

***Milestone Report –
Demonstrate Braided Material
with 3.5 g U/kg Sorption
Capacity Under Seawater
Testing Condition***

***(Milestone M2FT-15OR0310041 –
1/30/2015)***

Fuel Cycle Research & Development

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SUMMARY

This report describes work on the successful completion of Milestone M2FT-15OR0310041 (1/30/2015) entitled, “Demonstrate braided material with 3.5 g U/kg sorption capacity under seawater testing condition”. This effort is part of the Seawater Uranium Recovery Program, sponsored by the U.S. Department of Energy, Office of Nuclear Energy, and involved the development of new adsorbent braided materials at the Oak Ridge National Laboratory (ORNL) and marine testing at the Pacific Northwest National Laboratory (PNNL). ORNL has recently developed four braided fiber adsorbents that have demonstrated uranium adsorption capacities greater than 3.5 g U/kg adsorbent after marine testing at PNNL. The braided adsorbents were synthesized by braiding or leno weaving high surface area polyethylene fibers and conducting radiation-induced graft polymerization of itaconic acid and acrylonitrile monomers onto the braided materials, followed by amidoximation and base conditioning. The four braided adsorbents demonstrated capacity values ranging from 3.7 to 4.2 g U/kg adsorbent after 56 days of exposure in natural coastal seawater at 20 °C. All data are normalized to a salinity of 35 psu.

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ACRONYMS

Ads.	adsorbent
AO	amidoximation
°C	degree Celsius
cm	centimeter
DI	deionized
DMF	dimethylformamide
dia.	diameter
DOG	degree of grafting
EB	electron beam
g	gram
HDPE	high density polyethylene
ICP-OES	inductively coupled plasma optical emission spectroscopy
in	inch
kg	kilogram
kGy	kilogray
KOH	potassium hydroxide
L	liter
µm	micron
M	molar (moles per liter)
MeV	million electron volts
mg	milligram
min.	minute
ml	milliliter
MΩ	megaohm
MSL	Marine Sciences Laboratory
ORNL	Oak Ridge National Laboratory
PNNL	Pacific Northwest National Laboratory
PLA	polylactic acid
ppb	parts per billion
ppi	picks per inch
ppm	parts per million
psi	pounds per square inch
PTFE	polytetrafluoroethylene
PVC	poly(vinyl chloride)
PSU	practical salinity units
RIGP	radiation-induced graft polymerization
RT	room temperature
s	second
THF	tetrahydrofuran
UHMWPE	ultrahigh molecular weight polyethylene
Vol.	volume
wt%	weight percent
w/w	weight/weight

FUEL CYCLE RESEARCH & DEVELOPMENT

Milestone Report - Demonstrate Braided Material with 3.5 g U/kg Sorption Capacity Under Seawater Testing Condition

(Milestone M2FT-15OR0310041 – 1/30/2015)

1. INTRODUCTION

This report describes the development of ORNL's braided and leno woven adsorbents and marine testing activities conducted at Pacific Northwest National Laboratory (PNNL). The purpose of this document is to report on the successful completion of Milestone M2FT-15OR0310041 (1/30/2015) entitled, "Demonstrate braided material with 3.5 g U/kg sorption capacity under seawater testing condition".

The world's oceans represent a vast and as yet untapped source of uranium that is readily available to the United States.[1] Uranium, at approximately 3.3 ppb, is considered a conservative element in seawater, meaning its concentration varies in direct proportion to changes in salinity. Since seawater is slightly basic ($\text{pH } 8.0 \pm 0.4$), uranium exists primarily as $[\text{UO}_2(\text{CO}_3)_3]^{4-}$. It is estimated that the total sum of uranium in seawater is approximately 4.5 billion metric tons.[2] This amount is approximately 1000 times larger than the known amount of uranium from mineral reserves on land.[3] This reserve, combined with a suitable production cost for the extraction of uranium, can contribute to the growing international nuclear industry. Researchers in many countries—including the United States,[4-6] Japan,[7-9] Great Britain,[2] Germany,[10, 11] Russia, China,[12] India,[13] South Korea,[14] Turkey,[15] and others—have been inspired to develop adsorbents to recover this untapped supply of uranium contained in world's oceans since the 1960s.

2. PREPARATION OF BRAIDED AND LENO WOVEN ADSORBENTS

2.1 Manufacture of Polyethylene Fiber and Braiding and Leno Weaving of Adsorbents

The adsorbents were prepared by melt-spinning high surface area, hollow-gear-shaped polyethylene fibers at Hills, Inc., using polylactic acid (PLA) as the second polymer, then braided at Steeger USA or leno woven at Philadelphia University. The braids were made with the #17 polyethylene fibers (Aspun 6835) and contained four unidirectional tri-axial fibers in the middle "spine" section, fiber tow densities of 5 or 25 picks per inch (ppi) in the loop sections and were approximately 8-11 inches wide. The braiding machine and a representative example of a braid made at Steeger USA are shown in Figure 1.



Figure 1. Braiding machine (left) and a representative braid made at Steeger USA (right).

The leno woven fabrics were made with #8 polyethylene fibers (Aspun 6850) and were woven in a half leno, single cloth version. These fabrics were composed of two leno woven fiber tow pairs in the middle “spine” section (total of 4 unidirectional tow yarns), a plain weave on the outer edges of the loop sections (removed after weaving) and each fabric was approximately 12-inches wide. The leno weaving machine and the half leno single cloth that was made at Philadelphia University are shown in Figure 2.



Figure 2. Leno weaving machine (left) and the L2 half leno single cloth made at Philadelphia University (right).

