

# The Uranium from Seawater Program at the Pacific Northwest National Laboratory: Overview of Marine Testing, Adsorbent Characterization, Adsorbent Durability, Adsorbent Toxicity, and Deployment Studies

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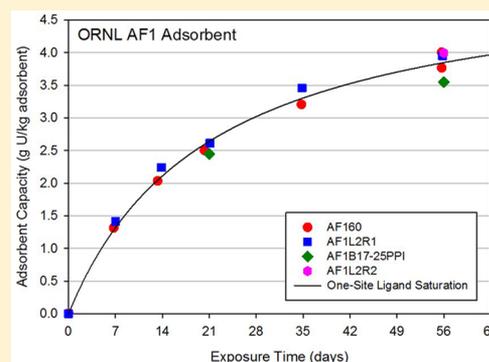
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## Supporting Information

**ABSTRACT:** The Pacific Northwest National Laboratory (PNNL) is evaluating the performance of adsorption materials to extract uranium from natural seawater. Testing consists of measurements of the adsorption of uranium and other elements from seawater as a function of time using flow-through columns and a recirculating flume to determine adsorbent capacity and adsorption kinetics. The amidoxime-based polymer adsorbent AF1, produced by Oak Ridge National Laboratory (ORNL), had a 56-day adsorption capacity of  $3.9 \pm 0.2$  g U/kg adsorbent material, a saturation capacity of  $5.4 \pm 0.2$  g U/kg adsorbent material, and a half-saturation time of  $23 \pm 2$  days. The ORNL AF1 adsorbent has a very high affinity for uranium, as evidenced by a 56-day distribution coefficient between adsorbent and solution of  $\log K_{D,56\text{day}} = 6.08$ . Calcium and magnesium account for a majority of the cations adsorbed by the ORNL amidoxime-based adsorbents (61% by mass and 74% by molar percent), uranium is the fourth most abundant element adsorbed by mass and seventh most abundant by molar percentage. Marine testing at Woods Hole Oceanographic Institution with the ORNL AF1 adsorbent produced adsorption capacities 15% and 55% higher than those observed at PNNL for column and flume testing, respectively. Variations in competing ions may be the explanation for the regional differences. Hydrodynamic modeling predicts that a farm of adsorbent materials will likely have minimal effect on ocean currents and removal of uranium and other elements from seawater when farm densities are  $<1800$  braids/ $\text{km}^2$ . A decrease in uranium adsorption capacity of up to 30% was observed after 42 days of exposure because of biofouling when the ORNL braided adsorbent A18 was exposed to raw seawater in a flume in the presence of light. No toxicity was observed with flow-through column effluents of any adsorbent materials tested to date. Toxicity could be induced with some non-amidoxime based adsorbents only when the ratio of solid adsorbent to test media was increased to part per thousand levels. Thermodynamic modeling of the seawater–amidoxime adsorbent was performed using the geochemical modeling program PHREEQC. Modeling of the binding of Ca, Mg, Fe, Ni, Cu, U, and V reveal that when binding sites are limited ( $1 \times 10^{-8}$  binding sites/kg seawater), vanadium heavily outcompetes other ions for the amidoxime sites. In contrast, when binding sites are abundant, Mg and Ca dominate the total percentage of metals bound to the sorbent.



## 1. INTRODUCTION

Extracting uranium from seawater can provide a sustainable and economically viable supply of uranium fuel for nuclear reactors.<sup>1</sup> Toward this aim, the Fuel Resources Program at the U.S. Department of Energy's Office of Nuclear Energy is investigating

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uranium adsorbent technology to extract uranium from seawater. Natural seawater is a complex multicomponent biogeochemical system, with low trace element content, and it contains natural organic matter that can complex solution ions and coat surfaces. Moreover, multioxidation-state elements can exist out of their normal thermodynamically predicted reduction–oxidation state because they become involved with or influenced by biological processes. Because of this, laboratory performance studies with salt solutions or synthetic seawater cannot reliably mimic the natural seawater environment and its influence on the adsorption processes. The Pacific Northwest National Laboratory's (PNNL) Marine Science Laboratory (MSL) is currently evaluating the performance of uranium adsorption materials being developed for seawater extraction under realistic marine conditions with natural seawater. This effort is aimed at evaluating adsorption materials being developed by Oak Ridge National Laboratory (ORNL), universities participating in the Nuclear Energy University Program (NEUP) of the U.S. Department of Energy (DOE), and with international collaborators including the Japan Atomic Energy Agency and the Chinese Academy of Science.

Laboratory studies with artificial seawater have often suggested that unusually high uranium adsorption capacities are possible, often 10–100 g U/kg adsorbent<sup>2–6</sup> compared to natural seawater studies with amidoxime-based adsorbents, which have reported maximum levels of approximately 3–4 g U/kg adsorbent.<sup>7–10</sup> This comparison suggests that artificial seawater testing of uranium adsorbent materials is not necessarily a good predictor of adsorbent performance in natural seawater. Simulated seawater studies often use U concentrations well above seawater levels (3.3 ppb), which may perturb the natural speciation of U in seawater and produce unrealistic conditions for the interaction between the U in solution and the adsorption media. Moreover, laboratory studies often exclude critical transition-metal elements (e.g., vanadium, iron, copper, and zinc) that could compete for binding sites on the adsorbent or do not include the proper abundance of Ca, Mg, and  $\text{CO}_3^{2-}$  to produce the dominant solution forms of U in seawater,  $\text{Ca}_2[\text{UO}_2(\text{CO}_3)_3]^{10}$ ,  $\text{Ca}[\text{UO}_2(\text{CO}_3)_3]^{2-}$ , and  $\text{Mg}[\text{UO}_2(\text{CO}_3)_3]^{2-}$ .<sup>11</sup>

This paper provides an overview of the marine testing program and adsorbent characterization activities that have been conducted at PNNL's Marine Science Laboratory in Sequim, Washington beginning in 2012. Additional and specific details of this program are in several companion papers, many in this special issue.<sup>12–17</sup> Specific attention is given here to describing the marine testing infrastructure and program at the MSL in Sequim, WA. Other activities being conducted at the MSL include marine testing at other coastal locations, hydrodynamic modeling efforts to assess impacts from the deployment of a farm of braided adsorbents, toxicity studies of adsorbent materials, biofouling investigations to determine impacts on adsorbent capacity, advanced imaging techniques and thermodynamic modeling to characterize and predict the binding of U and other elements with amidoxime-based adsorbent material, and investigations of nanostructured metal oxides for the collection and recovery of uranium from seawater.

## 2. MATERIALS AND METHODS

**2.1. Site Location.** PNNL's Marine Science Laboratory is located along the coast of Washington within the Strait of Juan de Fuca at the mouth of Sequim Bay (Figure 1). The Sequim Bay watershed is very small and has no major riverine system to dilute the seawater within Sequim Bay from typical coastal conditions. Illustrated in Figures S1 and S2 are records of salinity and pH,



**Figure 1.** Location of PNNL's Marine Sciences Laboratory on Sequim Bay along the Washington coast.

respectively, beginning in January 2012 when the marine testing program began. The variability in both salinity and pH over the testing period is quite small. The average salinity is  $30.6 \pm 0.8$  psu ( $n = 1008$ ,  $\text{CV} = 2.7\%$ ) and the average pH is  $7.83 \pm 0.12$  ( $n = 988$ ;  $\text{CV} = 1.5\%$ ). There is no clear seasonal pattern in salinity variations. pH varies with season primarily because of seasonal variations in the intensity of algal photosynthesis and microbial respiration process, which remove and introduce  $\text{CO}_2(\text{g})$  from solution, respectively, and from solubility changes in  $\text{CO}_2(\text{g})$  as a function of temperature. In general,  $\text{CO}_2(\text{g})$  is more soluble in cold water, which results in lower pH during winter months. These processes result in a pH shift between a summer high of around 8.1 to a winter low of approximately 7.6 pH units.

**2.2. Ambient Seawater Exposure Systems.** Marine testing was conducted using ambient seawater from Sequim Bay, WA. The MSL has a seawater delivery system that can provide ambient seawater into a "wet laboratory" for scientific investigations. Ambient seawater is drawn by pump from a depth of  $\sim 10$  m from Sequim Bay through a plastic pipe. Raw seawater is pumped directly into the laboratory for use. Filtered seawater is obtained by first passing raw seawater through an Arkal Spin Klin filter system (nominal pore size  $40 \mu\text{m}$ ) to remove large particles. The partially filtered seawater is then stored in a large volume ( $\sim 3500$  gal) reservoir tank outside the laboratory. This seawater is gravity fed into the laboratory research facilities through PVC piping where it can be passed through additional filtration to remove finer particles if needed at the point of use. Two types of exposure systems were employed in this program: flow-through columns for testing of loose fibers and other loose materials

and a recirculating water flume for testing of braided adsorbent material.

