber. Whether this seawater caused reduction in amidoxime groups may contribute to the uranium adsorption capacity of the adsorbent is unknown and deserves further investigation.

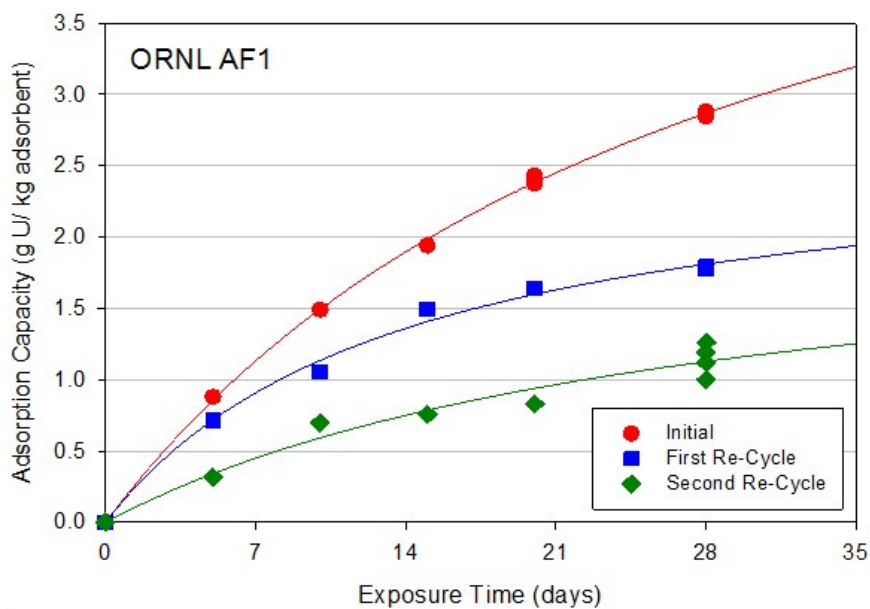


Figure 7. Time-dependent measurements of uranium adsorption capacity of ORNL-AF1 braid adsorbent recycled using 1 M Na_2CO_3 and 1 M H_2O_2 leaching. All data were normalized to a salinity of 35 psu.

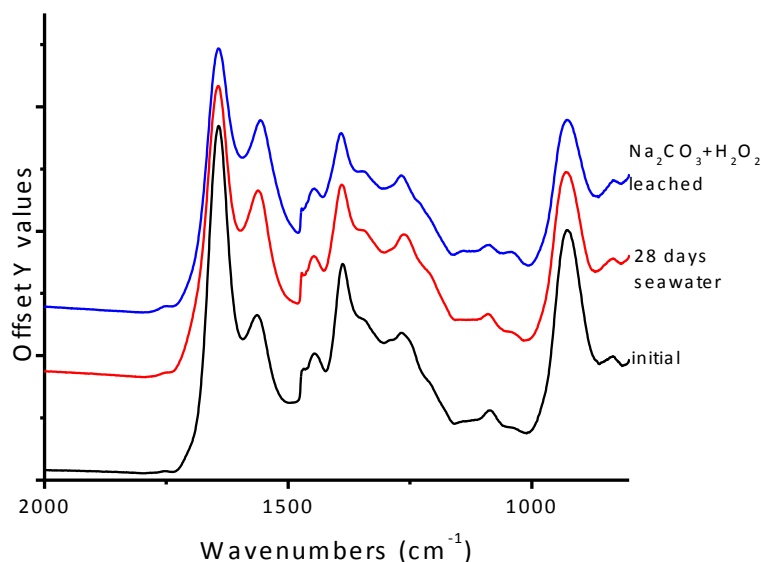


Figure 8. FTIR spectra in the region 800–2000 cm^{-1} of the ORNL-AF1 braid adsorbents eluted by the Na_2CO_3 – H_2O_2 method. The spectra are normalized to the $-\text{CH}_2-$ asymmetrical stretching peak at 2918 cm^{-1} .

