Uranium Recovery from Seawater using Amidoxime-based Braided Polymers Synthesized from Acrylic Fibers

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Abstract

Global demand for nuclear energy is expected to rise in the coming decades. To meet these growing needs, new uranium resources must be explored. One of the potential alternatives to traditional uranium mining is oceanic uranium. The capture and recovery of uranium from the ocean has been under investigation for some time, with many recent studies focused on amidoxime-based adsorbents. These adsorbents, while able to achieve high uranium recovery capacities are, nevertheless, expensive to produce and adsorb a significant amount of hard to remove vanadium. The purpose of this study is to evaluate the adsorption performance of amidoxime-based polymer braids synthesized from acrylic fibers that are designed to significantly cut polymer synthesis and conditioning costs. Adsorption experiments were performed in a meso-scale recirculating raceway flume system at environmental conditions, approximately 10.8^{o}C, with 40-micron prefiltered seawater over 28 days for small and large sized polymer braids. For both braid sizes, the adsorption of vanadium was far lower on the acrylic adsorbent considered in the present study than on previously tested adsorbents developed at Oak Ridge National Laboratory (ORNL AF1 and AI8). The small acrylic braids also outperformed both ORNL materials with respect to uranium adsorption under similar conditions. Adsorption modeling was used to simulate the performance at higher temperatures based on 20^{o}C experiments previously performed with these materials. Simulation results indicated that the small acrylic braids would have a somewhat less significant advantage with respect to uranium adsorption over both ORNL AF1 and AI8 at 20^{o}C and will continue to outperform both ORNL adsorbents at 31^{o}C. Vanadium adsorption on the small acrylic braids was less than one third of the vanadium adsorption on either AF1 or AI8 for all temperatures. This behavior indicates that the newly developed acrylic adsorbents are able to achieve superior uranium

adsorption compared to other amidoxime adsorbents previously developed, while being cheaper to produce and adsorbing significantly less vanadium.

1. Introduction

The global energy generating capacity of nuclear power is expected to increase by as much as 45% over the next fifteen years.[1] If this growing demand were to be sustained entirely using conventional nuclear fuel resource then roughly 20% of the world's identified uranium reserves that can be extracted for less than $260 per kg would be consumed by 2035.[1] This would include a large majority, if not all, of the uranium that can be obtained from existing and planned mines. As a result, global uranium mining would need to be continually expanded over the coming decades to ensure an adequate supply of fuel resources for nuclear energy. The expansion of uranium mining is, however, quite problematic given the long term potential for such operations to contaminate the surrounding environment with various heavy metals and radionuclides.[2,3] These environmental concerns, alongside potential political resistance to new mines and the steady exhaustion of easily accessible uranium ores, will lead to instability in the uranium market long before the world's known reserves are depleted. As such, the development of technologies that can extend the usable lifetime of existing nuclear fuels or the exploration of alternative nuclear fuel sources will be essential to ensuring the long term sustainability of nuclear energy. One potential alternative to traditional uranium mining as a resource of nuclear fuel is the uranium dissolved in the world's oceans. The oceanic reserve of uranium is more than 500 times larger than all known terrestrial uranium resources with an approximate mass of 4.5 billion metric tons.[4] This vast reserve could meet global uranium demand for well over a millennium without many of the environmental impacts associated with terrestrial uranium

mining. Nevertheless, uranium is distributed throughout the world's oceans at a low average concentration of approximately 3.3 ppb.[4] This concentration level makes the recovery of oceanic uranium a particularly challenging task requiring the techniques used to be both highly selective and relatively inexpensive.

The recovery of uranium from seawater has been an area of interest since at least the early 1950s. Numerous materials have been examined during the nearly seven decades long period since then, though amidoxime based adsorbents are currently considered the most promising.[4] Development of amidoxime based adsorbents for uranium recovery from seawater began in Japan during the early 1980s. These early studies led to a number of marine tests during the 1990s and early 2000s.[5-7] Marine testing of amidoxime materials during this period culminated in the work of Seko and coworkers, who were able to recover 1 kg of uranium, with a capacity of 2.85 mg/g adsorbent, using a passive adsorbent system deployed for 240 days.[8] In the United States, the US Department of Energy has sponsored research into the recovery of uranium from seawater since 2010.[9] Through this program Oak Ridge National Laboratory (ORNL) has continued to develop amidoxime based adsorbents significantly improving upon earlier Japanese designs.[10,11] Other recent studies in this area have also examined amidoxime based materials not derived from the designs previously studied by the Japanese.[12-14] Despite these capacity improvements and considerable reductions in recovery costs relative to the Japanese adsorbents, the cost of uranium recovery with these materials remains too high for the process to be commercially viable.[15] Adsorbent deployment is also an area of concern not only from the cost perspective but also with respect to natural complications, such as biofouling, which can significantly reduce adsorption capacity.[16,17] Attempts have been made to reduce deployment costs by incorporating adsorbent systems into existing infrastructure such as off-shore wind

turbines.[18,19] Deployment costs, however, only represent about 30% of the total cost of uranium recovery, meaning that cost savings in this area alone will not be sufficient to make the recovery of uranium from seawater commercially viable.[15] Thus we must also seek other means to reduce overall the cost of uranium recovery.