2.2 Irradiation and Grafting of Braided and Leno Woven Adsorbents

Prior to irradiation of the braids and leno woven fabrics, the PLA polymer was removed by submerging the fabrics in excess tetrahydrofuran (THF) at 60°C overnight. This process was repeated three times, and the fibers were then filtered and dried under vacuum at 50°C. After drying, the fabrics were secured on each end with polypropylene plastic ties to prevent unravelling, and were cut into individual samples. The samples were then pre-weighed and placed inside a plastic glove bag and sealed under nitrogen in double-layered plastic bags. The bags were then put inside an insulated Styrofoam® container and placed on top of a bed of dry ice pellets, then sealed with a layer of cardboard on top of the container. The fibers were irradiated for 16 passes under the electron beam to a dose of approximately 150-200 kGy using 4.4-4.8 MeV electrons and 1 mA current from an RDI (Radiation Dynamics Inc.) Dynamitron electron beam machine. The total irradiation time was approximately 22 minutes.

The irradiation and grafting activities were conducted off-site at NEO Beam— Mercury Plastics, Inc. in Middlefield, Ohio. Figure 3 shows the electron beam set-up for irradiating the fabrics, which shows the sealed Styrofoam® insulated box, containing dry ice and several fabric

samples. The insulated box was positioned on top of a computer-controlled, screw-driven, translating table and placed underneath the 4-ft-wide scan horn of the electron beam machine that is contained within a concrete vault. During irradiation of the fibers the speed of the translating table was approximately 0.54 in/s.



Figure 3. Electron beam set-up used for irradiating braids and leno woven fabrics.

After irradiation, the fabrics were immersed in flasks containing previously de-gassed AF1 grafting solutions. The flasks were then placed in an oven at 60–70°C for 18–20 hours for grafting. The braids were grafted in 1000 ml Erlenmeyer reaction flasks, whereas the leno woven fabrics were grafted in 950 ml Ace-Glass pressure bottles. After the grafting reaction was complete, the fabrics were drained from the solution and washed with dimethylformamide (DMF) to remove any monomers or co-polymer by-products. The fibers were then washed with methanol to remove the DMF and dried under vacuum at 50–60°C. The grafted fabrics were weighed to determine the % degree of grafting (%DOG). A summary of the four braided and leno woven AF1 adsorbents are shown on Table 1.

Table 1. Description of ORNL's AF1 braid and leno woven adsorbents.

AF1 Braided/Leno Woven Adsorbents	Fabric type	Fiber no.	Graft time (hrs.)	% DOG
AF1B17-5ppi	Braid-5ppi	#17	20	250
AF1B17-25ppi	Braid-25ppi	#17	20	271
AF1L2R1	Half Leno	#8	18	410
AF1L2R2	Half Leno	#8	19	319

2.3 Amidoximation and KOH Conditioning of Braided and Leno Woven Adsorbents

Before amidoximation of the braided and leno woven adsorbents was done, they were cut into samples weighing approximately 3 to 13 g and secured on each end of the braid with polypropylene plastic ties. The linear mass density for the dried braided and leno woven samples before amidoximation were approximately 2 g/inch and 5 g/inch, respectively. Amidoximation of the adsorbents was conducted using 10 wt% hydroxylamine hydrochloride in 50:50 (w/w) water/methanol (previously neutralized with KOH) and heated at 80°C for 24 hours in an oven. The samples were then filtered, and the process was repeated two more times for a total of 72 hours.

The reaction vessels used for amidoximation consisted of 950 ml or 1800 ml Ace-Glass® pressure bottles (rated at 60 psi maximum pressure at room temperature (RT)) and polytetrafluoroethylene (PTFE) screw tops. Care was taken to prevent floating of the adsorbent samples by wrapping several hollow cylindrically shaped Teflon® spacers (i.e., 6 x 0.5-inch dia. x 0.75-inch long) around the adsorbent samples using one fiber tow of ultrahigh molecular weight polyethylene (UHMWPE) fibers. After amidoximation the samples were washed under vacuum filtration with deionized water followed by a methanol rinse and dried at 50 °C under vacuum. Table 2 provides a summary of the amidoximation conditions and Figures 4 and 5 show the adsorbents after the amidoximation reaction.

Table 2. Summary of amidoximation (AO) conditions for braided and leno woven adsorbents.

Sample ID	Dry weight before AO (g)	Approx. dry length before AO (in.)	Vol. of AO soln. every 24 hours (ml)	Dry weight after AO (g)	% weight gain after AO	mg ads./ml AO soln. (3X)
AF1B17-5PPI	3.2	1.6	800	4.1	28.1	4.0
AF1B17-25PPI	4.7	2.4	800	6.0	27.7	5.9
AF1L2R1	10.1	2.0	1400	12.7	25.7	7.2
AF1L2R2	12.7	2.5	1400	16.0	25.9	9.1



Figure 4. Braided adsorbents after amidoximation reaction.