3. Potassium Bicarbonate Elution

The idea of eluting uranium from the amidoxime-based adsorbents with potassium bicarbonate solutions is based on the fact that the uranyl tris-carbonato complex is a very stable species in water. Based on the thermodynamic data of uranyl complexes with single molecule

glutarimidedioxime (H_2A) reported in the literature^{8, 9}, we performed thermodynamic equilibrium calculations to evaluate the distribution of uranyl species in bicarbonate solutions of different concentrations. At a low bicarbonate concentration (2.3×10^{-3} M) in the pH range 7–9, the uranyl ion is predominantly bound to amidoxime molecules in the form $UO_2(HA)A^-$ and the concentration of $UO_2(CO_3)_3^{4-}$ is <1% (Figure 9). The calculation supports the fact that adsorption of uranyl to amidoxime-based adsorbent occurs spontaneously in seawater. At high bicarbonate concentrations (1–3 M), uranyl tris-carbonato species becomes predominant in the system (Figure 10) suggesting elution of adsorbed uranium from amidoxime-based adsorbents is thermodynamically feasible.

Figure 10 shows the distribution ratio of $UO_2(CO_3)_3^{4-}$ over $UO_2(HA)A^-$ species in 1 M bicarbonate solution is about 4:1 at pH around 8. The pH of 1 M bicarbonate solution is about 8.2 and increasing bicarbonate concentration does not change the solution pH much because it is a buffer system. Further increase in bicarbonate concentration to 3M (pH 8.3) would result in a distribution ratio of $UO_2(CO_3)_3^{4-}/UO_2(HA)A^-$ greater than 100 suggesting near total elution of uranium from the adsorbent as uranyl tris-carbonato complex in the bicarbonate solution is thermodynamically possible. According to equation (2), the ratio of $UO_2(CO_3)_3^{4-}/UO_2(HA)A^-$ varies with the third power of bicarbonate concentration as shown by the following equation

$$[UO_2(CO_3)_3^{4-}]/[UO_2(HA)A^-] = [HCO_3^-]^3/K[H_2A]^2 \quad (2)$$

where K is the equilibrium constant of the reaction. According to equation (2), raising bicarbonate concentration triple-fold would increase the $[UO_2(CO_3)_3^{4-}]/[UO_2(HA)A^-]$ ratio by a factor 27 which appears consistent with the experimental data.

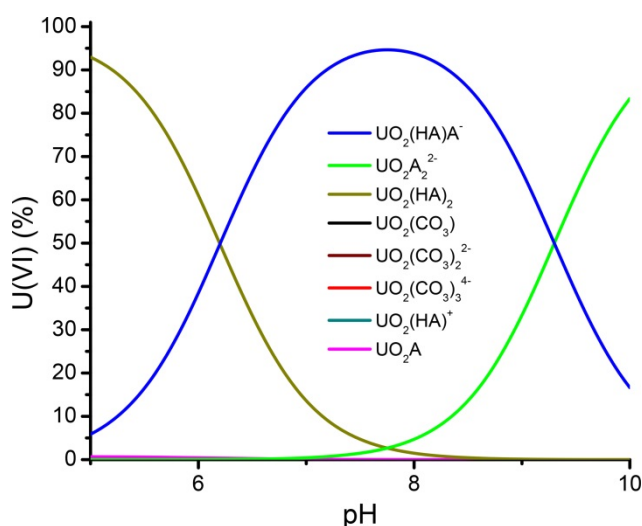


Figure 9. Distribution of uranyl species in water with uranium (9 ppm), carbonate (2.3×10^{-3} M), and single molecule glutarimidedioxime (H_2A , 0.504 M)