**2.2.1. Flow-through Column Exposures.** Figure S3 shows a diagram of the seawater delivery and manifold system used to expose adsorbent materials to 0.45  $\mu\text{m}$  filtered seawater in flow-through columns. Figure S4 is a picture of the manifold with flow-through columns attached. Seawater from a large outside storage reservoir is fed sequentially through 5  $\mu\text{m}$  and 1  $\mu\text{m}$  cellulose filters and then collected in a 180 L fiberglass reservoir tank termed a “head tank.” Seawater in the head tank is heated to the desired temperature using a 10 kW all titanium immersion heater. Temperature-controlled ( $20 \pm 1.5$  °C) seawater is drawn from the head tank with a pump (nonmetallic pump head) and passed through a 0.35 to 0.45  $\mu\text{m}$  poly(ether sulfone) (Memtrex MP, GE Power and Water) or cellulose membrane cartridge filter and into a 24-port PVC manifold. Water that is not used to expose adsorbent material passes through the manifold and is returned to the head tank. Pressure in the manifold is controlled with a gate valve at the outlet of the manifold. MSL has four separate 24-port manifolds, linked to three separate head tanks, permitting testing of 96 adsorbent materials in flow-through columns simultaneously. The flow rate of seawater passing through the columns is grossly controlled by varying the seawater delivery pressure in the manifold and then fine scale flow adjustments using a needle valve placed on the outlet of each flow-through column. A turbine flow sensor (DFS-2W, Clark Solutions) is attached to the outlet tubing to monitor and record the flow through each column. The signals from the sensors are captured by a homemade instrument package operated with National Instruments LabView software which displays in real time the flow rate of each column on the manifold and records integrated flow rate measurements in increments ranging from a few seconds to several hours. Temperature of the seawater flowing through the system was monitored and recorded at the outlet of columns using an Omega model HH804U hand-held meter equipped with a long lead and nonmetallic temperature probe. The temperature was recorded every 5 min by attaching the meter to a laptop computer using data recording and storage software provided with the instrument.

Adsorbent materials for seawater exposure were packed into columns and were held in place by a combination of glass wool and/or 3–5 mm glass beads. The flow-through column consists of a 0.75–1.5 in. inside diameter by 4–6 in. length Harvel Clear Rigid PVC piping with pipe thread fittings on each end. Polypropylene end-caps fitted with coarse diameter porous polyethylene frits (Bel-Art Products) and held in place with Viton o-rings were used to seal the ends of the column. Linear velocities in the column ranging between 0.5 and 10 cm/sec can be achieved by using different diameter columns and seawater delivery flow rates between 100 and 1500 mL/min. The standard test conditions used for this work were average linear velocities through a cross-sectional area within the packed glass bead bed region of the column of between  $>2.0$  and  $<2.5$  cm/sec. These velocities were achieved with a 1 in. ID column, packed with 5 mm glass beads, and a minimum flow rate of 250 mL/min. All column material was acid washed prior to use. Packed columns were mounted in one of the port positions on the seawater manifold (see Figures S3 and S4).

**2.2.2. Recirculating Flume Exposure System.** Recirculating flumes constructed of acrylic material were used for conducting exposure tests with braided adsorbent material under controlled temperature and flow-rate conditions. Several flumes have been constructed of varying dimensions (4–8 feet in length; 6–10 in.

in width; and 10 in. in height) to accommodate experimental needs. The specific dimensions and pump sizes were selected to allow the researchers to reproduce a range in linear velocities that one might encounter in a coastal marine environment ( $<10$  cm/s). Darkened acrylic material was used for studies with filtered seawater where no biological growth was desired and clear flumes were constructed for exposures with unfiltered seawater where light-stimulated biological growth was desired for biofouling studies. A side view depiction of the flume design is given in Figure S5, and a picture of the clear flumes used for biofouling studies is given in Figure S6.

Fresh seawater was constantly fed into the flume using the seawater manifold delivery system depicted in Figure S3. A tubing line was run from one or more of the manifold ports directly into the flume to achieve the desired seawater delivery rates up to 8 L/min. The rate of fresh seawater delivery was controlled using a needle valve mounted on one or more ports in the manifold.

Controlled water flow (linear velocity) within the flume was accomplished by recirculating water using a centrifugal water pump (Finish Thompson). The pump head was nonmetallic to minimize contamination concerns. Precise control of flow rate and linear velocity was achieved by putting a flow restriction (globe valve) at the outlet of the pump (Figure S5). The flow rate in the recirculating water was continuously monitored by placing a flow meter (Omega) in the line between the pump outlet and the flume inlet. The target for these studies was a flow rate that results in a linear velocity  $>2$  cm/sec. This linear velocity was chosen to be consistent with the linear velocity used in flow-through column studies. The linear velocity in the flume was determined using the cross-sectional area of the flume and the recirculation flow rate. For example, a linear velocity of 2 cm/s was achieved in a 6 foot flume (183 cm) with a cross-sectional area of 300  $\text{cm}^2$  by restricting the pump flow rate to 9 gpm (34 L/min). There was a slight increase in linear velocity due to the fresh seawater inflow (2–4 L/min), but it was small relative to the recirculation flow of 34 L/min.

The height of water in the flume was controlled by the height of the standpipe (overflow tube), which varied between approximately 6 and 10 in. (15–25 cm). Water within the system rose until it reached the height of the standpipe and then spilled out of the flume through the standpipe to drain. The normal operating height was 9 in. (23 cm).

The rate at which fresh seawater was fed into the system and the internal volume of the flume controlled the residence time of seawater in the system. For the above example, with the 6 ft. flume, the seawater residence time was 18.9 min. The time to recirculate water was much faster. At a recirculation flow rate of 34 L/min, the water in the flume was recirculated once every 1.7 min. Hence, the water in the flume can be considered well mixed and has been confirmed so with multiple samples in different areas in the flume.

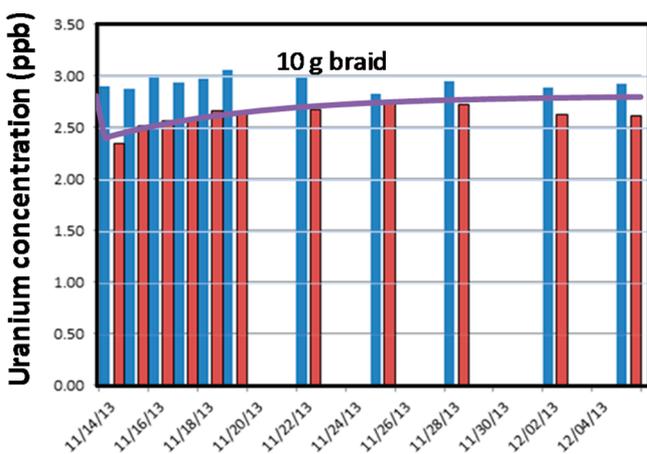
Braided adsorbents were placed into the flumes for exposure by attaching them to a short length of 1/4 in. polyethylene tubing with cable ties and inserting one end of the tubing into a small block mounted on the bottom of the flume into which a 1/4 in. hole has been drilled (Figure S7). Multiple braids could be mounted in a single flume if desired and are widely spaced ( $>20$  cm) to minimize any localized reductions in flow or uranium concentrations in the flume around upstream braids.

The ORNL adsorbent braids have a form factor that resembles a feather duster, consisting of “feather” like strands of material that protrude outward from a dense woven core (see Figure S7).

Time series samples of uranium and other trace element adsorption capacity are obtained by cutting of a small mass (~100 mg) of the “feathers” from the braided material using a pair of titanium-coated scissors. Replicate measurements taken from the feather region of the braids agree very well, but the dense core material has a much lower (10–50% of the feather values) and much more variable uranium concentration. The reduction in adsorption capacity within the core material likely arises from a restriction to the flow of seawater reaching core material due to the dense packing of the fibers. Clearly, this finding suggests that the form factor of the adsorbent material and the linear velocity of the seawater exposure are important to adsorption capacity.

The temperature of the seawater in the flume was monitored using an Omega model HH804U hand-held meter equipped with a long lead and nonmetallic temperature probe.

Illustrated in Figure 2 is an example of a flume experiment in which 10 g of ORNL AF1 adsorbent material (described later)



**Figure 2.** Time series measurements of fresh seawater input (blue bars) and internal flume (red bars) uranium concentrations determined during the course of a natural seawater flume experiment. The line drawn across the figure represents the predicted uranium concentration in the exit water from a mass balance model based on the mass of braid (10 g) used in the exposure, the uptake kinetics for the AF1 adsorbent at a temperature of 20 °C, and the input rate of fresh seawater to the flume of 1.5 L/min.

was placed in the flume and the fresh seawater inflow rate was set at 1.5 L/min. Under these conditions, the adsorbent material was able to remove uranium faster than was being supplied by the fresh seawater input, especially early in the exposure when the adsorbent was fresh and the extraction rate was faster. Drops in uranium and other elements in solution during a flume experiment can be minimized by working with small masses of adsorbent and supplying fresh seawater at a rate higher than it is being removed. Minimal drops (<5%) in uranium concentration were observed when the fresh seawater input flow rate was maintained >2.0 L/min and the total mass of adsorbent being exposed is <5 g. If larger masses of adsorbent are used for an exposure study, this guideline is used to proportionally adjust the inflow rate to match the mass of adsorbent. Small variations in inlet seawater and flume seawater uranium concentrations observed in Figure 2 are due to analytical error (~5%) and small changes in the salinity (typically ~3%) over the course of the experiment. Replicate measurements of uranium in seawater within the flume revealed that the seawater was well mixed, and there were no downstream areas of lower uranium concentration.