The remaining costs arise from the front-end costs of adsorbent production and the back-end costs associated with elution of the adsorbent, adsorbent regeneration, waste treatment, and the disposal of spent adsorbent material. Adsorbent production at the front end and the various costs at the back end represent about 33% and 37% of the total uranium recovery cost, respectively.[15] Additionally, the costs associated with alkaline treatment of the adsorbent, which is necessary at the front end for initial adsorbent conditioning and at the back end for adsorbent regeneration, represent most of the back-end and a notable portion of the front-end costs. ORNL's adsorbents are synthesized using radiation induced graft polymerization to attach amidoxime polymers to a polyethylene backbone and undergo alkaline treatment with potassium hydroxide.[20,21] Radiation induced graft polymerization is a highly controllable technique for producing sorbent materials that allows for precise tuning of adsorbent synthesis to maximize performance, however, its complexity greatly increase synthesis costs. Alternatives to potassium hydroxide have also been considered. One such alternative is sodium hydroxide (NaOH) which can reduce the total cost of uranium recovery by as much as 30% when used in place of potassium hydroxide.[15] The acrylic fiber based amidoxime adsorbent, termed the LCW adsorbent, considered in this study is intended to substantially reduce both the cost of alkaline treatment and that of adsorbent synthesis, while also increasing the durability of the adsorbent. This is achieved through simplified adsorbent synthesis based on the amidoximation of commercially available acrylic fibers and the use of NaOH for alkaline treatment. The

performance of these LCW adsorbents has not yet been examined extensively, thus the goal of this study is to assess the viability of these adsorbents for uranium recovery from seawater. Adsorption experiments were performed with ambient seawater at a temperature of 10.8 ± 0.7°C using braided LCW materials in a meso-scale raceway system (total volume of 0.9 m^3) to more realistically reflect deployment conditions. Such testing has rarely been used for performance evaluation of uranium adsorbents in the literature. Kinetic adsorption modeling is also performed to predict the adsorption loadings for relatively long-term seawater deployment (56 days) at temperatures up to 31°C. These performance simulations are then compared to ORNL's AF1[20] and AI8[21] adsorbents synthesized using radiation induced graft polymerization with itaconic acid (amidoxime/itaconic acid molar ratio of 7.57) and vinylphosphonic acid (amidoxime/vinylphosphonic acid molar ratio of 3.21) comonomers, respectively.

2. Methodology

2.1 Experimental Methodology

Adsorption experiments were conducted over a 28-day period using ambient seawater with an average temperature of 10.8±0.7°C in the meso-scale raceway system (MicroBio Engineering Inc, San Luis Obispo, CA, USA) shown in Figure 1 with additional images provided in Figure 2. The temperature of incoming seawater was not controlled as we have done in many of our experiments examining the amidoxime adsorbents developed at ORNL.[20-23] The system has a total volume of 0.9 m^3 and an average linear velocity in the raceway of 8.0 cm/s though given the nature of our system it is not likely to be uniform at all points in the raceway. This average velocity was chosen based on the work of Ladshaw and coworkers who determined that the velocity necessary to overcome external-mass transfer limitations to adsorption lies between

5.52 and 8.24 cm/s which is easily achievable in nature.[23] Thus, by maintaining an average flow velocity in the raceway on the upper end of that range, the adsorption of uranium and other metals will primarily be driven by the kinetics of the adsorption reaction and the effects of non-uniform flow in the raceway will be mitigated. The influent flow rate of fresh seawater entering the raceway was controlled to 3.6 m^3/hr. Ambient seawater was drawn by pump from Sequim Bay, WA, at a depth of ~10 m through a plastic pipe. Raw seawater was roughly filtered using an Arkal Spin Klin™ filter system (nominal pore size 40 μm) to remove large particles. The seawater pH in the flume was monitored daily using a VWR Scientific portable pH probe equipped with a temperature compensating glass electrode that was calibrated using National Institute of Standards and Technology (NIST) traceable buffers. Salinity in the flume was also measured on a daily basis using a YSI model Pro30 instrument. Both salinity and pH remained relatively constant during the experimental period, with values of 30.5±0.3 psu and 8.07±0.03, respectively.

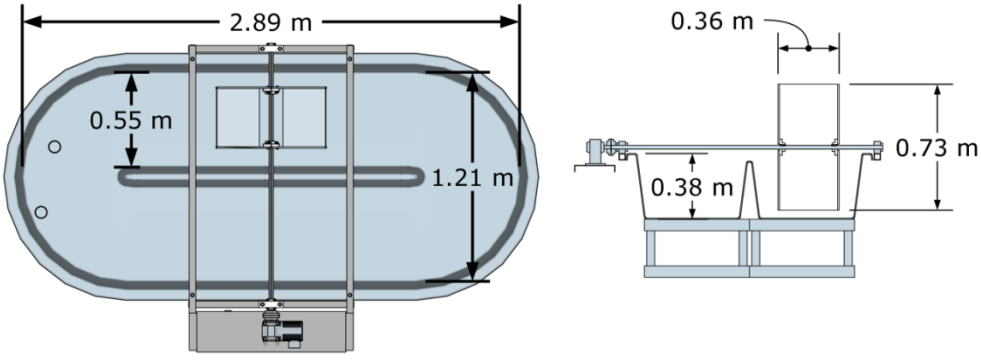

Figure 1. Schematic of recirculating flume system used in adsorption experiments (the schematic is a courtesy from the MicroBio Engineering Inc). This setup was operated at environmental conditions, at an average temperature of 10.8°C with 40-micron pre-filtered seawater, to more realistically simulate field deployment conditions.