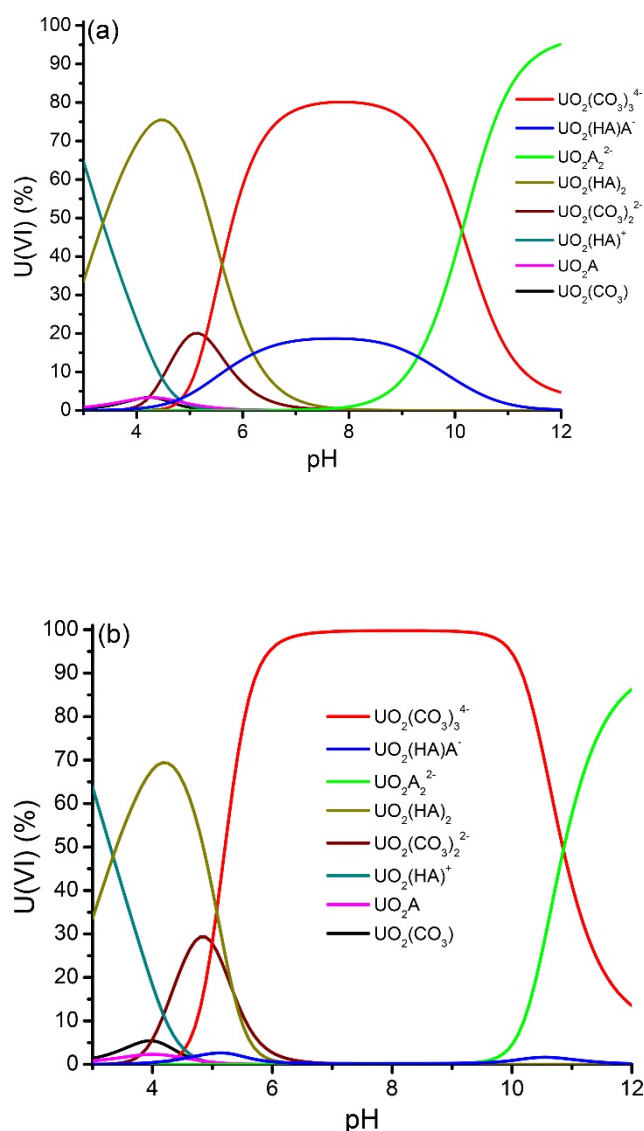


Figure 10. Distribution of uranyl species in water with uranium (0.252 M), single molecule glutarimidedioxime (H_2A , 0.504 M), and carbonate ((a) 1 M and (b) 3M)

Figure 11 shows the experimental results of leaching uranium from amidoxime-based polymer adsorbent using potassium bicarbonate solutions at different temperatures. Loading of uranium was performed using simulated seawater as described in a previous paper. Using 1 M potassium bicarbonate, about 83% of adsorbed uranium can be leached from the amidoxime-based adsorbent at room temperature (21 °C). In 3 M bicarbonate solution, about 92% of uranium can be eluted from the adsorbent at room temperature. Raising temperature to 40 °C would increase elution of uranium to about 88% by 1 M bicarbonate solution. Near total elution of uranium can be achieved with 3 M potassium bicarbonate at 40 °C within one hour. After the elution, the adsorbent is rinsed with water and can be reused for uranium adsorption again. In

simulated seawater experiments, the potassium bicarbonate elution method does not cause reduction of uranium adsorption capacity of the ORNL-AF1 adsorbent for 6 repeated cycles.

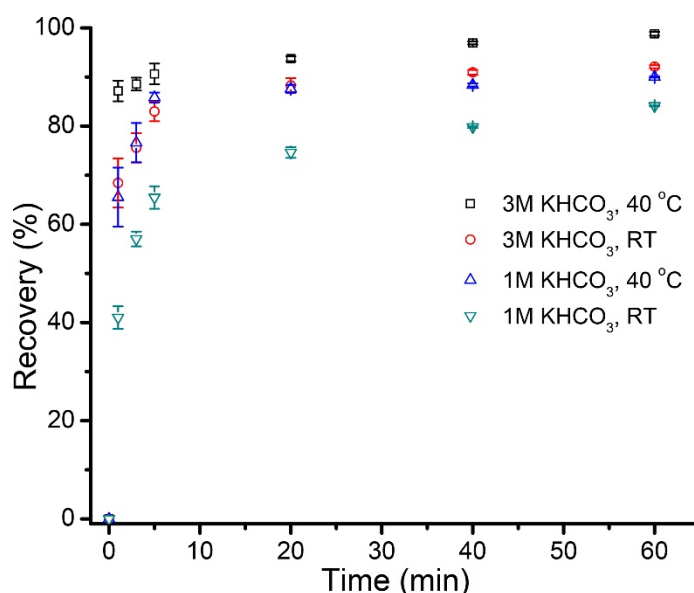


Figure 11. Rate of elution of uranium from ORNL-AF1 using different concentrations of KHCO_3 solution and at different temperatures.