### 2.3. Preparation of Adsorbent Materials for Testing.

Amidoxime-based polymeric adsorbent materials were prepared by Oak Ridge National Laboratory (ORNL). Details associated with the production of these materials are given in other papers in this special issue.<sup>18–22</sup> PNNL received three separate formulations of the ORNL adsorbent material, referred to as 38H, AF1, and AI8 formulations. Adsorbent materials were shipped dry to PNNL and were conditioned immediately before use. The conditioning procedure consists of soaking the braids or fibers in a 2.5% (~0.44 M) potassium hydroxide solution at 80 °C for 1–3 h. One mL of the KOH solution was used per mg of adsorbent material. Immediately upon conditioning, the adsorbent was rinsed with several volumes of deionized water. For flow-through column testing, a nominal mass of 50–100 mg of dry fiber adsorbent was packed into individual columns for mounting on the multiport manifold. The conditioned fiber was placed into a column and held in place with glass wool. Glass beads were used to fill the remainder of the void volume in the columns. For testing of braided adsorbent materials, the conditioned braids were held in deionized water until directly placed in the flume.

### 2.4. Water Quality, Temperature, and Flow-Rate Measurements.

Salinity and pH measurements were conducted daily. Salinity was determined using a hand-held YSI model Pro30 salinometer. pH measurements were made with a standard pH meter and probe that was calibrated weekly using NIST traceable buffers. The temperature of the seawater exposures was continuously monitored using an Omega model HH804U hand-held meter equipped with a long lead and nonmetallic temperature probe. Temperature data were logged every 10 min using software provided by Omega. The flow rate for flow-through column studies was continuously monitored using an in-line turbine-style flow sensor (Model DFS-2W, Digiflow Systems) placed at the outlet of the flow-through columns (see Figures S3 and S4). The flow-rate data from the individual sensors were integrated and logged every 10 min using a homemade data acquisition system controlled by National Instruments LabVIEW Software.

### 2.5. Determination of Uranium and Trace Elements on Adsorbent Materials.

Adsorbent materials exposed to seawater were washed with deionized water to remove salts and dried using a heating block. The dried fibers (50–100 mg) were weighed and then digested with 10 mL of a high-purity (Optima, Fisher Scientific) 50% aqua regia acid mixture (3:1; hydrochloric acid:nitric) for 3 h at 85 °C on a hot block. Analysis of uranium and other trace elements was conducted using either a PerkinElmer 4300 inductively coupled plasma optical emission spectrometer (ICP-OES) or a Thermo Scientific iCapQ inductively coupled plasma mass spectrometer (ICP-MS). Quantification with both instruments is based on standard calibration curves. Additional details are given in a companion paper in this issue.<sup>14</sup>

### 2.6. Determination of Uranium and Trace Elements in Seawater.

Determination of uranium and a select suite (e.g., V, Fe, Zn, Cu, Ni, Sr, Ti, Cr, Co, and Mn) of trace elements in natural seawater samples was conducted using a Thermo Scientific iCAP Q inductively coupled plasma mass spectrometer equipped with an Elemental Scientific seaFAST S2 sample introduction system. The seaFAST S2 automated sample introduction system incorporated online preconcentration utilizing a chelating ion-exchange resin (iminodiacetic acid and ethylenediaminetriacetic acid immobilized on a hydrophilic methacrylate polymer) for matrix elimination and online preconcentration of

trace and ultratrace elements from seawater.<sup>23</sup> Analytes were eluted off the column using 10% high-purity HNO<sub>3</sub>.

Uranium determinations in seawater were conducted using either the method of standard addition calibrations or the samples were preconcentrated using the seaFAST system.<sup>14</sup> Addition calibration is a variant of the standard additions method and is often used when all samples have a similar matrix. Instrumental calibration curves were prepared in Sequim Bay seawater that was diluted 20-fold with high purity deionized water and then spiked at four different concentration levels: 0.1, 0.2, 0.3, and 0.4 μg/L, along with a 2% nitric acid blank in diluted seawater. The seawater samples were then analyzed at 20-fold dilution with high-purity deionized (DI) water and then quantified using the matrix matched additions calibration curve. The standard reference material CASS-5 (nearshore seawater reference material for trace metals) available from the National Research Council Canada, which is certified for uranium (3.18 ± 0.10 μg/L), was also analyzed at a 20-fold dilution every 10 samples to verify the analytical results. The uranium recovery for the analysis of CASS-5 ranged from 93 to 99% (*n* = 9). Duplicate analyses and matrix spikes were conducted with each batch of samples. The relative percent difference for duplicates ranged from 1 to 5%, and the recovery of matrix spikes ranged from 93 to 109% (*n* = 11).

**2.7. Determination of Adsorbent Capacity and Kinetics.** Measurements of the adsorption of uranium and other elements from seawater as a function of time onto the adsorbent materials were used to determine the adsorbent capacity and adsorption rate (kinetics) of uranium and other elements. Quantification of the adsorption capacity and adsorption kinetics was conducted by determining a best-fit curve through the time course data set using a simple one-site ligand saturation model, parametrized using the software graphics program SigmaPlot:

$$q(t) = q_{\max} \frac{t}{K_d + t} \quad (1)$$

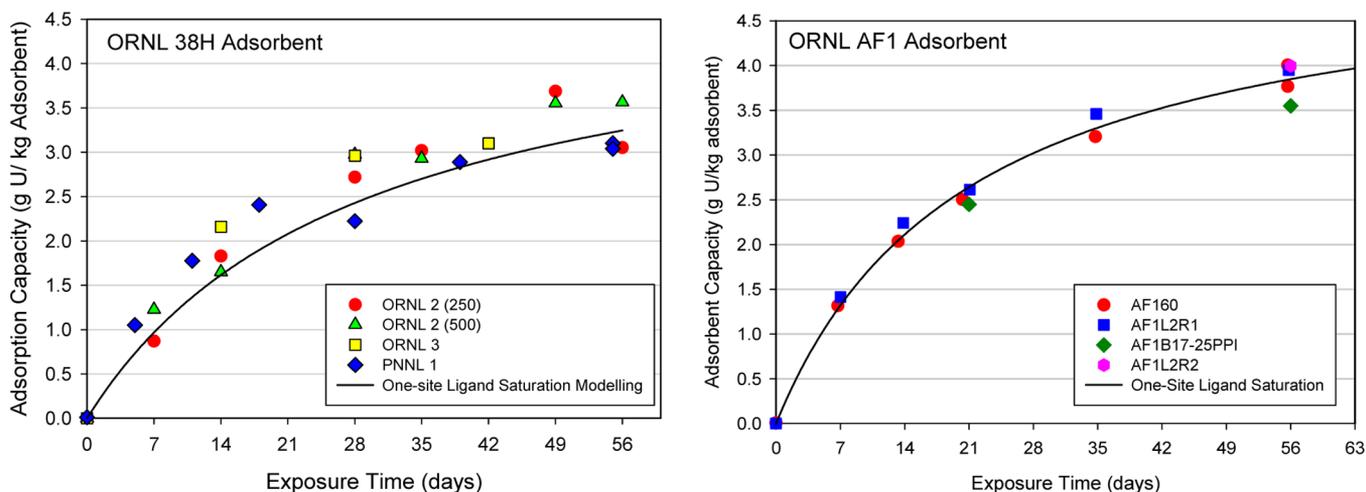
where  $q(t)$  is uranium capacity (g U/kg adsorbent) at time  $t$ ,  $t$  the exposure time (days),  $q_{\max}$  the adsorption capacity at saturation (g U/kg adsorbent), and  $K_d$  the half-saturation time (days). Binding is assumed to be a simple 1:1 ligand-binding site association. Because uranium uptake is slow, it is not clear how well this model will predict adsorption capacity outside of the specific operating conditions or time frame for which its parameters are optimized.