The braided LCW adsorbent was synthesized from textile grade acrylic fibers purchased from Kaltex consisting of 92% acrylonitrile and 8% methyl acrylate by weight. Amidoximation of the acrylonitrile monomers was carried out using a 3.0 w.t. % hydroxylamine solution made in a 1:1 by volume methanol-water mixture first at room temperature for one hr and then at 70ºC for 45 min. After amidoximation, the fiber was conditioned using a 1.0 M NaOH solution at room temperature for 24 hr. Fibers were rinsed with DI water several times at room temperature both before and after alkaline conditioning. The final composition of the LCW adsorbent is approximately 10% by weight acrylonitrile with the remainder split evenly between amidoxime and carboxylate yielding an amidoxime/carboxylate molar ratio of 0.83. These prepared fibers were then braided into large and small sized adsorbent braids with masses of 60 g and 10 g per braid, respectively (Figure 2). Additional details regarding adsorbent synthesis can be found in the work of Pan and coworkers.[24]

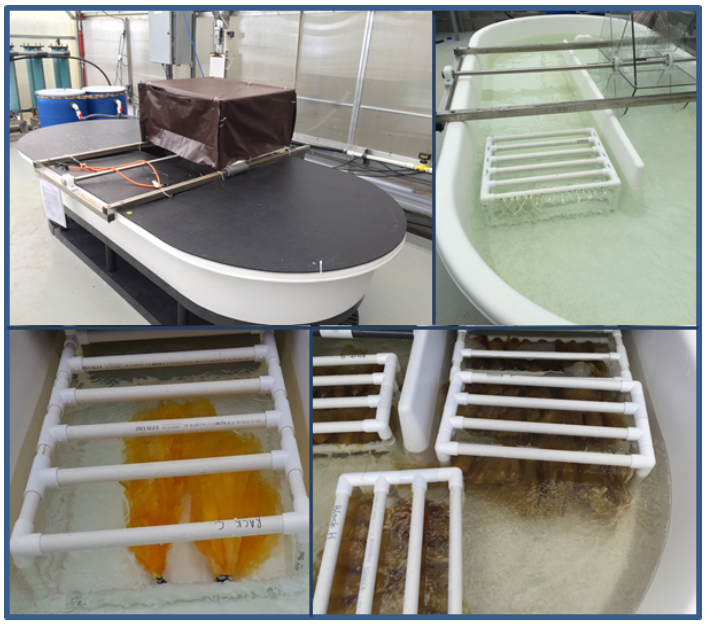

Figure 2. Covered (top left) and uncovered (top right) recirculating raceway flume used in adsorption experiments. Lightly loaded LCW large braids and heavily loaded LCW small braids are shown in the images on the bottom left and bottom right, respectively.

To hold the adsorbent braids in place, a series of cages were used with the layout shown in Figure 3. Adsorbents were grouped by braid size with large braids in Cage C and small braids in all other cages. The total adsorbent mass was about 980 g with 800 g of small braids divided evenly between the eight cages containing small braids and 180 g of large braids all in Cage C. Adsorbent snips were collected weekly from the tips of each of the adsorbent braids in Cages B and C using titanium-coated scissors and analyzed to determine the average adsorbed mass of uranium and other metals. This was done to help further mitigate the potential effects of non-uniform flow in the raceway. Sample snips were not collected form any of the braids in the other six cages in the raceway. The purpose of these additional cages was to obtain a large quantity of seawater exposed LCW adsorbent for a separate experiment that is beyond the scope of this study. Snipped samples were first washed with DI water and then dried at 80^{o}C using a heating block overnight.

Dried adsorbent snips were then digested in 15 mL of Fisher Scientific Optima grade 50% aqua regia acid solution consisting of a 3:1 hydrochloric-nitric acid mixture for three hr at 85^{o}C. Analysis of the digestate was carried out using a PerkinElmer 7300 inductively coupled plasma optical emission spectrometer (ICP-OES) and quantified based on standard calibration curves. The aqueous concentrations of uranium and vanadium in the raceway and feed seawater were determined using inductively coupled plasma mass spectroscopy with the on-line pre-concentration method.[25] This method was carried out using an Elemental Scientific seaFAST S2^{TM} equipped with a seaFAST PFA chelation column packed with ethylenediaminetriacetic/iminodiacetic acid ion exchange resin. Analytes were eluted off the column using 10% nitric acid and then nebulized for analysis by a Thermo Scientific ICap Q inductively coupled plasma mass spectrometer (ICP-MS).

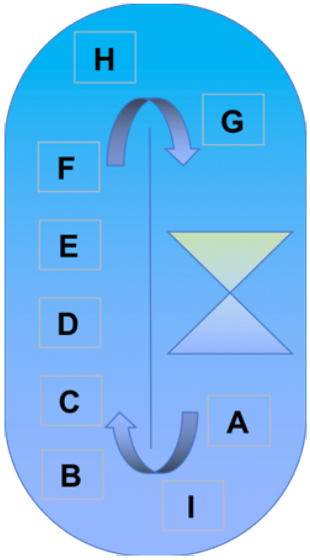

Figure 3. Schematic of the cages containing adsorbent braids in the raceway where Cage C contains three large braids (60 g per braid) and every other cage has 10 small braids (10 g per braid).