In real seawater experiments, other factors including adsorption of natural organic matter (NOM) can also affect the uranium adsorption capacity of the recycled adsorbent. NOM adsorbed on the surface of the adsorbent could change the rate of uranium adsorption in seawater and thus affect the adsorption capacity of the reused adsorbent. After several weeks of real seawater exposure, the ORNL-AF1 adsorbents typically exhibit a dark brown color, which is not observed in the simulated seawater experiments. Neither bicarbonate elution nor HCl leaching can remove the dark color. However, an alkaline solution soaking (e.g. 0.5 M NaOH) at room temperature can reduce the color of the seawater exposed braid sample from dark brown to light brown. Since NOM such as humic substances can be dissolved in alkaline solution, the observation provides a line of evidence that NOM adsorbs on the adsorbent in real seawater experiments.

The bicarbonate elution method was thus modified to add a NaOH soaking step to remove NOM from the adsorbent. The seawater-exposed adsorbent was treated first by the bicarbonate elution method to strip off uranium followed by a NaOH soaking (0.5 M, at room temperature for 3 hours) to remove NOM from the adsorbent. The uranium adsorption capacity of the initial ORNL-AI8 braid adsorbent was 2.87 ± 0.12 g U/kg adsorbent and that of the re-used adsorbent was 2.89 ± 0.10 g U/kg adsorbent after 28 days of exposure in natural seawater as shown in Figure 12. The uranium adsorption capacity of the recycled adsorbent remained virtually unchanged (Figure 12). Without the NaOH treatment, the recycled adsorbent with only

KHCO_3 elution showed about 45% reduction in uranium adsorption capacity in the seawater exposure experiment.

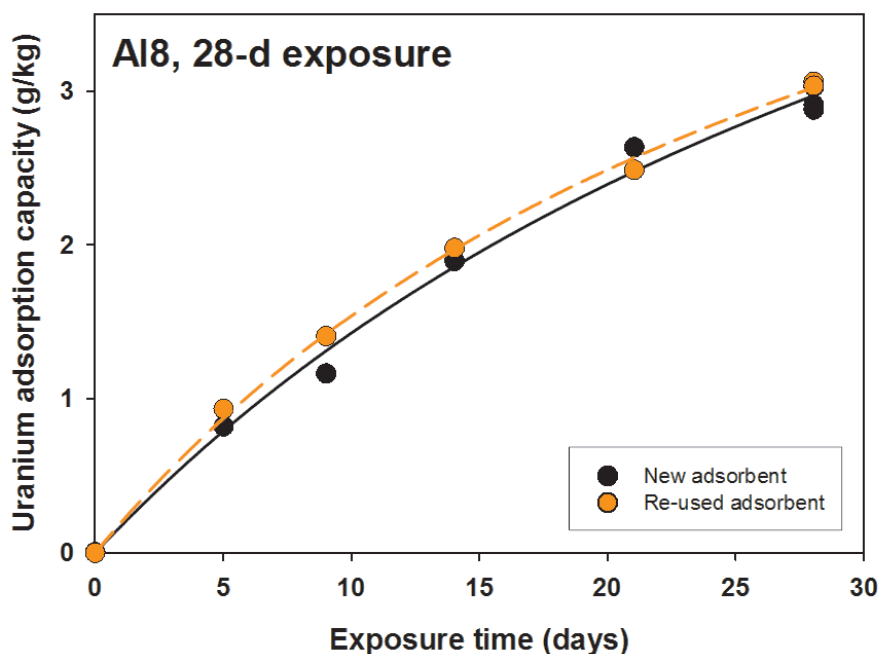


Figure 12. Comparison of rate of uranium adsorption by ORNL-AI8 polymeric braid adsorbent between the initial seawater exposure and first re-exposure after bicarbonate leaching. Seawater exposure was conducted at 20 °C for 28 days in a recirculating flume using Sequim Bay seawater.