The goal of this curve fitting process was simply to establish a predictive capability and generate information about the kinetics of the reaction and not to attempt to model the process controlling uranium binding onto amidoxime-based polymeric adsorbents. One-site ligand saturation modeling is often used in biomedical studies to describe saturation binding of a solution component onto a binding site. Other kinetic models, such as simple Langmuir kinetics, work equally as well to fit a curve to the data. The rate-limiting step controlling the kinetics of the adsorption of uranium onto amidoxime-based adsorbents is highly dependent on the characteristics of the exposure process and has been described by transport and kinetic models based on liquid film mass transfer, diffusion, or reaction kinetics.<sup>7,9</sup>

Prior to determination of adsorption capacity and kinetics, the individual capacity determinations were normalized to a salinity of 35 psu using a simple proportional adjustment based on the salinity observed when the sample was collected. For example, if the salinity was 30 at the time of the collection, or alternatively averaged 30 over the time of the collection, then the sample concentration would be adjusted by a factor of 35/30 to normalize it to a salinity of 35. The ability to normalize the uranium data to a common salinity for comparison purposes is possible because there is a well-defined relationship between the 238-U concentration in seawater and salinity of 3.187 μg U/kg of seawater.<sup>24</sup> This normalization removes the differences that result from exposures in seawater with varying salinity and hence uranium concentrations. This salinity normalization is also done for the other elements as well, but the normalization is less well-defined for nonconservative elements in seawater.

### 3. RESULTS AND DISCUSSION

**3.1. Adsorption Capacity and Adsorption Kinetics.** An example of the determination of adsorption capacity and adsorption kinetics using flow-through column testing is given in Figure 3. The results were obtained with multiple time series experiments using the ORNL amidoxime-based polymeric adsorbent material 38H produced in 2012 and an improved adsorbent, AF1, produced in 2013. The 38H adsorbent had a 56-day adsorption capacity of 3.30 ± 0.68 g U/kg adsorbent (normalized to a salinity of 35 psu).<sup>9</sup> Applying a one-site ligand saturation model predicts a saturation adsorption capacity of 4.89 ± 0.83 g U/kg of adsorbent material (normalized to a



**Figure 3.** Time-series measurements of the adsorption capacity of the ORNL amidoxime-based adsorbent material 38H (left panel) and AF1 (right panel).

**Table 1. Relative Abundance of Elements Absorbed by the ORNL AF1 Amidoxime-Based Adsorbent Material in Flow-through Column Tests<sup>a</sup>**

element	56-day adsorption capacity ( $\mu\text{g/g}$ adsorbent)	% of total (by mass)	element	56-day adsorption capacity ( $\mu\text{mol/g}$ adsorbent)	% of total (by molar percent)
Mg	16 500 $\pm$ 890	32.0 $\pm$ 1.7	Mg	678 $\pm$ 24	47.4 $\pm$ 1.7
Ca	15 100 $\pm$ 920	29.3 $\pm$ 1.8	Ca	378 $\pm$ 14	26.3 $\pm$ 1.0
V	10 700 $\pm$ 320	21.0 $\pm$ 3.0	V	210 $\pm$ 36	14.9 $\pm$ 2.5
U	3 420 $\pm$ 370	6.7 $\pm$ 0.7	Na	90.7 $\pm$ 28.5	6.2 $\pm$ 2.0
Na	2 090 $\pm$ 700	4.0 $\pm$ 1.4	Fe	23.0 $\pm$ 7.0	1.6 $\pm$ 0.5
Fe	1 280 $\pm$ 360	2.5 $\pm$ 0.7	Zn	16.4 $\pm$ 2.7	1.2 $\pm$ 0.2
Zn	1 070 $\pm$ 170	2.1 $\pm$ 0.3	U	14.4 $\pm$ 1.9	1.0 $\pm$ 0.1
Cu	646 $\pm$ 74	1.3 $\pm$ 0.1	Cu	10.2 $\pm$ 1.1	0.71 $\pm$ 0.08
Ni	381 $\pm$ 8.7	0.74 $\pm$ 0.02	Ni	6.50 $\pm$ 0.21	0.45 $\pm$ 0.02
Sr	132 $\pm$ 8.2	0.26 $\pm$ 0.02	Ti	1.50 $\pm$ 0.30	0.11 $\pm$ 0.02
Ti	72 $\pm$ 12	0.14 $\pm$ 0.02	Sr	1.50 $\pm$ 0.09	0.10 $\pm$ 0.01
Co	24 $\pm$ 4.1	0.047 $\pm$ 0.008	Co	0.41 $\pm$ 0.08	0.029 $\pm$ 0.006
Cr	18 $\pm$ 2.4	0.035 $\pm$ 0.005	Cr	0.35 $\pm$ 0.05	0.025 $\pm$ 0.004
Mn	17 $\pm$ 2.1	0.033 $\pm$ 0.004	Mn	0.30 $\pm$ 0.04	0.021 $\pm$ 0.003
Sum	51 400	100%	Sum	1430	100%

<sup>a</sup>Adsorption capacity is expressed in units of  $\mu\text{g}$  (element)/g adsorbent on the left-hand side of the table and  $\mu\text{mol}$  (element)/g adsorbent in the right-hand side of the table.

salinity of 35 psu) and a half-saturation time of  $28 \pm 10$  days. The AF1 adsorbent material had a 56-day adsorption capacity of  $3.9 \pm 0.2$  g U/kg adsorbent material (normalized to a salinity of 35 psu), a saturation capacity of  $5.4 \pm 0.2$  g U/kg adsorbent material (normalized to a salinity of 35 psu), and a half saturation time of  $23 \pm 2$  days. The fit of the data points to the one-site ligand saturation modeling curve provides an indication of the reproducibility of the testing process because all the testing was conducted with identical conditions. The earlier investigations with the 38H adsorbent were not as reproducible as the more current investigations with the AF1 adsorbent. A more rigorous discussion of the marine testing of the ORNL amidoxime-based polymeric adsorbent materials is given in a companion paper in this issue.<sup>13</sup>

Adsorbents which exhibit a high affinity and rapid uptake for the target element from aqueous solution are highly desirable. The amidoxime-based polymeric adsorbents described here have, admittedly, slower uptake kinetics compared to other high-affinity adsorbents which can reach equilibrium with a variety of elements in seawater in time frames of 1–1000 min. The relatively slow uptake kinetics of uranium on amidoxime-based polymeric adsorbents has been attributed to a reaction-limited process.<sup>7,9</sup>

### 3.2. Adsorbent Characterization: Elemental Specificity.

The amidoxime-based adsorbent materials are not specific for uranium, but also adsorb other elements from seawater.<sup>25,26</sup> Shown in Table 1, in order of adsorption capacity, is a listing of elemental abundance for a suite of trace elements absorbed by the ORNL AF1 adsorbent material. Note that the major doubly charged cations in seawater (Ca and Mg) account for a majority of the cations adsorbed (61% by mass and 74% by molar percent). For the AF1 adsorbent material, U is the fourth most abundant element adsorbed by mass and seventh most abundant by molar percentage. Improving the selectivity of the adsorbent will clearly result in a significant improvement in the adsorption capacity for uranium from seawater.

An assessment of the affinity of the adsorbent to extract uranium and other elements from seawater can be made by determining a 56-day, mass-weighted, distribution coefficient ( $K_{D,56\text{-day}}$ , L/kg):

$$K_{D,56\text{-day}} = \frac{C_{\text{ads}}}{C_{\text{sea}}} \quad (2)$$

where  $C_{\text{ads}}$  is the concentration of a given element observed on the adsorbent (in units of g of element/kg of adsorbent) and  $C_{\text{sea}}$  is the concentration of the element observed in the seawater exposure system (in units of g/L). It is important to distinguish that this distribution coefficient is not based on equilibrium concentrations, but rather on the observed capacities at 56 days, what is anticipated to be a typical deployment period to achieve a reasonable saturation. Because the adsorption kinetics are slow, > 90% saturation is not reached for most elements for hundreds of days. The distribution coefficient for uranium and several other elements on the ORNL AF1 adsorbent is given in Table 2. In general, the larger the  $K_D$  (or  $\log K_D$ ), the greater the affinity of the adsorbent to extract an element from solution.<sup>27,28</sup> Values of  $\log K_D > 4$  are considered to exhibit high affinity.<sup>27,28</sup>

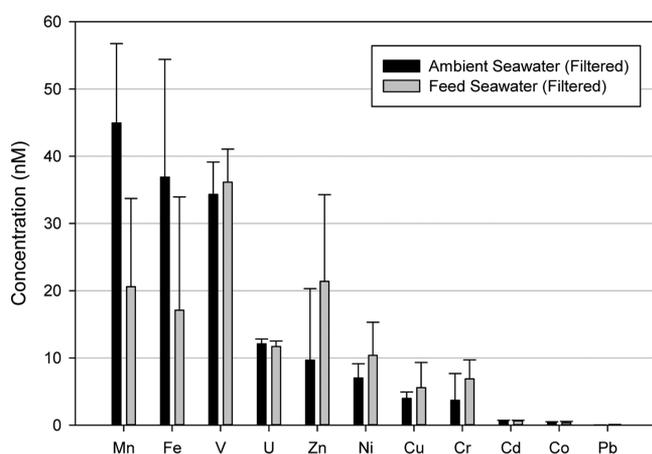
**Table 2. Adsorbent-Solution Distribution Coefficients Determined for the ORNL Amidoxime-Based Adsorbent Material AF160 after 56 Days of Exposure in the PNNL Seawater Test System<sup>a</sup>**

element	56-day adsorption capacity <sup>b,c</sup> (g/kg)	seawater concentration <sup>d</sup> ( $\mu\text{g/L}$ )	$\log K_D$ (L/kg)
V	11.2	1.84	6.78
Cu	0.895	0.49	6.26
U	3.36	2.77	6.08
Co	0.025	0.022	6.06
Ni	0.496	0.61	5.91
Zn	1.32	1.75	5.88
Fe	1.52	2.07	5.87
Mn	0.235	0.38	5.14
Cr	0.026	1.70	4.84
Ca	23.5	368 000	1.81
Mg	24.2	1 147 000	1.32

<sup>a</sup>Distribution coefficients ( $K_D$ ) are expressed as  $\log K_D$ . <sup>b</sup>Adsorption capacities were *not* normalized to a salinity of 35 to allow direct comparison between solution and adsorbent concentrations and calculation of  $\log K_D$ . <sup>c</sup>56-day adsorbent capacities were determined using one-site ligand saturation modeling of time-series measurements of adsorption capacity. <sup>d</sup>Measured filtered seawater concentration in the seawater exposure system. The values shown represent average values determined over approximately a 20 month period.