2.2 Modeling Methodology

The adsorption of uranium and other metals on amidoxime based fibers is primarily governed through adsorbent-adsorbate reaction kinetics and the various mechanisms of mass transfer including inter-particle, inter-phase, and intra-particle mass transfer.[26] At the average experimental linear velocity of about 8.0 cm/s, however, external mass-transfer limitations to adsorption are removed in the raceway flume and, as such, do not need to be considered.[23] To account for adsorption, all adsorbent-adsorbate reactions are assumed to proceed as reversible Langmuir type reactions (Equation 1) where C is the adsorbate concentration in the bulk phase, q is the adsorption capacity represented as mass adsorbed per mass of adsorbent, and L is the capacity still available for adsorption.

This available capacity L is in turn a function (Equation 2) of the theoretical maximum capacity (q_{max}) and q. Equations 1 and 2 can be combined to derive a kinetic expression for

adsorption (Equation 3) with forward and reverse reaction rate constants of k_f and k_r, respectively, which were determined iteratively from experimental results for small and large polymer braids. For the bulk phase, the system is treated as a series of perfectly mixed reactors defined by Equation 4. In this equation V is the reactor volume, M_a is adsorbent mass, C_j is the concentration of the j^{th} element in the reactor, Q_i is the i^{th} incoming flowrate, C_{ij} is the i^{th} influent concentration of the j^{th} element, Q_o the o^{th} outgoing flow, and q_j is the adsorbent mass of the j^{th} element. A series of 10 perfectly mixed reactors, corresponding to the nine adsorbent cages shown in Figure 3 and the section of the raceway where concentration is monitored, is considered when modeling is performed. The forward and reverse reaction rates and maximum adsorption capacity for uranium and vanadium are summarized in Table 1.

$$C + L \Leftrightarrow q \tag{1}$$

$$L = q_{\max} - q \tag{2}$$

$$\frac{\partial q}{\partial t} = k_f C q_{\max} - (k_f C + k_r) q \tag{3}$$

$$V \frac{\partial C_j}{\partial t} = \sum Q_i C_{ij} - \sum Q_o C_j - M_a \frac{\partial q_j}{\partial t} \tag{4}$$

Table 1. Forward (k_f) and reverse (k_r) reaction rate constants for uranium and vanadium and adsorbent max capacity (mol/kg adsorbent) for small (SB) and large (LB) LCW braids weighing 10 and 60 g, respectively, alongside ORNL's AF1 small braids.

		Uranium			**Vanadium**		
		SB	LB	AF1	SB	LB	AF1
k_f (m^3/mol/hr)	10.8°C	0.22	0.165	0.85	0.60	0.45	5.36
	20°C	0.81	0.608	1.65	1.30	0.975	5.56
	31°C	3.47	2.60	3.42	3.06	2.30	8.96
k_r (1/hr)	10.8°C	0.00129		0.00248	0.00171		0.000765
	20°C	0.00225		0.00213	0.00204		0.000752
	31°C	0.00418		0.00204	0.00248		0.000537

q_{max} (mol/kg)	5.23	1.47	5.23	1.47

3. Results and Discussion

After an exposure period of 28 days, at approximately 10.8°C, the salinity normalized uranium recovery rate for the small LCW braids in Cage B was 1.43 mg/g adsorbent while the large braids in Cage C had an uranium capacity of 1.17 mg/g adsorbent (Table 2). The disparity in uranium recovery between the small and large LCW braids can likely be attributed to complications arising from material scale-up. When tested by Pan and coworkers at 20°C, LCW braids of similar size and composition to the small adsorbent braids tested in this study attained a uranium adsorption capacity of 4.93 mg/g adsorbent over 28 days exposure to finely filtered (0.45 μm) seawater.[24] These results are, however, closer to the ideal adsorption performance since the aqueous concentration of trace metals in the experimental system used by Pan and coworkers is nearly constant. Thus, an estimate of the ideal capacity at 10.8°C can be made using the model previously described if a constant concentration is assumed. The predicted 28-day salinity normalized uranium adsorption capacity under ideal conditions is 2.05 mg/g adsorbent. As such, the disparity in uranium adsorption between data attained at 20°C and 10.8°C can largely be attributed to the effect of temperature. A similar effect has already been observed for the amidoxime based grafted fiber adsorbents developed at ORNL. In the case of ORNL's AF1 series adsorbent using 0.45 μm filtered Sequim Bay seawater, the salinity normalized 21-day recovery rate for small braids dropped from 2.5 mg U/g adsorbent at 20°C to 0.93 mg U/g adsorbent at 8°C.[22] For both AF1 and AI8 series adsorbents, cyclic amidoxime ligands are the primary sites for all trace metal adsorption.[27] The adsorption of aqueous uranium on these sites is highly endothermic and, as such, will increase alongside the ambient temperature.[22,28] Open-

chain amidoxime ligands are, however, the predominant site for adsorption on the LCW adsorbent.[21] Uranium adsorption on open-chain ligands is exothermic but this behavior can, nevertheless, be altered dramatically in the presence of certain comonomers.[28] Indeed, theoretical studies performed using density functional theory have indicated that uranyl ions may be adsorbed on mixed ligand complexes involving both open-chain amidoxime and carboxylate sites.[29,30] Further experimental characterization of the complexes formed on the LCW adsorbent is still needed, but it is expected that carboxylate plays some role in the adsorption of uranium.