The bicarbonate elution method also removes fractions of other metals including vanadium and iron from the seawater exposed adsorbent. In general, the KHCO_3 elution is more selective for removing U relative to transition metals from the adsorbent. About 88% of the uranium was recovered from the adsorbent under the specified elution conditions. Acid leaching (0.5 M HCl) is known to remove a significant portion of most elements, except vanadium but reusability of the adsorbent is a problem.

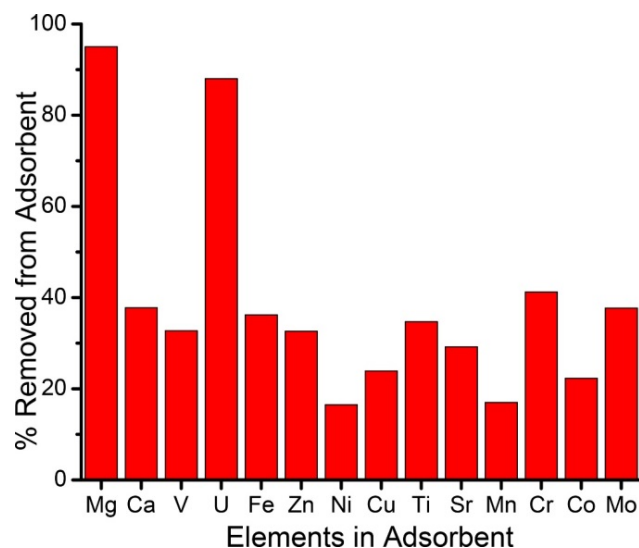


Figure 13. Amounts of uranium and other metals eluted from the ORNL AI-8 amidoxime-based polymeric braid adsorbent by 3 M KHCO_3 at 40°C for 24 hours. The adsorbent was exposed to seawater in a flume system at 20 °C for 42 days.

Potassium bicarbonate elution occurs at pH around 8.3, which is close to the pH of seawater and consequently causes minimal damage to the adsorbent. The FTIR spectra (Figure 14) indicate that after the KHCO_3 –NaOH coupled elution, both the 1643 and the 928 cm^{-1} band intensities remain unchanged, suggesting that the KHCO_3 –NaOH treatment would not alter the amidoxime groups present in the adsorbent.