The log  $K_D$  value for the ORNL amidoxime-based adsorbent AF1 for uranium is 6.08, a value which indicates that the adsorbent has a very high affinity for uranium. For comparison, Johnson et al.<sup>27</sup> determined log  $K_D$  values for uranium with a number of conventional and nonporous adsorbents. They determined log  $K_D$  values ranging from 2.0 for a manganese dioxide impregnated strong anion exchange resin to a log  $K_D$  of 4.8 for a hydroxypyridinone ligand (HOPO) installed on self-assembled monolayers on mesoporous support (SAMMS) using Galveston Bay seawater in batch studies with radiotracers. The ORNL AF1 adsorbent also has a very high affinity for vanadium and several other trace elements (Table 2). The affinity of the ORNL AF1 adsorbent for calcium and magnesium is low, but the concentrations of these elements in seawater are high, resulting in a significant retention of these elements on the adsorbent (Table 1).

**3.3. Trace Element Contamination Control.** Illustrated in Figure 4 is a comparison of collections of ambient seawater,



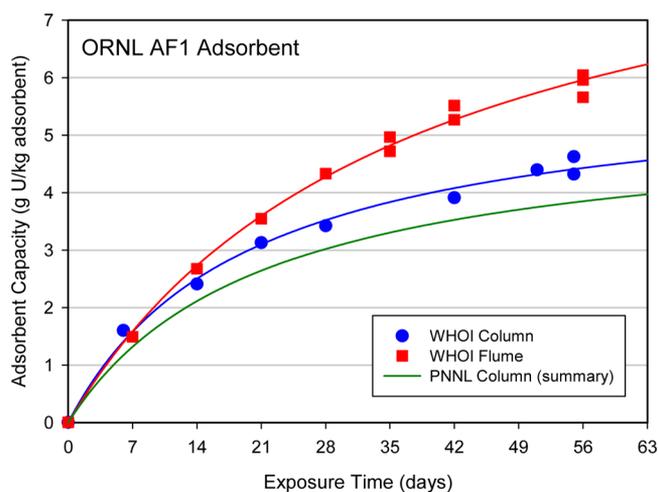
**Figure 4.** Comparison of trace element concentrations in filtered ambient Sequim Bay seawater with filtered seawater collected from the exposure system (feed seawater). The data represent approximately 72 collections of ambient seawater and 235 collections of feed seawater obtained between April 2014 and December 2015. Error bars represent 1 standard deviation about the average.

collected by hand, directly into acid-cleaned sample bottles, off a dock on Sequim Bay, with collections of the (filtered) seawater at a sampling point immediately before it enters into a flow-through column or a flume. The data comparison helps to illustrate the level of contamination that is imparted onto ambient Sequim Bay seawater by the water delivery system (pumps, storage tanks, PVC piping, exposure column or flume, and filtration units). The concentrations of uranium, vanadium, cadmium, and cobalt are nearly identical in both ambient and feed seawaters, suggesting no contamination exists for these elements. The most significant contamination occurs for zinc which is elevated in the feedwater 2.2 times over ambient levels. Chromium is elevated 87%, nickel 48%, and copper 40% over ambient seawater levels. Iron and manganese levels are actually lower in the feedwater than in Sequim Bay. This concentration reduction is likely due to oxidation and precipitation processes that take place in the storage reservoirs prior to delivery to the exposure systems.

The importance of the contamination needs to be visualized with respect to the affinity of the adsorbent to retain the contaminant (Table 1). For example, zinc is the seventh most abundant element the adsorbent retains by mass (2.1% Zn by mass) and sixth most abundant by molar percentage (1.1% Zn by

molar percentage). Hence, although zinc is significantly higher in the feedwater, its abundance in the adsorbent is not as significant as uranium (6.7% U by mass). Hence, reducing the zinc contamination would only marginally increase the retention of uranium on the adsorbent as a reduction in zinc would cause a shift in the equilibrium of all the elements on the adsorbent, not just uranium. The opposite effect would occur for iron and manganese if the concentrations were raised to represent Sequim Bay levels. The change due to increasing manganese would be minor because it is a minor component of the elements adsorbed on the adsorbent (Table 1). Collectively, conducting the testing of the adsorbent in ambient Sequim Bay seawater would result in reductions in adsorption capacity for U from the higher levels of iron and manganese and increases in adsorption capacity from reduction of the contaminants Zn, Cu, and Cr.

**3.4. Adsorbent Testing at Different Coastal Marine Locations.** Marine testing is being conducted at two other coastal locations, at the Woods Hole Oceanographic Institution (WHOI) and at the University of Miami's Broad Key Island Research Facility. These efforts were undertaken to characterize and confirm adsorbent performance determined at PNNL with another coastal marine environment with different oceanographic conditions. Illustrated in Figure 5 is a comparison of column and



**Figure 5.** Comparison of uranium adsorption capacity results for the ORNL AF1 adsorbent between column and flume exposures at Woods Hole Oceanographic Institution with flow-through column exposures at PNNL. The PNNL data are the same results as shown in Figure 3 for the AF1 adsorbent. All data have been normalized to a salinity of 35 psu, and the exposures were all at a temperature of 20 °C. Replicate samples were obtained at selected data points, providing an indication of the good reproducibility of the capacity determinations.

flume exposure methods at WHOI with the flow-through column testing at PNNL shown in Figure 3. One-site ligand saturation modeling results for these exposures are given in Table 3. These comparisons were all conducted with the ORNL AF1 adsorbent at a temperature of 20 °C.

The exposures conducted at WHOI produced significantly higher capacities than observed at PNNL. Fifty-six-day adsorption capacities in the WHOI flow-through column studies were 15% higher than the same studies at PNNL, and the flume exposures were 55% higher than the flow-through column studies at PNNL. Moreover, the flume results at WHOI are 35% higher than the flow-through column studies at WHOI. These regional differences in adsorption capacity cannot be explained

**Table 3. One-Site Ligand Saturation Modelling of the Experimental Data Illustrated in Figure 5**

experiment	saturation capacity <sup>a,b</sup> (g U/kg adsorbent)	56-day adsorption capacity <sup>a,b</sup> (g U/kg adsorbent)	half-saturation time <sup>b</sup> (days)
WHOI column	5.97 ± 0.27	4.43 ± 0.20	19.4 ± 2.4
WHOI flume	9.84 ± 0.48	5.96 ± 0.29	36.4 ± 3.7
PNNL column	5.30 ± 0.20	3.85 ± 0.14	21.1 ± 2.0

<sup>a</sup>Normalized to a salinity of 35 psu. <sup>b</sup>Predicted using one-site ligand saturation modeling.

by variations in the uranium concentration because all the data are normalized to a salinity of 35 psu. In addition, previous studies with many column and flume exposures at PNNL produced very similar results,<sup>13</sup> suggesting that the exposure method is not a likely reason for the difference between the column and flume results obtained at WHOI.

One possible explanation for the differences in U adsorption capacity is due to temporal or spatial variations in the concentrations of other elements (see Table 1) or water quality parameters such as dissolved organic carbon. The WHOI column study was conducted between December 2014 and January 2015, while the WHOI flume study was conducted in March and April of 2015. Both V and Fe adsorption capacity were elevated during the column study, opposite to that of U, consistent with an enhanced competition from V and Fe which lowered the U adsorption capacity. Seawater measurements of V concentrations observed for the WHOI column study were also higher ( $1.66 \pm 0.08 \mu\text{g/L}$ ) than that observed during the flume study ( $1.39 \pm 0.12 \mu\text{g/L}$ ), consistent with that observed on the adsorbent. While these data are limited in scope and warrant additional testing for confirmation, they nonetheless suggest that variations in seawater concentration of V, and to a lesser extent other elements, may have a large impact on U adsorption capacity.