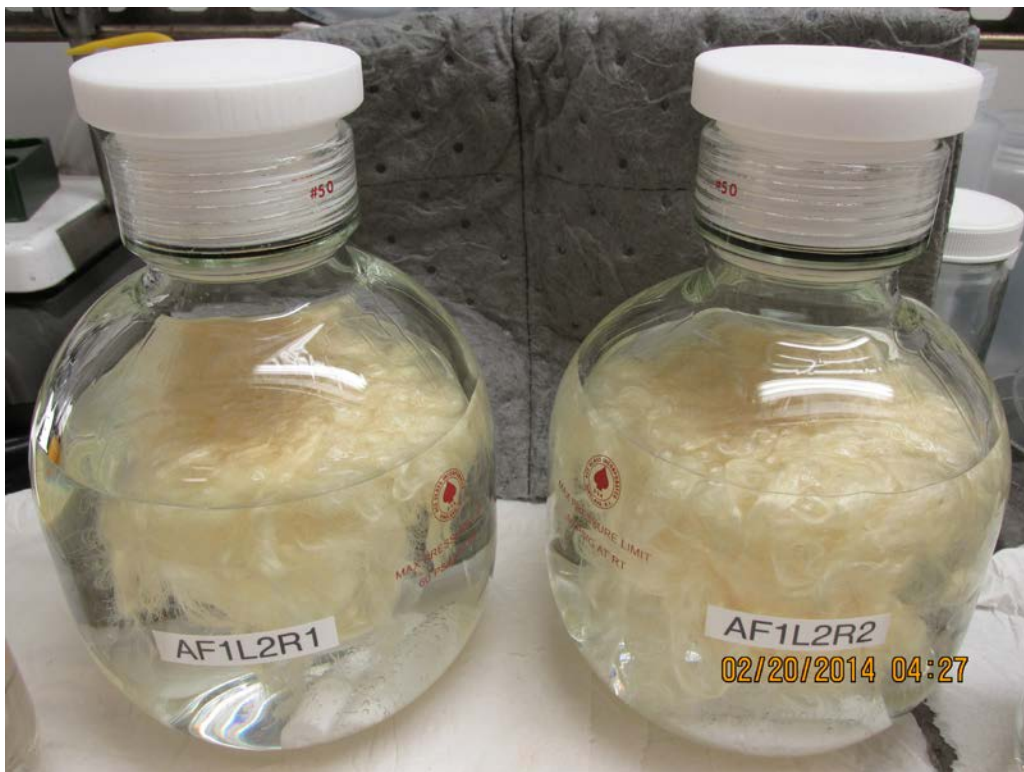


Figure 5. Leno woven adsorbents after amidoximation reaction.

2.4 Laboratory Screening of Braid and Leno Woven Adsorbents at ORNL

Before sending the adsorbents to PNNL, small samples of each of the dried amidoximated braided and leno woven fabric adsorbents were KOH-conditioned and tested at ORNL using the laboratory screening protocol described below in order to determine their uranium adsorption capacity.

2.4.1 KOH Conditioning

Approximately 15 mg of each amidoximated braided and leno woven fabric adsorbent was added to a flask containing 15 mL of 2.5 wt % KOH and heated for 3 hours at either 70 or 80°C. The fibers were then filtered using a vacuum filtration system with a low extractable borosilicate glass holder through a hydrophilic polyethersulfone membrane with low extractable and washed with 18.2 MΩ water until the pH of the excess water in the fiber was neutral. This process was done while keeping the adsorbent wet at all times. This is because, in earlier studies, it was found that if the fibers dried out, the capacity would significantly decrease.

2.4.2 Laboratory Screening Protocol of Braid and Leno Woven Adsorbents at ORNL

Since typical capacity determinations with real seawater take 30–60 days to complete, a rapid screening protocol was developed that contains a higher level of uranium to quickly and efficiently determine the uranium adsorption capacity. Normal seawater contains 140 ppm

bicarbonate ions, 10,500 ppm sodium ions, 19,000 ppm chloride ions, and 3.3 ppb uranium as the tricarbonat complex $\{[\text{UO}_2(\text{CO}_3)_3]^{4-}\}$ with a pH of 7.5–8.4. The test solutions that are used in our laboratory screening protocol contained 140 ppm bicarbonate ions from sodium bicarbonate, 10,516 ppm sodium ions and 16,136 ppm chloride ions from sodium chloride, and 7–8 ppm uranium ions from dissolving uranyl nitrate hexahydrate in 18.2 megaohm water at a pH of approximately 8. A sample of the solution was collected prior to sorbent addition to determine the initial uranium concentration before the adsorption experiment. Each of the KOH-conditioned braided adsorbent samples was then equilibrated with 750 ml test solutions for 24 hours at room temperature with constant shaking at 250-500 rpm. Previous testing determined that these conditions were sufficient for the fibers to reach equilibrium within 24 hours. After shaking was completed, an aliquot of each solution was put into a 12-mL plastic cap vial for uranium analysis via inductively coupled plasma optical emission spectroscopy (ICP-OES). The initial and final solutions were then analyzed using a Perkin Elmer Optima 2100DV ICP-OES. Using the difference in uranium concentration of the solution, the uranium adsorption capacity is determined, using Eq. (1).

$$\text{Uranium adsorption capacity} = \left(\frac{\text{initial Uranium conc. (mg/L)} - \text{final Uranium conc. (mg/L)}}{\text{g of dry adsorbent}} \right) \times L \text{ solution}$$

The ICP-OES was calibrated using 6 standard solutions ranging from 0-10 ppm, which were prepared from a 1000 ppm uranium in 5 wt.% nitric acid stock solution, and a linear calibration curve was obtained. A blank solution of 2–3 wt. % nitric acid was also prepared and washouts were monitored between samples to ensure no uranium was carried over into the next analysis. In addition, 5 ppm Yttrium in 2 wt% nitric acid was used as an internal standard, which was prepared from 1000 ppm stock solution (procured from High-Purity Standards, North Charleston, USA). The sample solution and the internal standard solution were introduced by using the Non HF Internal Standard Addition Kit for ICP-OES (Perkin-Elmer) as shown in Figure 6 below.

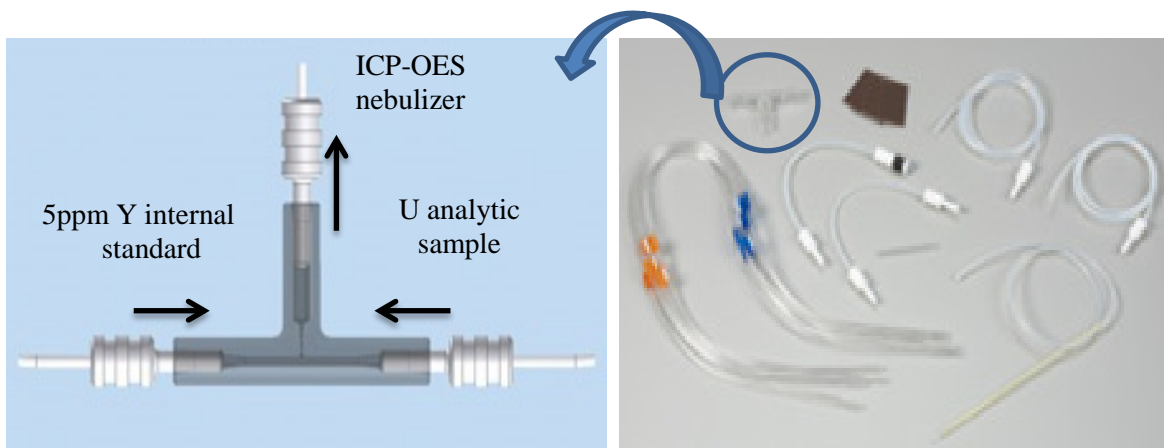


Figure 6. Internal Standard Addition Kit for ICP-OES (Perkin-Elmer).

