Milestone Letter Report

Work Package: Advanced Adsorbent Development by Radiation-Induced Grafting, WP FT-14OR0310011, WBS 1.02.03.10, B&R code AF5855

Milestone: M3FT-14OR0310013

Title: Complete braided adsorbent for marine testing to demonstrate 3g-U/kg-adsorbent

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Objective
Complete braided adsorbent for marine testing and demonstrate a capacity of 3g-U/kg-adsorbent.

Progress
ORNL has manufactured four braided adsorbents that successfully demonstrated uranium adsorption capacities ranging from 3.0-3.6 g-U/kg-adsorbent in marine testing at PNNL. Four new braided and leno woven fabric adsorbents have also been prepared by ORNL and are currently undergoing marine testing at PNNL. Detailed information on the uranium adsorption capacity results, marine testing and adsorbent preparation is described below.

Results – Braided Adsorbents - Uranium Adsorption Capacity
Four ORNL adsorbents underwent marine testing in a plastic flume at PNNL over a period of 42 days and the uranium adsorption capacities ranged from 3.0-3.6 g-U/kg-adsorbent. A summary of these results is shown in Table 1 and the capacity is shown in Figure 1 as a function of exposure time. After 42 days all adsorbents showed an adsorption capacity of $\geq$ 3 g-U/kg-adsorbent and the capacity could be higher at longer exposure times.

Table 1. Uranium adsorption capacity results for AF1 braids in seawater.

AF1 Braid Adsorbents	KOH Conditioning (2.5 wt% KOH)	Flume Position	Capacity at 42 days* (g-U/kg-ads.)	Estimated Capacity at Saturation* (g-U/kg-ads.)	Half-Saturation Time (days)
AF1B17-2-25ppi	1 hr. 60°C	1	3.10	4.68 ± 0.26	23 ± 3
AF1B17-2-5ppi	1 hr. 80°C	2	3.57	5.78 ± 0.19	26 ± 2
AF1B17-2-5ppi	1 hr. 60°C	3	3.33	7.33 ± 0.61	48 ± 6
AF1B17-2-25ppi	1 hr. 80°C	4	3.00	7.01 ± 2.30	53 ± 27

* Capacity normalized to salinity of 35 psu

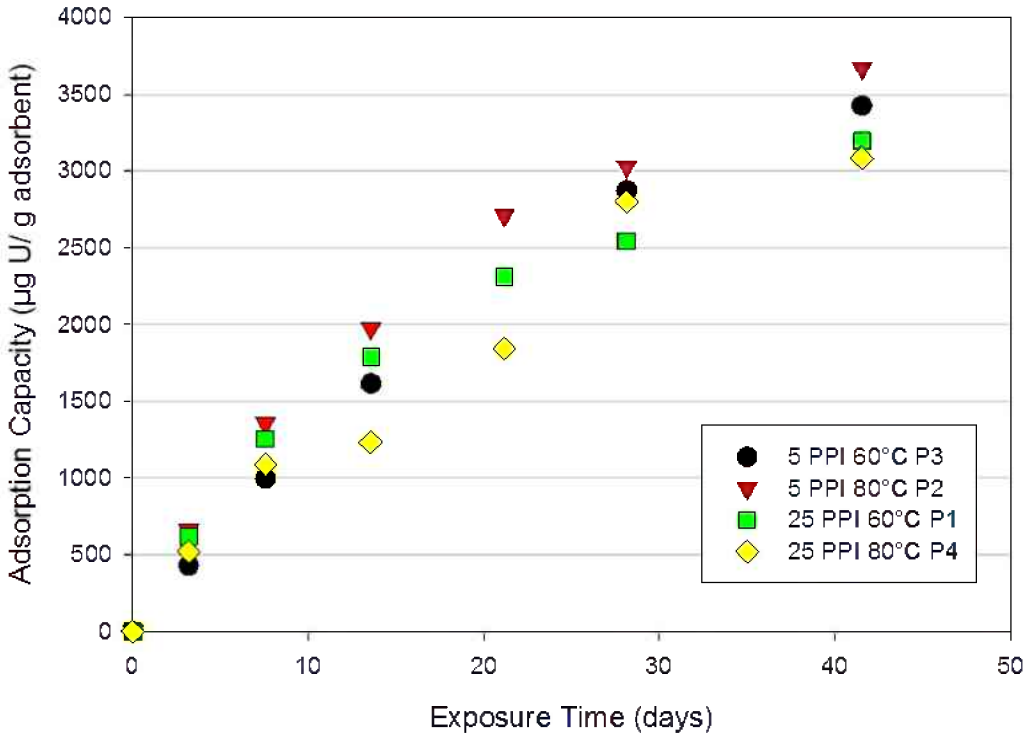
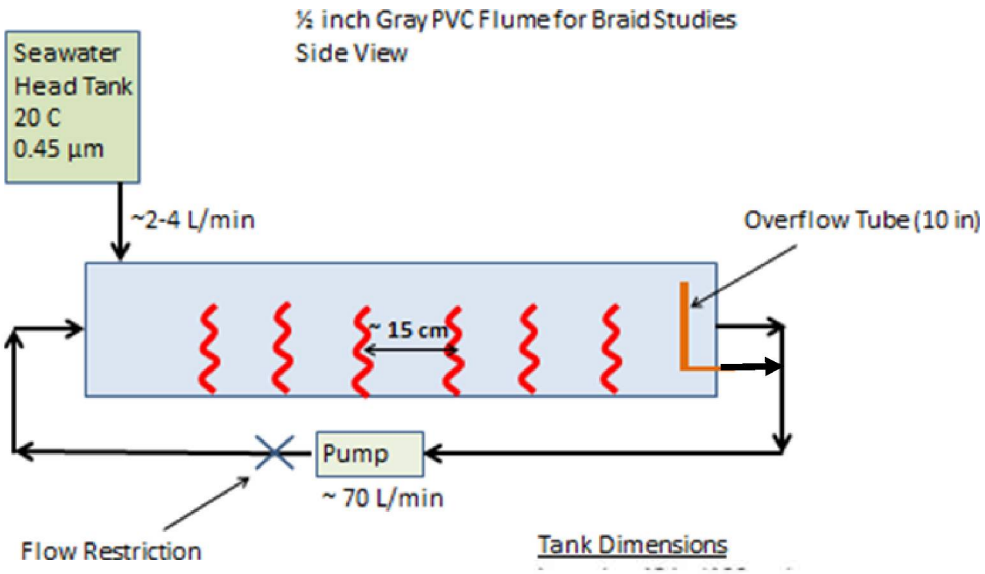