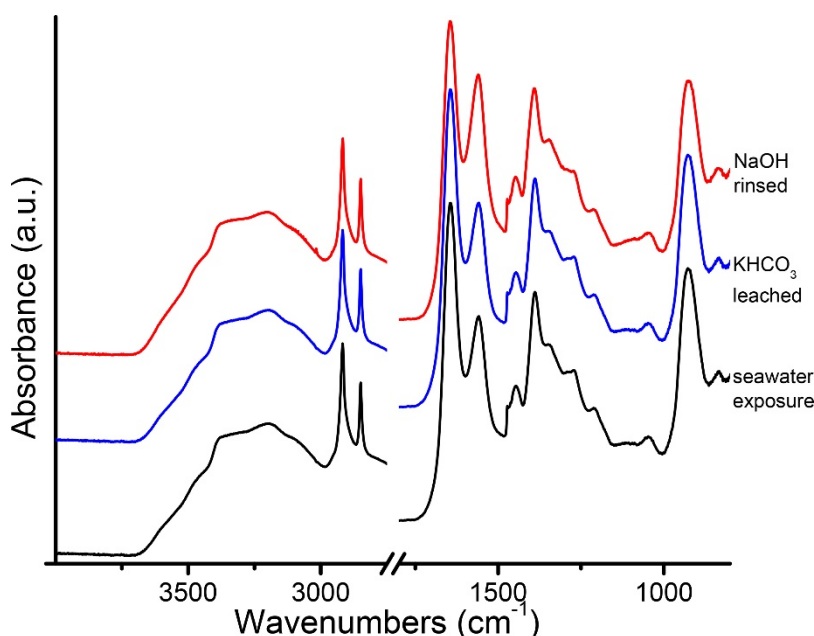


Figure 14. FTIR spectra of the ORNL amidoxime-based polymer adsorbent after 42 days seawater exposure, 3 M KHCO_3 elution at 40 °C for 24 hours, and followed by a NaOH soaking (0.5 M, at room temperature for 3 hours). (Note: The spectra were normalized to the $-\text{CH}_2-$

asymmetrical stretching peak at 2918 cm^{-1} . There is no characteristic adsorption band between 2750 and 1800 cm^{-1} .)

After the first re-use, the uranium adsorption capacity started to decrease with subsequent re-use (Figure 15). This observation is puzzling. It appears to suggest that the ORNL-AI8 fiber material is probably not stable over long term exposure to seawater. In a separate experiment, we took weekly FTIR spectrum of an ORNL-AF1 braid sample exposed to seawater over a period of 8 weeks in the same flume system. The changes in FTIR spectra over the 8 week period are shown in Figure 16. The FTIR spectra clearly show that the 928 cm^{-1} peak (N–O stretching) and the 1643 cm^{-1} peak (C=N stretching) become smaller over time while the 1559 cm^{-1} peak ($-\text{COO}^-$ stretching) increases with time. The decrease in peak intensity of the N–O stretching and the increase in peak intensity of the COO^- stretching of the fiber suggest possible conversion of amidoxime to carboxylate groups during its exposure to seawater. This change of peak intensity is not observed in the bicarbonate elution process shown in Figure 14. The stability of fiber material during long term exposure in seawater is a separate issue which deserves further investigation.

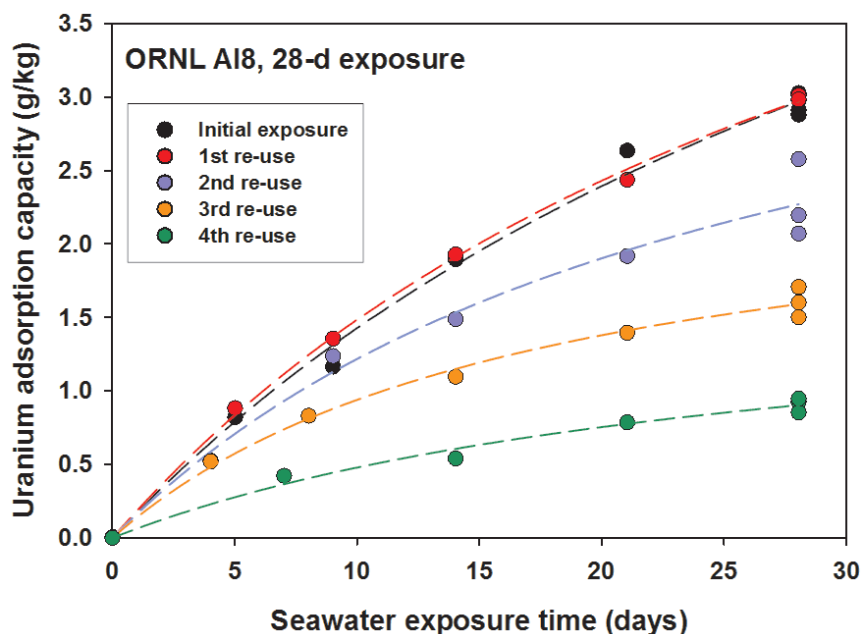


Figure 15. Uranium adsorption rates of the ORNL-AI8 braid adsorbent for 5 repeated use using the bicarbonate elution method. All data are normalized to a salinity of 35.