To ensure accuracy and reproducibility of the measurements (and no sample carryover), the following protocol was used after calibration.

- A. Analysis of the uranium solution (described above) before fiber was added.

- B. Analysis of the sample solutions was conducted and, between each sample, the blank solution was analyzed to ensure no uranium was carried over into the next analysis.

The uranium adsorption capacity results for the braided and leno woven adsorbents are shown in Figure 7 and ranged from 168 to 193 g U/kg adsorbent. As shown in the figure, there were differences in the capacities of the adsorbents that were KOH conditioned for 3 hours at 70°C (red) versus 80°C (blue). Investigations are currently on-going at ORNL and PNNL to optimize the KOH conditioning parameters.

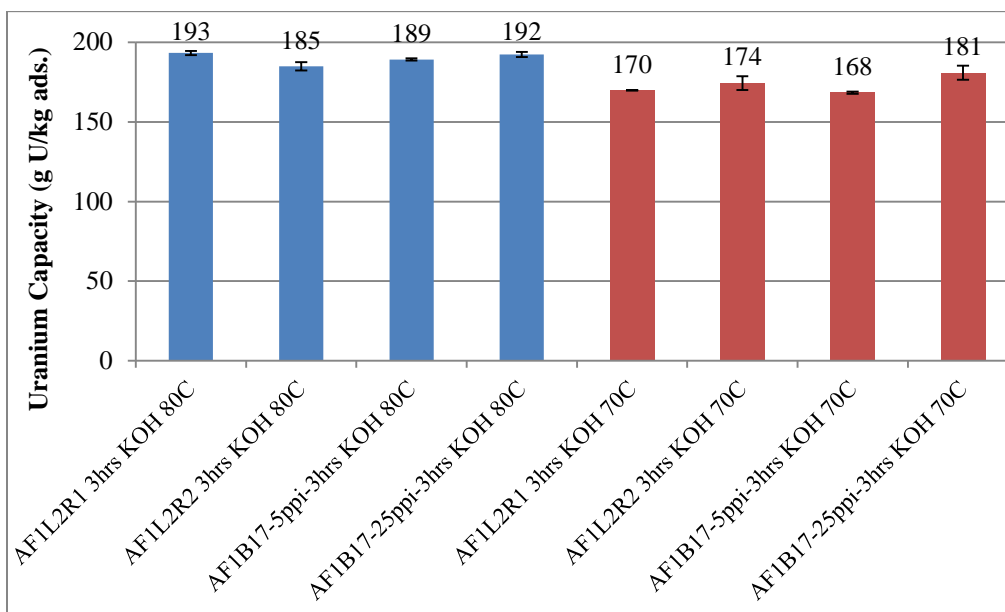


Figure 7. Uranium adsorption capacity results on braided and leno woven adsorbents from laboratory screening at ORNL.

After laboratory screening was completed the braided and leno woven adsorbent samples (Figures 8-11) were shipped to PNNL for KOH conditioning and marine testing in two different flumes of seawater.

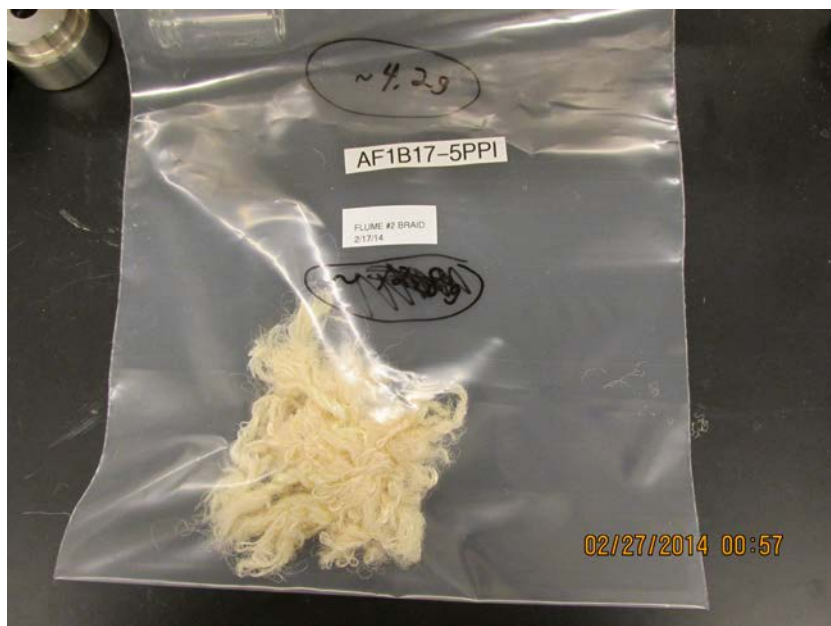


Figure 8. Braided adsorbent (AF1B17-5ppi) after AO and washing/drying.