Dissolved organic carbon (DOC) concentration is another factor which is known to affect the adsorption of elements from solution onto adsorptive materials.<sup>27–29</sup> The DOC concentration at WHOI during the flow-through column and flume studies were  $1.10 \pm 0.06 \text{ mg/L}$  and  $1.67 \pm 0.72 \text{ mg/L}$ , respectively. The average DOC background concentration in Sequim Bay seawater is  $0.89 \pm 0.19 \text{ mg/L}$ . One would assume that elevating DOC would result in lowering the adsorptive capacity of an adsorbent. Because the highest adsorptive capacity at WHOI was observed when DOC was higher, this argues against a significant impact from DOC on adsorption capacity. Supporting this hypothesis, adsorptive capacities obtained at Sequim Bay were lower than at WHOI, where DOC concentrations in Sequim Bay were lower than at WHOI. Organic material was also suggested not to play a significant role in the adsorption of uranium on a number of conventional and nanoporous adsorbents.<sup>27</sup> While this indirect evidence suggests that DOC is not important in adsorbing uranium from seawater on amidoxime-based polymeric adsorbents, a detailed investigation controlling critical adsorptive parameters is nonetheless warranted to reliably assess the impact of DOC on the adsorption of uranium from seawater.

**3.5. Marine Deployment Assessments.** Mining the sea for uranium at viable scales will require deployment of expansive “kelp-like farms” of adsorbent material that must be shown not to harm marine biota and the marine ecosystem. The program at PNNL has been investigating several key issues related to deployment of a farm of adsorbent material, including reduction in ocean currents from deployment of a farm of “kelp-like”

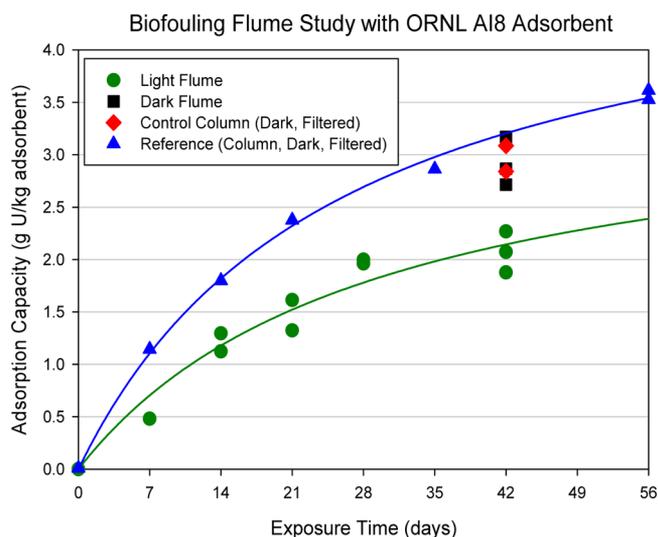
adsorbent material, and removal of uranium and other trace elements from a flow-field within a farm of adsorbent material.

Concern about reduction in coastal currents is being addressed by assessing the form drag from a braid adsorbent farm using hydrodynamic modeling. Wang et al.<sup>30</sup> applied the model to a 670 km<sup>2</sup> adsorbent farm with a spacing density of 1780 moorings/km<sup>2</sup>. They observed a reduction in ambient currents of 4–10%. This reduction is fairly minor compared to the reduction in currents through a kelp forest (up to 50%) and is not anticipated to have significant impact in the open ocean at the mooring densities used in this evaluation.

There is also concern that a commercial scale deployment of braided-mooring farms, which would cover a large area (~680 km<sup>2</sup>), could modify background oceanic uranium and other selected trace element concentrations. Not only could this result in unknown environmental impacts, but it would also affect the overall efficiency of the adsorbent farm, because the downstream part of the farm would be receiving already-depleted uranium waters. To address this concern, hydrodynamic model simulations of the concentration and distribution of uranium and trace elements within a farm of braided adsorbents as a function of deployment time, water depth, and farm density are currently being investigated. The rate of uranium uptake was temperature- and time-dependent based on information obtained from laboratory studies at PNNL with amidoxime-based polymeric adsorbents. Initial results show a maximum decrease in uranium concentration of only 0.3% with a farm of ~0.23 km<sup>2</sup>, a low-density placement of ~334 braids/km<sup>2</sup>, a current velocity of 20 cm/s, and a water temperature at 30 °C. Under these operational conditions, the change in uranium concentration within the flow field is very small. This current assessment was conducted on a very small field (0.23 km<sup>2</sup>) with low-density spacing compared to the field size (~100 km<sup>2</sup>) that would be required to produce viable amounts of uranium for energy production.<sup>31,32</sup> Increasing the density and size of the farm will of course increase the uptake of uranium in the flow-field.

**3.6. Biofouling Investigations.** The deployment of a kelp-like structure into the marine environment, like the braided adsorbent materials being developed to extract uranium from seawater, provides a surface to which a wide variety of marine organisms can attach. This process is referred to as biofouling.<sup>33–35</sup> A major effort in the development of the uranium adsorbent technology at PNNL is to test the performance of the uranium adsorption materials in natural seawater under realistic marine conditions, including unfiltered seawater containing marine biofouling organisms. When the ORNL braided adsorbent A18<sup>36</sup> was exposed to raw seawater in a flume in the presence of light (to allow photosynthetic growth), a decrease in U adsorption capacity of up to 30% was observed after 42 days of exposure due to biofouling (Figure 6).<sup>15</sup> An identical raw seawater exposure with no light exposure showed little or no impact on adsorption capacity from biofouling. These results suggest that deployments below the photic zone would mitigate the effects of biofouling, resulting in greater yields of uranium extraction from seawater, though this needs to be considered relative to reduced adsorption in generally colder waters at depth.

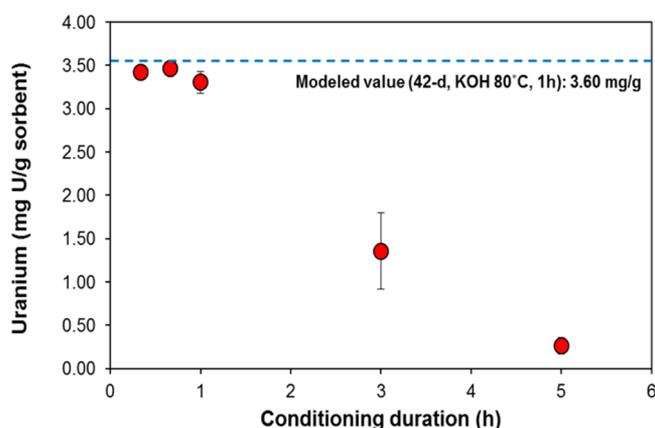
**3.7. Toxicity Testing.** To be able to deploy a large-scale farm of adsorbent material into the marine environment, it will first be necessary to demonstrate that the material is not harmful to marine life or the marine environment. PNNL has been conducting toxicity testing of adsorbent materials produced by program participants using the “Microtox” aquatic toxicity test.<sup>16</sup> The test is being applied to direct contact with solid adsorbents



**Figure 6.** Comparison of U capacities as a function of time in a flume exposure experiment with the ORNL adsorbent AI8. Shown are four experiments: darkened flume to minimize photosynthetic growth (squares), a flume exposed to light to stimulate growth (circles), a flow-through column exposure with AI8 conducted with filtered seawater ( $0.45 \mu\text{m}$ ) to exclude biofouling organisms (diamonds), and for reference a set of absorption data (triangles) from an experiment that was conducted with the ORNL AI8 adsorbent in a flow-through column exposure with filtered ( $0.45 \mu\text{m}$ ) seawater prior to the current experiment.

and aqueous column effluents containing adsorbent material. The Microtox assay measures the luminescence of the bioluminescent marine bacterium *Aliivibrio fischeri* (ATCC 49387), an indicator of metabolism in the organism, after a 30 min exposure to a test sample.<sup>37</sup> No toxicity was observed with column effluents of any adsorbent materials tested to date.<sup>16</sup> Toxicity could be induced with some nonamidoxime-based adsorbents only when the ratio of solid adsorbent to test media was increased to part per thousand levels. The sustained seawater contact with adsorbent ( $\sim 30$  min) necessary to illicit toxicity at this high adsorbent:seawater ratio ( $\sim 1$  kg adsorbent/1 g of seawater) are not likely to be encountered in the marine environment under anticipated deployment conditions.