Figure 1. Uranium adsorption capacity results as a function of exposure time for AF1 braids in seawater.

Adsorbent Composition and Marine Testing

The above-mentioned braided adsorbent samples were each approximately 3-3.5 inches long and 6-inches wide and were composed of AF1 grafting formulation, #17 high surface area polyethylene fibers and braided with fiber densities of either 5 or 25 picks per inch (ppi). Prior to marine testing, the adsorbents were conditioned with 2.5 wt. % potassium hydroxide (KOH) at PNNL for 1 hour, at either 60°C or 80°C, then washed with distilled water until the pH of the excess water was neutral, and kept wet at all times. The wet adsorbents were placed in a flume at one of four different positions wherein position 1 was closest to the inlet (more turbulent region) and position 4 was closest to the outlet (more laminar region). The linear velocity and temperature of the seawater was 2.0 cm/s and 20°C, respectively. Figure 2 is a schematic and the flow conditions for the PNNL flume that was used in the braid studies, and Figures 3-4 show the flume containing the ORNL braid adsorbents.



Inside dimensions: 8' L x 12" D x 8.5" W
Overflow height = 10 inches (6-11)
Fresh Seawater Inflow = 3.5 L/min (0-5)
Recirculation Rate = 60 L min (10-120)
Water Volume = 125 L
Water Residence Time: < 35 min.
Linear Velocity = 2.0 cm/s (0.5-8)

Figure 2. Schematic and flow conditions of PNNL flume.

Figure 3. PNNL flume.

Figure 4. ORNL braids in flume.

During the 6-week (42-day) exposure period, the braids experienced several color changes with time. Initially they were white, then changed to yellow, and finally to progressively darker shades of orange (Figure 5). 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 inductively coupled plasma (ICP) instrument.