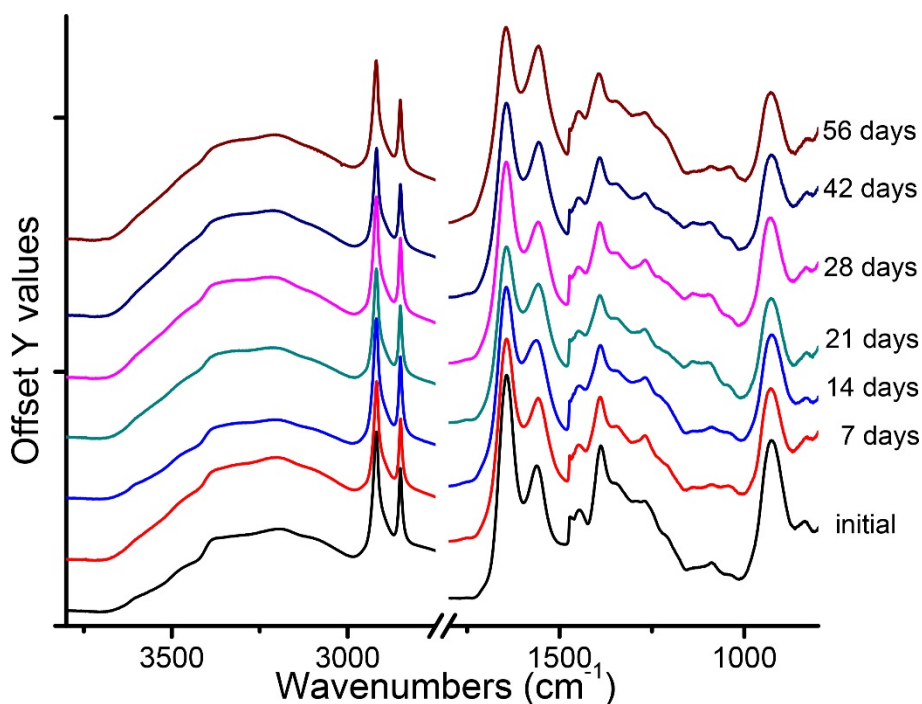


Figure 16. Changes in FTIR spectrum of an ORNL-AF1 braid adsorbent over a period of 56 days of exposure to seawater in a recirculating flume system at 20 °C. The spectra were normalized to the $-\text{CH}_2-$ asymmetrical stretching peak at 2918 cm^{-1} . There is no characteristic adsorption band between 2750 and 1800 cm^{-1} .

Conclusions

Our FTIR results indicated that the KOH conditioning (2.5% KOH at 80 °C for 3 hours) did cause conversion of amidoxime to carboxylate groups attached to the polymer adsorbent. In addition, some physical damage to the polymer structure was also observed by SEM (Scanning Electron Microscope) after the KOH conditioning. The consequence of this harsh KOH treatment was a reduction of the uranium adsorption capacity of ORNL-AF1 in real seawater flume experiments. The damaging effect of KOH conditioning may be minimized using milder conditions such as lower temperature or shorter reaction time. However, if uranium elution is not performed in acid solution, the KOH reconditioning step may not be necessary for reusing the adsorbent.

Two non-acid elution methods have been developed by the project for elution of uranium from ORNL-AF1. Both elution methods do not require KOH conditioning for reusing the adsorbent. One method uses a mixture of sodium carbonate and hydrogen peroxide solution as eluent, removing uranium from the adsorbent to form a very stable uranyl-peroxo-carbonato complex in the leaching solution. The second method uses a high concentration (3M) potassium bicarbonate solution to remove uranium from the adsorbent to form uranyl tris-carbonato complex in the bicarbonate solution. This process can be considered as the reverse reaction of the uranium adsorption process because of the high concentration of bicarbonate used in the

solution. Thermodynamic calculations based on the known formation constants of uranyl tris-carbonato and uranyl amidoxime complexes were performed and the predictions are consistent with the experimental observation. The potassium bicarbonate elution occurs at a pH close to the pH of seawater and consequently causes minimal damage to the adsorbent.

Publications Derived from the Project

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Acknowledgements

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