Table 2. Concentration in feed seawater and salinity normalized 28-day adsorption capacities on small braids in Cage B (LCW-B) and Cage C large braids (LCW-C) for uranium, vanadium, iron, zinc, and copper.

	Concentration	**LCW-B**		**LCW-C**	
	nM	mg/g	µmol/g	mg/g	µmol/g
Uranium	12.8	1.43	6.01	1.17	4.92
Vanadium	36.2	1.90	37.25	1.26	24.71
Iron	545.3	1.86	33.21	1.71	30.54
Zinc	22.1	0.44	6.77	0.31	4.77
Copper	7.5	0.03	0.47	0.02	0.31

Another possible contributor to the disparity between the uranium adsorption capacity attained in this study and the previous study at 20°C is biofouling. Coarse filters, such as the 40-µm pore size filter used in this study, allow microorganisms to infiltrate the system and colonize the adsorbent braids. This leads to a reduction in the materials adsorption capacity, though it also offers a more realistic idea of the adsorbent's capacity when deployed in the open ocean. Capacity loss from biofouling can be as high as 30% under worst case conditions in the laboratory (i.e., fully exposed to light) at 20°C.[31] For the experiments in the present study, it is

highly unlikely that the adsorbents would experience worst case capacity losses since the raceway was covered leaving the braids in complete darkness for most of the experiment. This inhibits the growth of photosynthetic microbes, which play an important role in microbial colonization of the adsorbent braids. Park and coworkers previously showed that in a dark flume feed with coarsely filtered seawater (150 μm pore size), adsorbents accumulated 75% less microbial mass than adsorbents exposed to light after 42 days at 20°C.[31] At this significantly reduced biomass, the disparity between the capacities of the adsorbent in the coarsely filtered dark flume and the finely filtered control flume was negligible. Additionally, the lower temperature of the present experiment is likely to at least somewhat inhibit microbial growth.[32] Thus, while some biomass accumulation is expected on the adsorbent, it is unlikely to have a significant impact on the adsorption capacity.

Trace elements including iron, copper, zinc, and vanadium are also adsorbed and are competitors to uranium for amidoxime adsorption sites.[10,17,27] For this study, the salinity normalized mass of vanadium adsorbed over the 28 day exposure period was 1.9 mg/g adsorbent for small LCW braids in Cage B and 1.26 mg/g adsorbent for large LCW braids in Cage C. Compared to the materials developed at ORNL, vanadium adsorption on the LCW adsorbent is quite low for the same vanadium aqueous concentration. At 8ºC, the adsorbed mass of vanadium after 28 days exposure to Sequim Bay seawater for ORNL's AF1 and AI8 adsorbents formulated in small braids was approximately 8.5 mg/g adsorbent and 8.0 mg/g adsorbent, respectively.[22] This makes the vanadium/uranium ratio (w/w) for the ORNL adsorbents ~8 at 8ºC; while the ratio for the LCW adsorbents tested in the present study is ~1.3 for braids of a similar size at around 10.8ºC. Indeed, one unique feature of the LCW adsorbents is their much lower vanadium adsorption.[24] This reduction in vanadium adsorption is attributable to the open-chain amidoxime

ligands that make up the vast majority of binding sites on the LCW adsorbent. Vanadium has a significantly lower binding affinity for these sites than it does for the cyclic sites that dominate adsorption on the ORNL materials.[33-35] An additional benefit of this reduced affinity is that the elution of adsorbed vanadium should be significantly easier for the LCW adsorbent. When adsorbed to cyclic amidoxime sites, vanadium removal requires harsh acidic treatment to effectively strip bound vanadium.[36] Acidic treatment damages the adsorbent, significantly reducing its reusability which is critical to the economic viability of uranium recovery from seawater.[37] Thus, by substantially reducing the mass of vanadium adsorbed, the need for acidic treatment is also substantially reduced if not entirely eliminated. This, therefore, gives the LCW adsorbent greater longevity allowing the material to be redeployed more times than the ORNL developed adsorbents. These additional deployments, in turn, directly translate into a greater mass of uranium recovered per kg adsorbent over the usable lifetime of the LCW adsorbent and a lower overall cost of uranium recovery.

Of the remaining trace elements, iron is the most important with the second highest adsorbed mass after vanadium on a molar basis. The 28-day iron adsorption capacity was 1.90 mg/g adsorbent for the Cage B small braids and 1.71 mg/g adsorbent for the Cage C large braids. This adsorption rate is roughly on par with the adsorption of vanadium and several times greater than that of uranium, in terms of molar adsorption, while having a total aqueous concentration, in feed seawater, about 15 times higher than the concentration of vanadium. Iron speciation in seawater is, however, very complex with a large proportion of aqueous iron in both organic and inorganic forms that are unavailable for adsorption on amidoxime sites.[27] Thus, based solely on the total aqueous concentration, it is difficult to accurately assess the performance of the LCW materials with respect to their selectivity for iron over uranium. Adsorption of copper on both

samples is effectively negligible with only about 30 μg adsorbed per g adsorbent on the small braids in Cage B. Lastly, while the molar adsorption of zinc is comparable to uranium, the binding affinity of the amidoxime ligands for zinc is not precisely known, though it appears to be weak.[11,27]