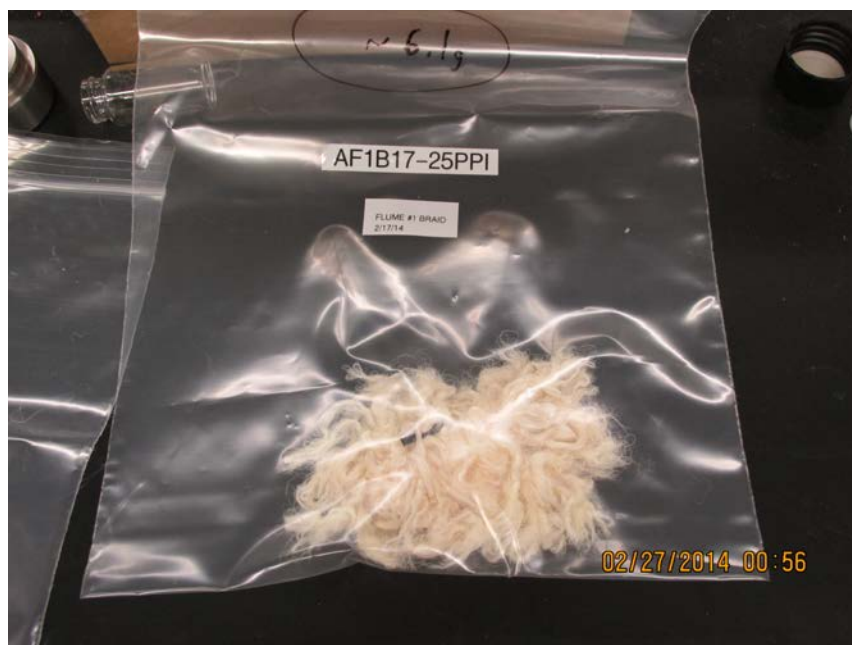


Figure 9. Braided adsorbent (AF1B17-25ppi) after AO and washing/drying.

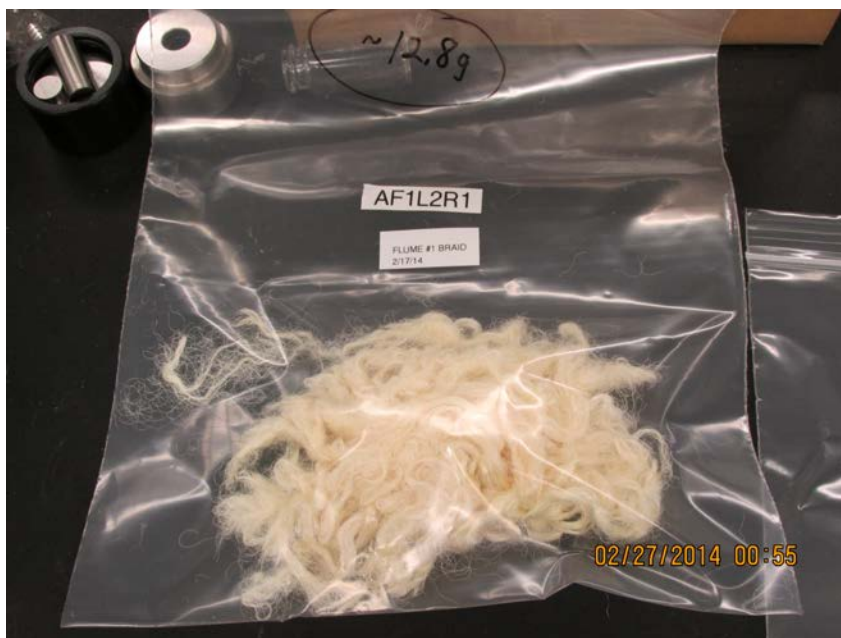


Figure 10. Leno woven fabric adsorbent (AF1L2R1) after AO and washing/drying.

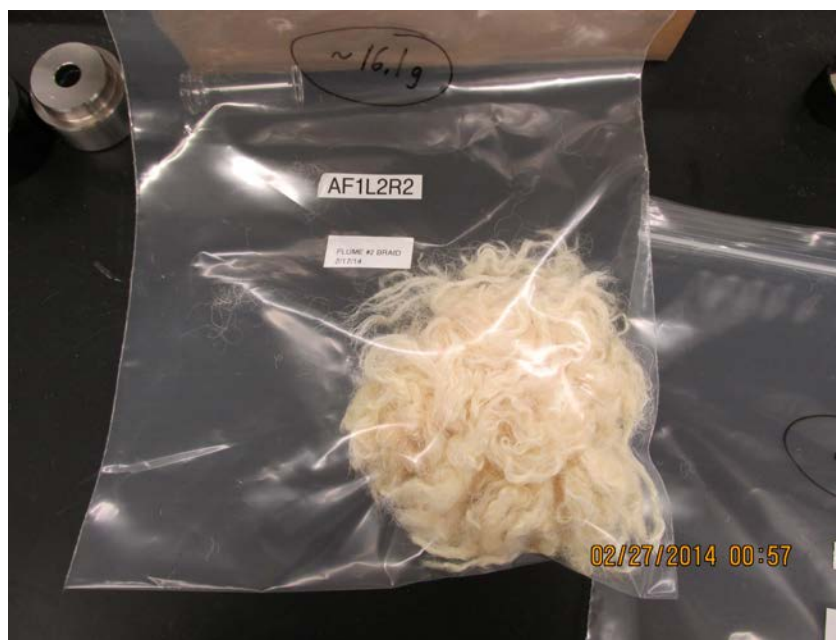


Figure 11. Leno woven fabric adsorbent (AF1L2R2) after AO and washing/drying.

3. Marine Testing of Braided and Leno Woven Adsorbents at PNNL

Immediately prior to exposure to natural seawater the four braided and leno woven adsorbents were conditioned with 2.5 wt.% (~0.44M) potassium hydroxide (KOH) at PNNL for 1 hour at 80°C. The adsorbent to solution ratio that was used for conditioning was 1 mL of the KOH solution per mg of adsorbent material. After conditioning, the braids were immediately washed

with deionized water until the pH of the rinse water was neutral. The braids were kept in deionized water solution until deployed for testing.

Exposure of the braid samples to filtered (0.45 μm) natural seawater was conducted in small flumes in which the internal water was constantly recirculated using a pump system. Temperature in the system was also controlled by feeding fresh temperature controlled seawater from a head tank into the flume at a rate of approximately 3.5 L/min. The water level in the flume was maintained at a constant height by varying the height of the overflow tube. The linear velocity and temperature of the seawater during exposure was 2.0 cm/s and 20°C, respectively. These conditions are identical to that of marine testing using columns at PNNL.