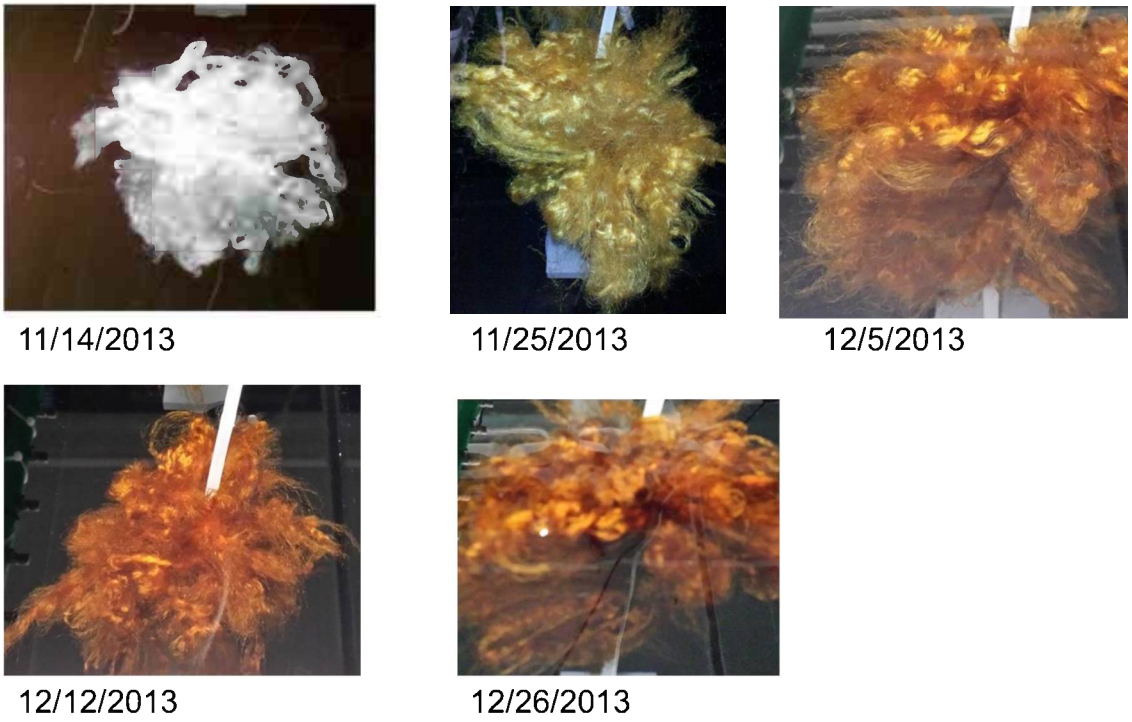


Figure 5. AF1 braid adsorbent - color changes with time during seawater exposure.

Figure 6 shows the braid adsorbents once they were removed from the flume after 42 days of exposure. It is worth noting that the flume position appeared to influence the color of the braid with the braids in positions 1 and 2 (more turbulent region) appearing much darker than the braids in positions 3 and 4 (less turbulent region). PNNL is currently interrogating and dissecting each braid including the feather and core regions and determining the uranium adsorption capacities.