The adsorption capacity for uranium and vanadium of both the Cage B small braids (Figure 4a) and Cage C large braids (Figure 4b), and the aqueous concentration of uranium and vanadium (Figure 5) over the experimental period were simulated using the modeling methodology previously described. As noted previously, estimates of the adsorption capacity were made by adjusting the forward and reverse rate constants for braid sizes. Initially, this approach underpredicted the aqueous concentration in the flume, thus a correction was applied reducing the total simulated adsorbent mass by 15%. Most of this correction can be attributed to the random distribution of amidoxime and carboxylate sites in the LCW adsorbent. This randomness allows for regions of the adsorbent to have higher concentrations of either amidoxime or carboxylate than the overall average. Regions with a higher concentration of amidoxime contain a large number of adsorption sites but are less accessible to adsorbates since these regions are significantly less hydrophilic than regions containing a more even mixture of amidoxime and carboxylate.[20,21] Conversely, regions rich in carboxylate are highly accessible but do not contain a sufficient number of adsorption sites to effectively capture diffusing adsorbates. Thus, a certain proportion of sites will not be effectively utilized. Another contributor to this correction is that, when the braids are attached to the cage frame, the base of the braid is tightly bound significantly constricting the flow of seawater through that region of the braid. Thus the adsorbent mass located in the constricted area is, aside from material on the surface of the braid, unavailable for adsorption. Biofouling was assumed to have no impact on

the capacity of the adsorbent in the raceway. With this rate information, it is possible to simulate the adsorbent's 56-day and saturated adsorption capacities. These are summarized for the Cage B small braids and Cage C large braids in Table 3. The predicted salinity normalized adsorption capacities on the Cage B small braids for uranium and vanadium are 2.32 mg and 2.89 mg per g adsorbent at 10.8°C, respectively. For the large braids in Cage C, the predicted salinity normalized capacities were 1.74 mg uranium and 2.17 mg vanadium per g adsorbent at 10.8°C.

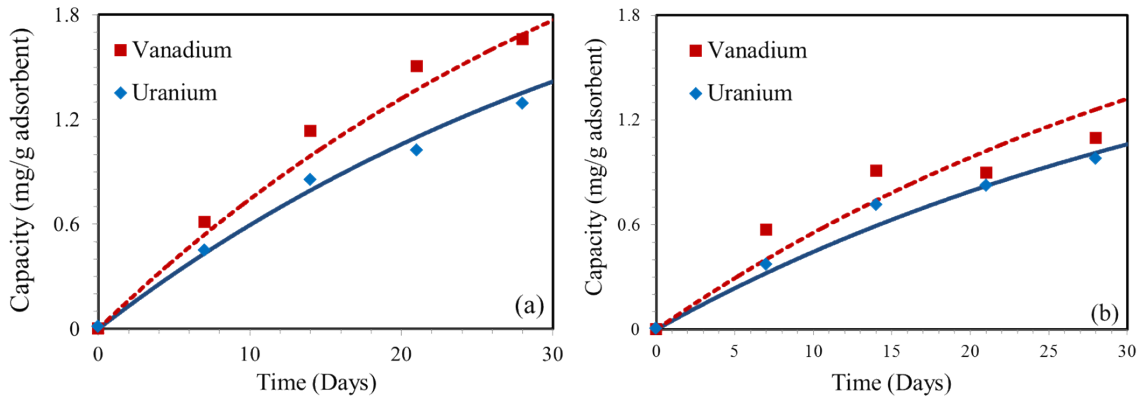

Figure 4. Simulated (lines) and experimental adsorption capacities (mg adsorbate/g adsorbent) for vanadium and uranium over a 28-day exposure period for (a) Cage B small braids and (b) Cage C large braids in the raceway. The analytical error is approximately 5%, as reported by Gill et al. (2016).[10]

Based on the work of Kuo and coworkers,[22] the uranium adsorption capacity of ORNL's AF1 and AI8 adsorbents can be simulated at our experimental temperature in Sequim Bay seawater. This results in a salinity normalized uranium adsorption capacity of 1.68 mg/g adsorbent for AF1 and 1.36 mg/g adsorbent for AI8 at 10.8°C after 56 days. With respect to vanadium, at the lowest temperature examined by Kuo and coworkers (8°C), the salinity normalized vanadium adsorption capacities after 56 days for AF1 and AI8 in Sequim Bay seawater were 12.5 mg/g adsorbent and 14 mg/g adsorbent, respectively. Thus at reduced

temperatures, the small LCW braids are expected to significantly outperform both the AF1 and the AI8 adsorbent small braids with respect to uranium capture, while also adsorbing substantially less vanadium.

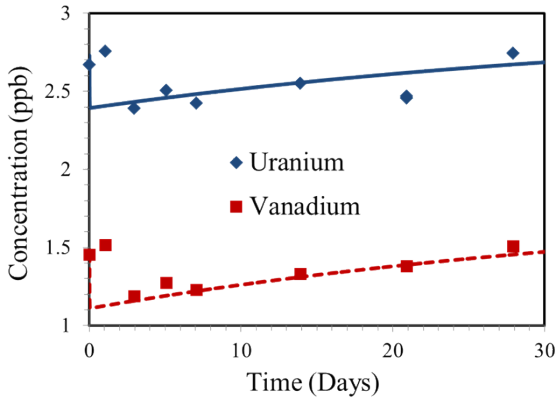

Figure 5. Measured and simulated (lines) aqueous concentrations (ppb) for uranium and vanadium in the raceway over a 28-day exposure period. The analytical error is approximately 5%, as reported by Gill et al. (2016).[10]