Two separate and identical flumes (Flume A and B) were used for seawater exposure. Each flume contained one braid and one leno woven adsorbent. To fix the adsorbents in place in the flume, they were attached to a short length of ¼ inch polyethylene, and the tubing was inserted into a hole drilled into a block fixed to the bottom of the tank. The adsorbents were placed near the flume inlet of the water recirculation system, which is a turbulent region of the flume.

Figure 12 is a schematic and the flow conditions for the PNNL flume that was used in the marine studies, and Figures 13-14 show Flume A and two of the ORNL braid and leno woven adsorbents.

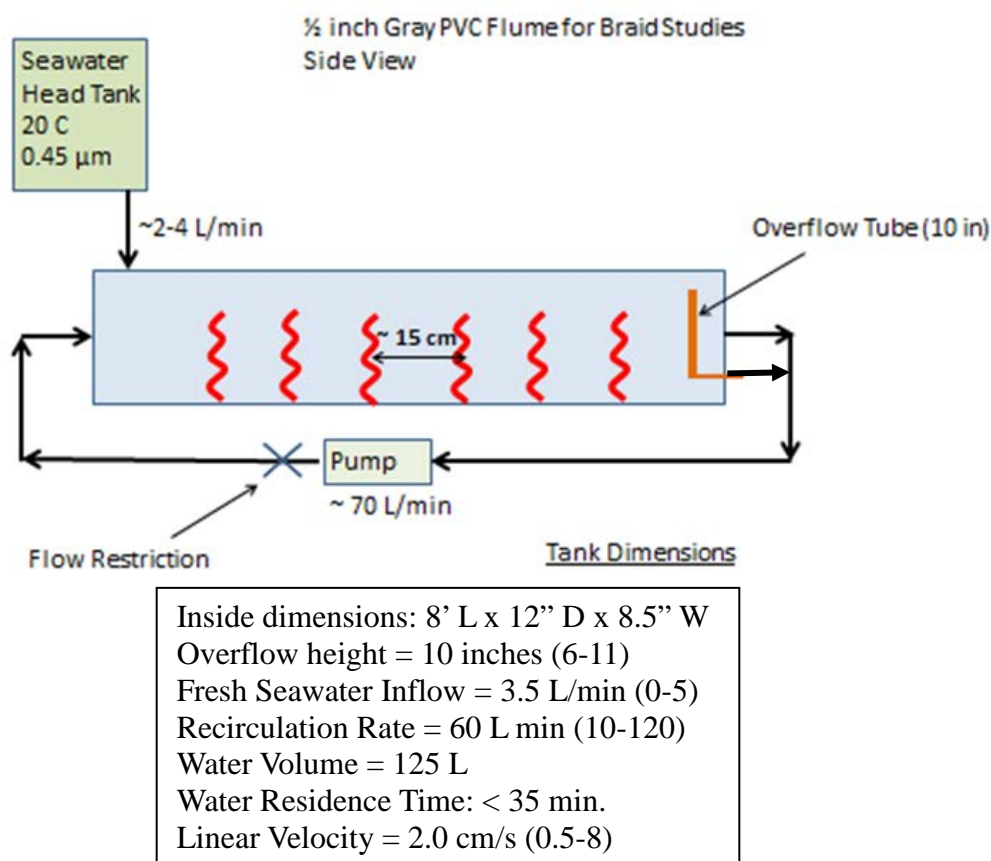


Figure 12. Schematic and flow conditions of PNNL flume.



Figure 13. PNNL flume.



Figure 14. ORNL's braid and leno woven adsorbents after KOH conditioning (left) and after submersion in PNNL's flume on day one (right).

The seawater was quantitatively monitored for pH, temperature, salinity, and trace-metal concentrations over the experimental period. Salinity and temperature were determined using a hand-held salinometer (YSI, Model 30). Temperature was determined using a temperature logger (RDXL4SD, OMEGA Engineering, Stamford, CT, USA). The logger was set to record the outlet temperature of seawater at least every 10 min. Discrete samples of seawater were collected periodically during the exposure period of the feedwater and the water passing through the columns for measurement of uranium and a suite of trace elements (e.g., V, Cu, Ni, Zn, Fe, and Mn).

During the 8-week (56-day) exposure period, the adsorbents experienced several color changes with time. Initially they were white, then quickly changed to yellow, and finally to progressively

darker shades of orange (Figure 15). Throughout the course of seawater exposure snips of the feather portions of each braid were collected and the uranium adsorption capacity was determined using an (ICP-OES) instrument.