**3.8. Adsorbent Characterization.** **3.8.1. FTIR and SEM Investigations.** It is well-documented that conditioning of polymer fiber adsorbents grafted with amidoxime and carboxylic acid groups with alkaline media prior to use is necessary to achieve optimal adsorption performance.<sup>8,20,38–45</sup> Spectroscopic and imaging techniques can be used to examine changes in the abundance of key functional groups grafted onto the polymer fiber and in physical appearance as a result of conditioning treatments and extended exposures in natural seawater.<sup>12,46</sup> Fourier transform infrared spectrometry (FTIR) spectra reveal that conditioning the ORNL adsorbent AF1 with 2.5% KOH (0.44 M KOH) at  $80^\circ\text{C}$  for periods of time ranging between 20 min and 5 h removes the proton from the carboxylic acids and also converts the amidoxime groups to carboxylate groups in the adsorbent.<sup>46</sup> The degree of conversion of the amidoxime group to carboxylate groups continuously increases with conditioning time, with optimal uranium adsorption capacities after 42 days of exposure in natural seawater when the conditioning time was 20–60 min (Figure 7).<sup>12,46</sup> With prolonged KOH treatment ( $>1$  h) at  $80^\circ\text{C}$ , SEM imaging shows that physical damage to the adsorbent material occurs which can lead to a significant



**Figure 7.** Uranium adsorption capacity of the ORNL adsorbent AF1 after 42 days of exposure in natural seawater as a function of the initial KOH conditioning time in 2.5% KOH at  $80^\circ\text{C}$ . The blue line represents the predicted adsorption capacity of the AF1 adsorbent determined from several previous measurements with the AF1 adsorbent using on-site ligand saturation modeling after 42 days of exposure.

reduction in the adsorbent's uranium adsorption capability in real seawater during extended exposure times ( $>21$  days).<sup>46</sup> Moreover, FTIR evidence shows that conversion of amidoxime groups to carboxylate groups also occurs during 42 days of seawater exposure, resulting in a loss of about 20% of the amidoxime groups.<sup>12</sup>

**3.8.2. Development of Novel Nanostructured Sorbent Materials.** A range of novel and commercial sorbent materials were quantified for chemical affinity, adsorption kinetics, and capacities with the goal of providing improved performance characteristics for uranium recovery from seawater. Sorbent materials with high affinity surface chemistries for uranium such as diphosphonic acid, phosphonic acids, and hydroxypyridinones installed upon high surface area nanostructured supports provided superior performance for the capture of uranium from seawater.<sup>17</sup> Select commercial phosphorus-based sorbent materials, such as Ln Resin and Diphonix Resin, also performed well. Some inorganic sorbent materials such as manganese, iron, and titanium oxides have been reported to be effective for the collection of uranium from seawater. Recent work found that high surface area nanostructured manganese and iron oxides to be very effective for the collection of uranium from seawater, and the best performing inorganic materials were composed of composite iron manganese oxides.<sup>47</sup> The prototype nanostructured sorbent materials, with both organic and inorganic surface chemistries, have similar or better capacities than amidoxime materials and typically much faster kinetics. The faster kinetics enable much higher production levels (uranium produced as a function of time) potentially improving economics and alleviating issues such as biofouling that become a problem for long-duration marine exposures.

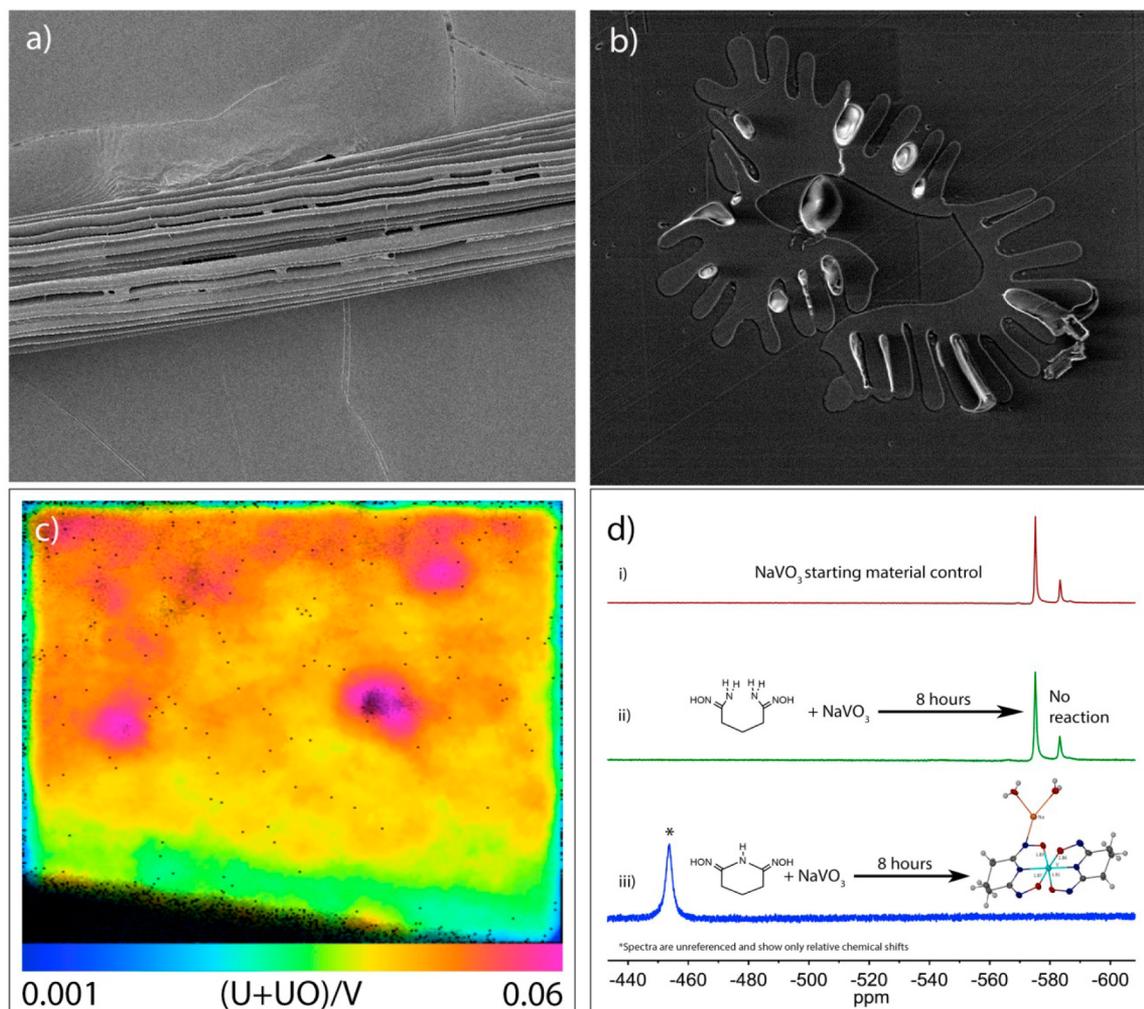
Various alternative configurations of the preferred nanostructured sorbent materials were explored for the trace level extraction of uranium from large seawater volumes. Efforts focused on the means to minimize problems such as back-pressure and chemical and biological fouling while enabling rapid high-volume processing. Prototype composite thin films composed of a polymer binder and preferred sorbent materials demonstrated excellent performance for uranium collection from seawater with the rapid kinetics enabling fast collection and resulting in short processing cycles with high uranium recovery rates from seawater.<sup>17</sup> Recovery of the U from the nanostructured

sorbents, from both organic and inorganic, could be achieved with carbonated or acidic stripping solutions. While these initial evaluations are promising, additional work with natural seawater are needed to optimize and confirm initial findings and determine the actual viability of using these novel materials and methods described to achieve recovery of uranium and other trace minerals from the sea.

**3.8.3. Advanced Imaging Investigations.** Advanced imaging and chemical characterization instruments available at PNNL and ORNL are being used to characterize the binding of major, minor, and trace elements in seawater to the amidoxime functionalized HDPE polymers developed at ORNL (Figure 8). Secondary ion mass spectrometry (SIMS) and nanoSIMS are being used to map the distribution of specific ionic species along the length of the modified HDPE polymer. Scanning electron microscopy (SEM) provides a view of the structure of the polymer fibers at length scales ( $<1 \mu\text{m}$ ) more closely approaching the regime where chemical interactions are taking place. Finally, NMR, both solution-phase and solid-state, allows determination of the affinity and specificity of the reactive amidoxime binding ligands (mono- and bis-amidoxime as well as the cyclic imidioxime) toward primary seawater species (e.g., Ca, Mg, U, V, Fe, Cu, Ni).