To estimate the performance of the LCW braids at higher temperatures, at least one additional reference point is needed. Thus, it was assumed that at 20°C adsorption on the LCW braids under ideal conditions is comparable to the performance results attained by Pan and coworkers.[24] From these data, the forward and reverse rate constants for adsorption of vanadium and uranium can be estimated and used in the adsorption model. With this kinetic information, the salinity normalized adsorption capacities in the raceway can be estimated at 20°C. The simulated 56-day capacities for uranium and vanadium at 20°C on the Cage B small braids are 5.20 mg and 4.82 mg/g adsorbent, respectively (Table 3). Once again, the LCW adsorbent outperforms both the AF1 and AI8 adsorbents for samples of similar braid size though to a slightly lesser degree than at 10.8°C, adsorbing 33% more uranium than the AF1 adsorbent at

20°C compared to 38% more at 10.8°C. Additionally, the adsorption of vanadium is still substantially lower than the 13 mg/g adsorbent on AF1 small braids and 16 mg/g adsorbent on observed AI8 small braids.[22]

Table 3. Simulated salinity normalized 56-day and saturated capacities (mg/g adsorbent) in the raceway for adsorption of uranium (U) and vanadium (V) on small and large sized LCW braids and on ORNL's AF1[22] grafted adsorbent.

		Small Braid		**Large Braid**		**AF1**	
		U	V	U	V	U	V
56-day Capacity (mg/g adsorbent)	10.8°C	2.32	2.89	1.74	2.17	1.68	12.6
	20°C	5.20	4.82	3.89	3.60	3.71	13.1
	31°C	10.34	7.28	7.72	5.43	7.86	22.2
Saturation Capacity (mg/g adsorbent)	10.8°C	3.08	3.83	2.31	2.88	1.73	17.4
	20°C	6.50	6.88	4.88	5.18	3.93	18.17
	31°C	14.90	13.09	11.20	9.93	8.36	32.4

On the larger braids, 56-day salinity normalized adsorption is simulated to be about 33% lower than on the small braids for both uranium and vanadium. This estimate was obtained by assuming that the impact of adsorbent scale up remains constant at all temperatures. With experimentally determined rate information for 10.8°C and an estimate of the rate constants at 20°C, a rough estimate of the forward and reverse rate constants can be obtained at other temperatures using the Arrhenius equation and then applied to the adsorption model. Thus, the simulated 56-day 31°C uranium and vanadium capacities are 10.34 mg/g adsorbent and 7.28 mg/g adsorbent, respectively, for the Cage B small braids. At 31°C and for adsorbent braids of similar size, the LCW adsorbent outperforms both the AF1 and AI8 series adsorbents which have 56-day capacities of 7.8 mg/g adsorbent and 6.5 mg/g adsorbent, respectively. Thus the LCW materials are expected to outperform ORNL's AF1 and AI8 adsorbents of similar size at all relevant temperatures, while also having a substantially reduced affinity for vanadium.

Considering the LCW's potential for lower cost production and conditioning, they may offer an avenue to notably reduce the cost of uranium recovery from seawater.

These estimates, however, only reflect the recovery rates of the adsorbent when it is first deployed. In practice, we must be able to repeatedly deploy these materials with relatively small capacity losses to ensure that uranium recovery is cost effective. The mass of uranium recovered from a potential deployment campaign depends upon how many times the adsorbent can be deployed and how much of its adsorption capacity is retained across each deployment. At this point in time, the LCW material has not been studied sufficiently to determine its reusability. Nevertheless, we have previously estimated the potential recovery of a theoretical deployment campaign for ORNL's AF1 adsorbent by assuming that AF1 may be deployed up to ten times and that five percent of its adsorption capacity is lost after each deployment.[27] Applying this same assumption to the LCW adsorbent, we can estimate the recovery of uranium and vanadium in seawater at 31^{o}C for a deployment campaign lasting up to one year for one kg of adsorbent for a number of different campaigns with varying lengths of deployment (Figure 6). For the LCW small braids, the ideal deployment period is estimated to be 42 days which, over the course of a year, results in a simulated uranium recovery of 63.7 g/kg adsorbent deployed. This rate of recovery is 18.8% higher than AF1's estimated uranium recovery under the same conditions. Simultaneously, the mass of vanadium adsorbed is estimated to be 43.3 g/kg adsorbent on the LCW small braids compared to 136.1 g/kg adsorbent on ORNL's AF1. As such, under the predicted ideal circumstances, the mass of adsorbent needed to abstain one kg of uranium per year using the LCW adsorbent is 15.7 kg. This would require that roughly 330,000 tonnes of adsorbent be produced annually to recover an equivalent amount of uranium to the total consumption of the United States in 2016.[1] As a comparison, approximately 390,000 tonnes of

ORNL's AF1 adsorbent would need to be produced annually to achieve the same annual uranium recovery using the same deployment criteria.