Day 1



Day 2



Day 4



Day 5



Day 6



Day 7



Day 8



Day 11



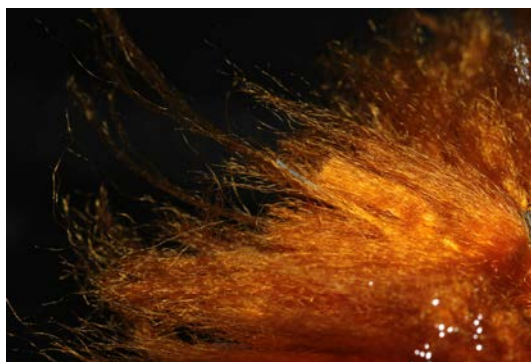
Day 12



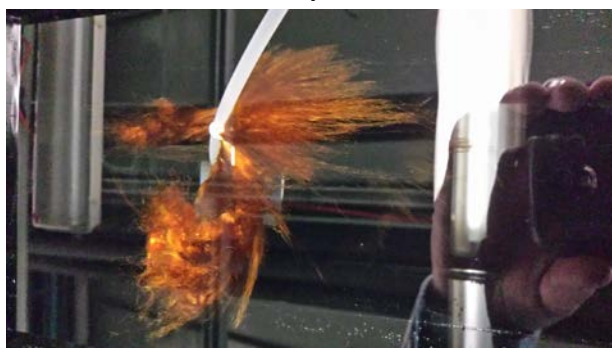
Day 13



Day 18



Day 20



Day 27



Day 32

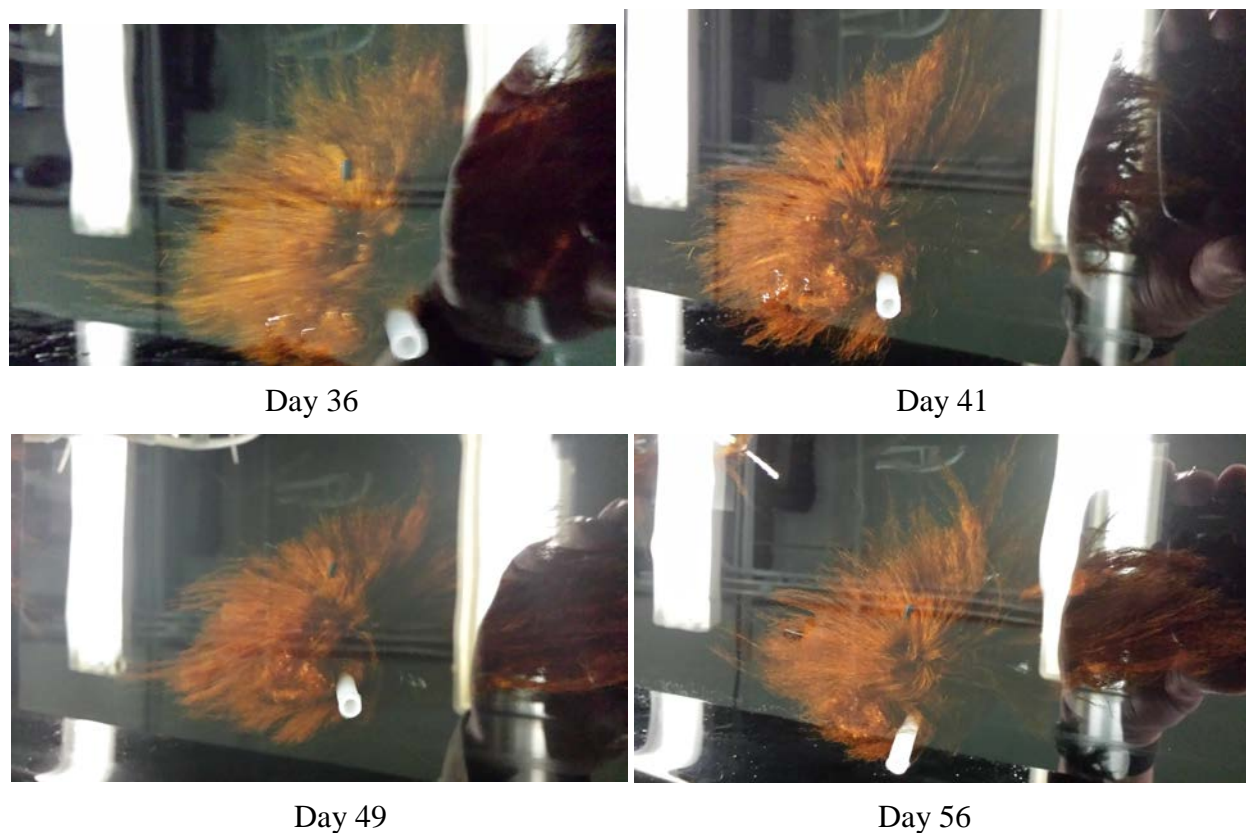


Figure 15. AF1 adsorbents – color changes with time during seawater exposure.

Figure 16 shows the braid (AF1B17-25 ppi - MSL 3439-2) and leno woven (AF1L2R1- MSL 3439-1) adsorbents after they were removed from Flume A, after 56 days of seawater exposure.



Figure 16. ORNL's AF1 braid and leno woven adsorbents after removal from flume.

4. Sample Handling and Analytical Procedures at PNNL

Srips of the braid taken from the “feathers” of the adsorbent were placed in 50 mL pre-cleaned vials and thoroughly washed with deionized (DI) water to remove salts. Complete removal of salts was verified with a salinometer. The dry weight of the exposed samples was determined after heating at 70 °C for several hours using a heated block. The dried fibers (50–100 mg) were then digested with 5–10 mL of high-purity (Optima, Fisher Scientific) concentrated aqua regia acid mixture for 2+ hours at 80 °C using a heated block. High-purity DI water was added to dilute acid solution to the desired concentration range for uranium analysis.

Analysis of uranium and selected elements (e.g., Ca, Mg, V, Fe, Cu, Ni, Cd, Zn, Ba, Co, Mn, Sr, Ti, and Al) in the adsorbent digestates was conducted using a Perkin-Elmer ICP-OES instrument following standard practices. Determination of uranium in natural seawater samples was conducted at PNNL using ICP-MS and the method of standard addition calibrations. 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 DI water and then spiked at four different concentration levels of 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 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% ($n = 15$). 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% ($n = 7$).