SIMS and nanoSIMS analysis showed a large amount of V, Ca, and Fe bound to the polymer support in addition to relatively smaller amounts of U. This is consistent with findings from elsewhere in the uranium from seawater program and further suggests that an understanding of how these species effect the ability of U to bind to the sorbent in addition to how effectively the U can be recovered from the sorbent through various elution conditions under development elsewhere in the program. The results from the SIMS analysis suggest that there are a number of heterogeneous binding modes along the fiber resulting in islands of high concentrations of U as well as other constituents along the fiber length. NMR experiments ( $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{51}\text{V}$ , and  $^{14/15}\text{N}$ ) with small molecule ligands that represent the monoamidoxime, bis-amidoxime, and cyclic imidioxime have revealed that the acyclic monoamidoxime binds U much more readily than V. However, the cyclic species, which can form along the polymer backbone, binds V very tightly.<sup>48</sup>

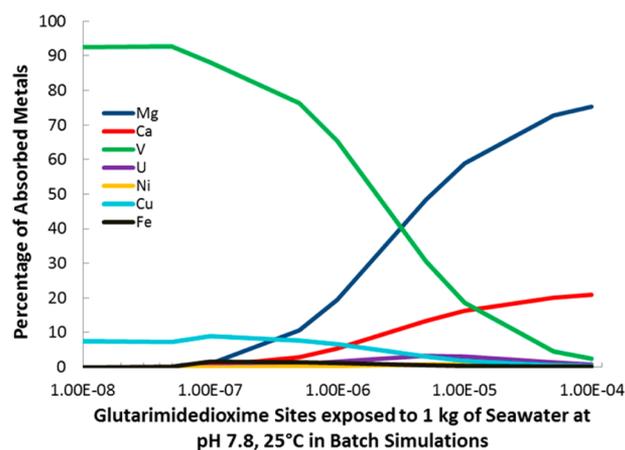
**3.8.4. Thermodynamic Modeling.** Thermodynamic modeling of the major seawater species retained on amidoxime-based adsorbents was performed using the geochemical modeling program PHREEQC to help improve our understanding of the selectivity of the adsorption process.<sup>49</sup> Seawater was modeled



**Figure 8.** (a) Helium ion microscopy (HIM) of the AI8 amidoxime-based polymer fiber from ORNL. (b) Scanning transmission electron microscopy (STEM) image of the cross-sectional area of the AI8 fiber after sectioning on an ultramicrotome. (c) nanoSIMS image of the AI8 fiber showing the ratio of total U to V found along the fiber where there are “hotspots” of U formed along the length of the fiber. (d)  $^{51}\text{V}$  NMR spectra (unreferenced) that show the preferential binding of (i)  $\text{NaVO}_3$  by the (iii) cyclic imidioxime over the (ii) acyclic ligand. These spectra were taken in  $\text{D}_2\text{O}$  and are unreferenced. The crystal structure from iii is an actual solved structure for the 2:1 binding motif of the cyclic imidioxime with V.

using Pitzer's specific ion interaction parameters, and the composition was defined by Pilsen<sup>50</sup> and corrected to 31 psu salinity.<sup>51</sup> Minor species concentrations (Fe, Cr, Cu, Ni, Pb, V) were included based on assays performed at MSL. Standard thermodynamic parameters were obtained from the MINTEQA database available with PHREEQC and supplemented with the latest values for uranium species from the OECD-NEA database.<sup>52</sup> Amidoxime was treated as an ion-exchange material within the model, and thermodynamic parameters were obtained from studies on the complexation of the glutarimidedioxime monomer in collaboration with the Rao research group at Lawrence Berkeley National Laboratory.<sup>11,53–58</sup>

One of the current hypotheses for reduction in uranium binding in natural seawater is the competition for amidoxime binding sites by more highly concentrated calcium and magnesium ions, and by more tightly binding vanadium species. To test this, modeling of the binding of Ca, Mg, Fe, Ni, Cu, U, and V from batch interactions with seawater was performed across a variety of concentrations of the amidoxime binding group, representing the range from a large excess of amidoxime groups (determined by the remaining concentration of protonated binding groups) and a highly limited concentration of amidoxime groups relative to the seawater constituents. The relative concentration of the bound metals was then determined from the simulations, and the results appear in Figure 9.



**Figure 9.** Results of simulations of ion exchange with bound glutarimidedioxime groups and natural seawater for multiple concentrations of glutarimidedioxime sites.

The results of the simulations provide unique insight into the local physical binding situation. In the highly limited case ( $1 \times 10^{-8}$  binding sites/kg seawater), vanadium heavily outcompetes other ions for the amidoxime sites, with only a small amount of copper making up the balance of the bound metals. Relative to the long-time scale experiments performed at MSL, this highly limiting case represents the situation in which the binding sites on the adsorbent fiber are all located in highly accessible locations with good local mixing, where they are constantly fed fresh seawater.

In contrast, the case in which a large excess of binding sites exists ( $1 \times 10^{-4}$  binding sites/kg seawater) represents the case in which stagnant areas are present within the fiber structure and access to new binding sites is controlled by diffusion from the surface or fresh flowing areas. In this case, magnesium and calcium dominate the total percentage of metals bound to the sorbent; however, this is only because of the large total quantity of these ions in solution. Examination of the solution concentration

at the end of the simulations shows that vanadium, copper, iron, uranium, and nickel (in order) are a small percentage of the metals absorbed because they are depleted from the solution, and that weakly binding calcium and magnesium are adsorbed in high concentrations only because of the excess of binding sites. This result suggests a stratification of the bound ions in the amidoxime functionalized fibers.

When the simulation results are compared with the experimental results presented in Table 1, the concentrations in the recovered experimental fibers appear to fall within the  $5 \times 10^{-6}$  to  $1 \times 10^{-5}$  binding sites/kg seawater range, which suggests significant diffusional limitations on the seawater binding. This finding is in agreement with a previous investigation with flow-through experiments in columns in which adsorbent kinetics were attributed to mass-transfer limitations arising from interparticle diffusion through the immobilized fibrous adsorbent in a confined space.<sup>7</sup> However, this region also shows the highest percentage recovery of uranium from the simulation, suggesting that the fiber may already be optimized relative to the Sequim Bay water chemistry. Regional or seasonal variations in the seawater chemistry, such as those observed at WHOI, may shift this optimization.

#### 4. SUMMARY AND CONCLUSIONS

The activities at PNNL's Marine Science Laboratory in Sequim in the development of technology to extract uranium from seawater are focused on understanding how uranium adsorptive materials perform and behave in marine systems under realistic conditions. A major focus of the marine testing program is to determine adsorptive capacity and kinetics in natural seawater. The technology has steadily improved over three years since the program began testing such that the current formulations of amidoxime-based adsorbents prepared by ORNL have a 56-day adsorption capacity that is 18% higher than the original formulations produced in 2012 (3.9 versus 3.3 g U/kg adsorbent). Japanese scientists have reported adsorption capacities for amidoxime-based adsorbents deployed in seawater ranging from 0.6 to 1.5 g U/kg adsorbent after 7–30 days of exposure.<sup>8,25,59</sup> One-site ligand saturation modeling predicts that the ORNL AF1 adsorbent would retain 1.3 g U/kg adsorbent after 7 days and 3.2 g U/kg adsorbent after 30 days of exposure. These adsorption capacities for the ORNL adsorbent are approximately 2 times higher than that reported by the Japanese scientists for amidoxime-based polymeric adsorbents for similar exposure periods. This comparison does not take into account differences in adsorption capacity due to temperature or water quality parameters (e.g., DOC) which we are aware affect adsorption capacities.<sup>27–29</sup>

Conducting testing investigations in different coastal marine environments helps to critically evaluate and demonstrate the effectiveness and robustness of the adsorption technology and provides insight into adsorption mechanisms with a contrasting coastal marine environment. The significant capacity differences observed between testing of a common batch of adsorbent material both off the coast of Washington and Massachusetts, using a common testing protocol, points to the critical role that variation in the concentration of the minor elements (e.g., V, Fe, Cu, and Zn) and perhaps water quality parameters (e.g., DOC) play in the retention of uranium from seawater at a common salinity.

Extraction of uranium from seawater at viable scales will necessitate deployment of expansive “kelp-like farms” of adsorbent material that must be shown not to harm marine biota and the marine ecosystem. Investigations at PNNL have

demonstrated that (1) deployment of an adsorbent farm will not significantly impact ocean currents or (2) reduce uranium concentrations within the flow-field to levels that will reduce the performance of the adsorbents, if the farm density is <334 moorings/km<sup>2</sup>; (3) adsorbents are not toxic, unless the ratio of solid adsorbent to test media was increased to part per thousand levels, a case not likely to be encountered in the marine environment during an adsorbent deployment.

Studies to characterize the amidoxime-based adsorbent material and its interaction with seawater have revealed the following: (1) The treatment of amidoxime-based adsorbents with alkaline solutions prior to use in seawater has a significant impact on adsorption capacity in extended seawater deployments. (2) There are a number of heterogeneous binding modes along AF1 adsorbent produced by ORNL resulting in islands of high concentrations of U as well as other constituents along the fiber length. (3) The acyclic monoamidoxime binds U much more readily than V, while the cyclic species, which can form along the polymer backbone, binds V very tightly. (4) When amidoxime binding sites are highly limited ( $1 \times 10^{-8}$  binding sites/kg seawater), vanadium heavily out-competes other ions for the amidoxime sites. In contrast, when there is a large excess of binding sites exists ( $1 \times 10^{-4}$  binding sites/kg seawater), magnesium and calcium dominate the total percentage of metals bound to the sorbent.

Collectively, the marine testing and characterization results provide a better understanding of the interactions between seawater and the adsorptive material enabling enhancements in the design and development of new materials that are more efficient, reusable, and ultimately provide better uranium recover from seawater, all features that lead to a reduction in the overall cost of extracting uranium from seawater.<sup>9,32,60,61</sup>

## ■ ASSOCIATED CONTENT

### ● Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: [10.1021/acs.iecr.5b03649](https://doi.org/10.1021/acs.iecr.5b03649).

Additional data and photos of experimental setup (PDF)

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### Notes

The authors declare no competing financial interest.

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