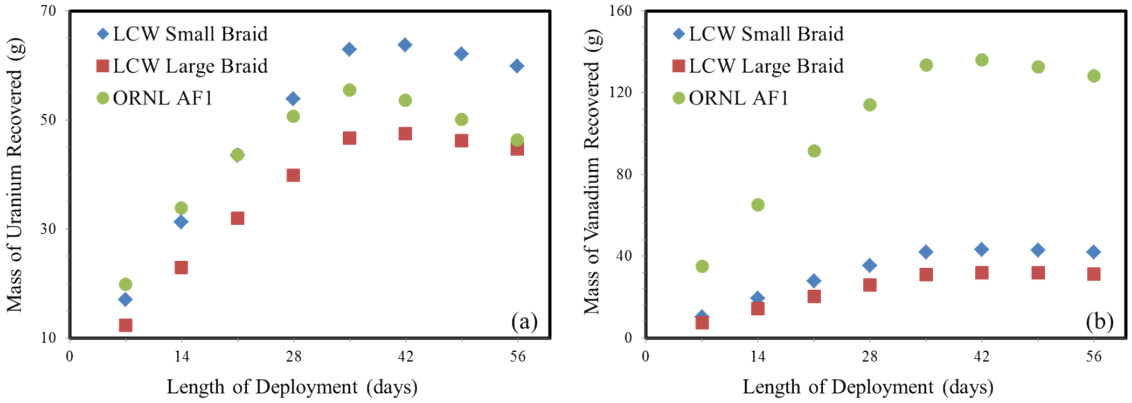

Figure 6. Estimated mass in grams of (a) uranium and (b) vanadium recovered at 31°C for both small and large LCW braids and for ORNL's AF1 braids per kg adsorbent deployed per year for varying lengths of deployment, assuming the material is deployed up to ten times and that five percent of the material's adsorption capacity is lost after each deployment.

4. Conclusions

The recovery of uranium from seawater has been an area of significant interest for the past seven decades with many recent studies focusing on amidoxime based materials. Nevertheless, the cost of uranium recovery remains high with a large portion of this arising from the costs associated with synthesizing the adsorbent and from purchasing the chemicals needed for alkaline treatment during initial conditioning and adsorbent regeneration. This study examines the efficacy of an amidoxime adsorbent derived from acrylic fibers, termed the LCW adsorbent, compared to two amidoxime based adsorbents previously developed at ORNL. The major difference between the LCW and ORNL adsorbents that is intended to substantially reduce the cost of uranium recovery is that the LCW adsorbent is produced directly from commercially

available acrylic fibers, significantly simplifying adsorbent synthesis when compared to the more complex radiation induced graft polymerization used for the ORNL adsorbents.

Adsorption experiments were performed with adsorbent braids of two different sizes in a recirculating raceway flume system for 28 days. The small-size LCW braids were found to consistently outperform the larger braids in the raceway with respect to uranium adsorption, though the adsorption of vanadium and other competing ions was also higher. Vanadium adsorption was, nevertheless, substantially lower on the LCW adsorbent than on the ORNL developed adsorbents. This can be attributed to the open-chain amidoxime ligands that are the predominant adsorption sites on the LCW adsorbent, which have a much lower affinity for vanadium than the cyclic sites on the ORNL adsorbents. A substantially reduced affinity for vanadium is particularly advantageous since it essentially eliminates the need for the harsh treatments necessary for vanadium elution leading to improved adsorbent reusability. The disparity between adsorption of large and small braids suggests a potentially inhomogeneous adsorbent quality when adsorbent size was scaled up. The results were then used for modeling of adsorption kinetics and the simulation of 56-day capacity outcomes.

At the experimental temperature of ~10.8°C, the 56-day uranium capacity was simulated for the small-sized braids to be 2.32 mg/g adsorbent compared to a simulated 1.68 mg and 1.36 mg/g adsorbent for ORNL's AF1 and AI8 adsorbents of similar size. The small braids were simulated to continue outperforming both ORNL adsorbents at up to 31°C. Across all temperatures, the small braids' uptake of vanadium was also significantly lower than for both the AF1 and AI8 adsorbents. Thus, the LCW adsorbents are expected to outperform both AF1 and AI8 adsorbents under most temperatures for realistic deployment. Using the simulated uranium capacities at 31°C, a number of theoretical deployment campaigns were considered for the LCW

adsorbent and ORNL's AF1. The estimated maximum uranium recovery attained from these simulations was 63.7 g/kg LCW deployed per year which is 18.8% higher than AF1 achieved under the same conditions. For this rate of recovery, approximately 330,000 tonnes of the LCW adsorbent would need to be produced annually to generate a mass of uranium equal to the demand of the United States in 2016. This behavior, combined with their lower production and alkaline treatment costs, makes the LCW material a potentially attractive adsorbent for uranium resource recovery from seawater. The LCW adsorbents are also shown to adsorb significantly less vanadium, thus effectively eliminating the need for harsh elution of the adsorbent and increasing its reusability.

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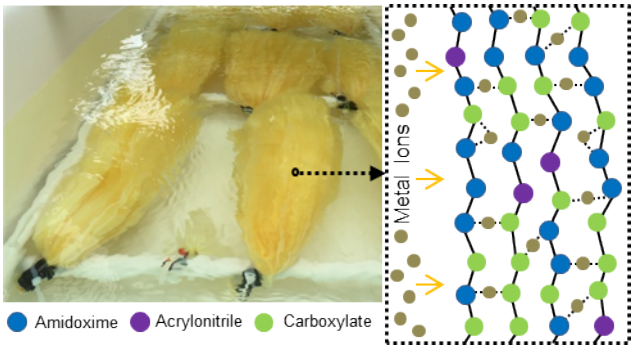
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