Analysis of other trace elements in seawater samples, such as V, Cu, Ni, Zn, Fe, and Mn, was also conducted by ICP-MS at PNNL following sample preconcentration and seawater matrix elimination. Seawater samples of 40 mL were preconcentrated by sodium borohydride reductive precipitation (5% solution, w/v) of an iron and palladium mixture (~0.5 mL of 1:1 solutions of 1000 µg/L) spiked into the samples. A 0.25 mL volume of a 2% (w/v) ammonium pyrrolidine-dithio-carbamate (APDC) solution was also added to the samples prior to reductive precipitation to complex trace elements and facilitate interaction with the Fe/Pd precipitate. Following precipitation of the Fe/Pd mixture, the samples were centrifuged at 2500 rpm for 30 min, and the overlying water was carefully decanted off the precipitate. The precipitate was dissolved with 0.1 mL of concentrated high-purity nitric acid (Optima grade, Fisher Scientific) and diluted to a suitable volume (~5 mL) for analysis with DI water. This scheme produced a sample preconcentration of approximately 8-fold, depending on the exact starting and final solution volumes. This analytical method for seawater is based on the reductive precipitation preconcentration techniques described by Nakashima et al.,[16] Sella et al.,[17] and Skogerboe et al.[18]

5. Marine Testing Results on Braided and Leno Woven Adsorbents

A summary of the marine testing results for the four ORNL AF1 braided and leno woven adsorbents that underwent seawater exposure testing in plastic flumes at PNNL over a period of

56 days at a linear velocity of 2.0 cm/s and a seawater temperature of 20 °C are shown in Table 3. The uranium adsorption capacities ranged from 3.7 to 4.2 g U/kg adsorbent. Also shown in Table 3 are the predicted saturation capacities and half-saturation times obtained from one-site ligand saturation modelling of the individual time course data that are shown in Figure 17.

Table 3. Uranium adsorption capacity results for AF1 braids and leno woven adsorbents after 56 days of seawater exposure.

ORNL AF1 Braid/Leno Woven Adsorbents¹	Flume Position	Adsorption Capacity at 56 days^{2,3} (g U/kg ads.)	Estimated Capacity at Saturation^{2,3} (g U/kg ads.)	Half- Saturation Time (days)
AF1L2R1	A1	4.11 ± 0.15	6.25 ± 0.15	29.2 ± 1.4
AF1B17-25 ppi	A2	3.72 ± 0.28	5.50 ± 0.30	26.8 ± 3.0
AF1L2R2	B1	4.11 ± 0.18	6.20 ± 0.19	29.5 ± 1.9
AF1B17-5 ppi	B2	4.22 ± 0.47	7.21 ± 0.51	39.7 ± 5.1
All 4 adsorbents		4.04 ± 0.18	6.29 ± 0.19	31.2 ± 1.9

¹2.5 wt% KOH conditioning for 1 hr/80 °C

²Capacity normalized to salinity of 35 psu

³Predicted using one-site ligand saturation modelling of time series data (Figure 17)

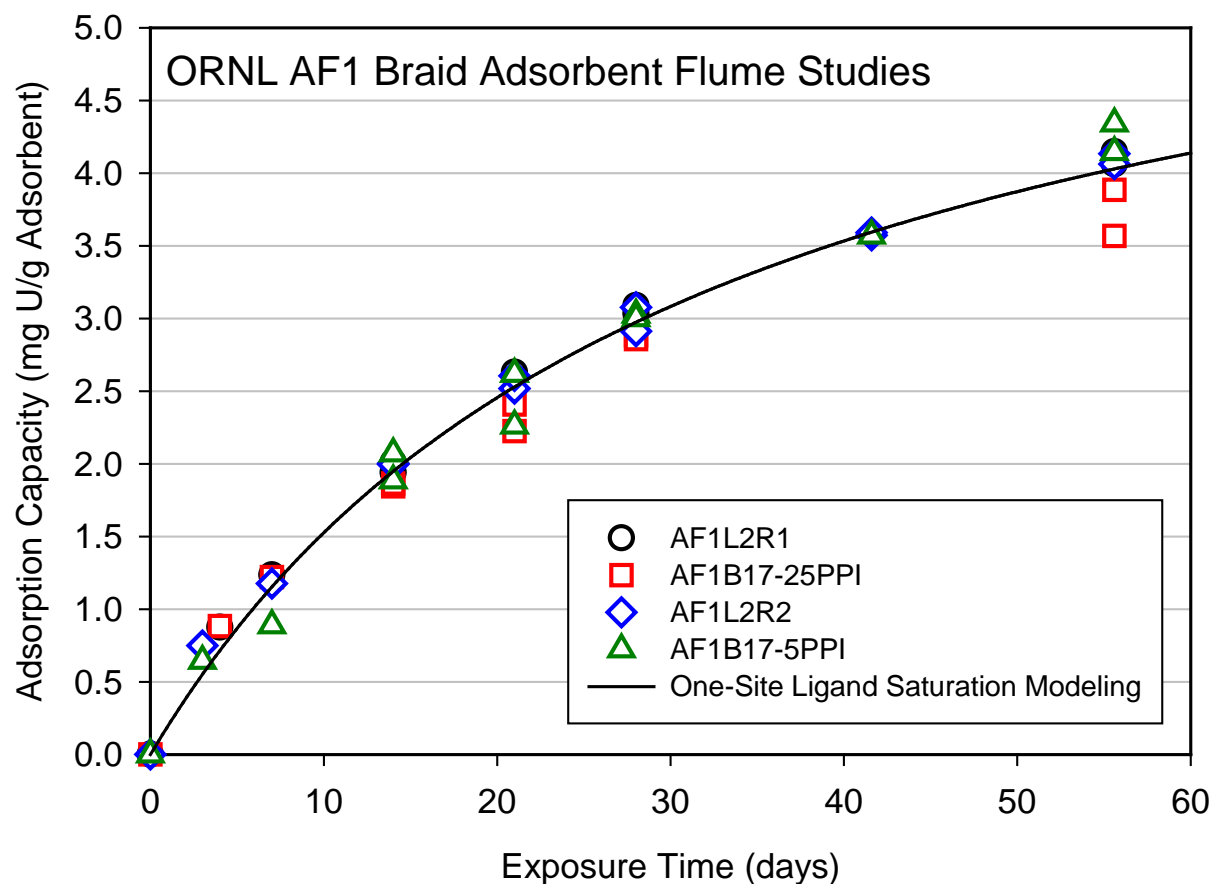


Figure 17. Uranium adsorption capacity results as a function of exposure time for AF1 braid and leno woven adsorbents in flumes with flowing natural seawater.

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7. Appendix A: References

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