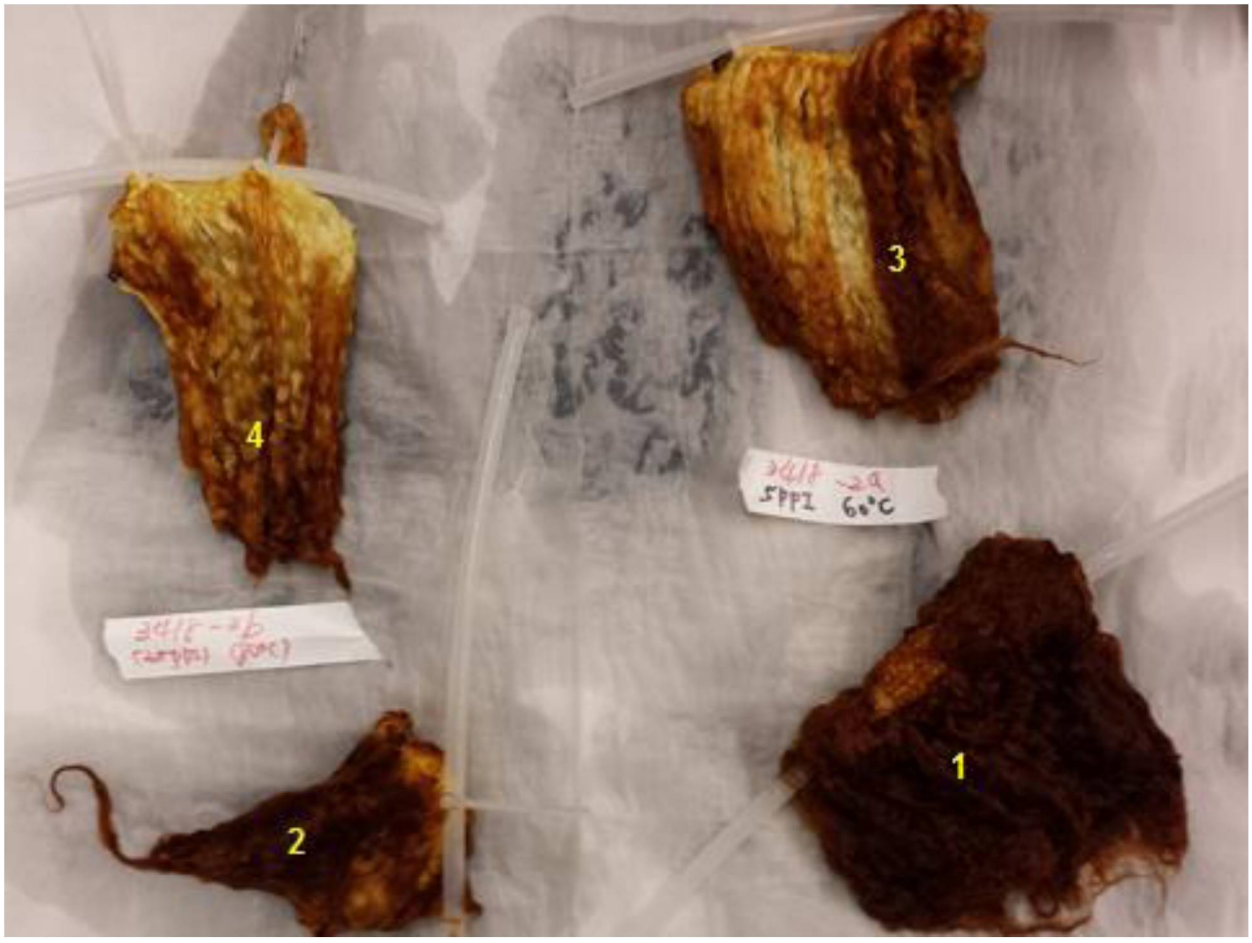


Figure 6. ORNL AF1 braid adsorbents after removal from flume.

Figure 7 shows the uranium concentration versus time at the flume inlet and outlet during seawater braid testing. It is worth noting that the concentration of the uranium in the flume during testing was below the typical uranium concentration in the oceans (3.3 ppb) and is a function of the braid mass, braid adsorption capacity, braid adsorption kinetics and seawater in-flow rate.

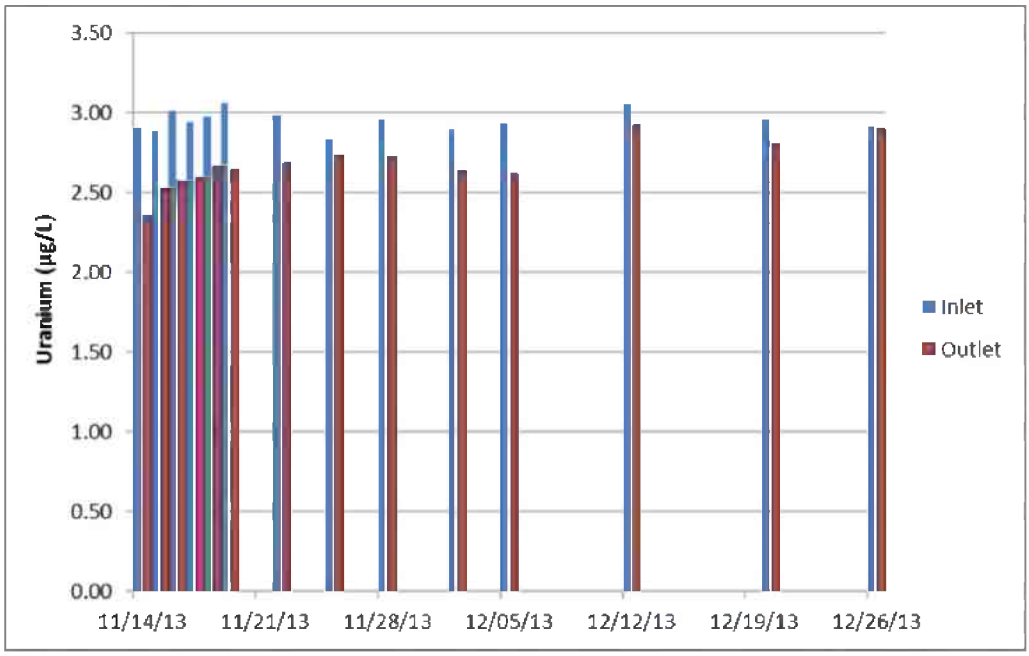


Figure 7. Uranium concentration vs time at flume inlet and outlet.

Adsorbent Preparation

In addition to the four AF1 braid adsorbents that were marine tested at PNNL, four new AF1 braids and leno woven fabric adsorbents were prepared by ORNL and are currently undergoing marine testing at PNNL. A summary of the four braid adsorbents that have already been marine tested at PNNL (shaded) and the four new adsorbents are shown on Table 2.

Table 2. ORNL AF1 braid and leno woven fabric adsorbents.

AF1 Adsorbent (KOH conditioning)	Fabric type	Fiber no.	Graft time (hrs.)	% DOG	AO conditions
AF1B17-2-25ppi (1 hr. 60°C)	Braid-25ppi	#17	1.5	275	1X52 hrs.
AF1B17-2-5ppi (1 hr. 80°C)	Braid-5ppi	#17	1.5	253	1X <52 hrs.
AF1B17-2-5ppi (1 hr. 60°C)	Braid-5ppi	#17	1.5	253	1X <52 hrs.
AF1B17-2-25ppi (1 hr. 80°C)	Braid-25ppi	#17	1.5	275	1X52 hrs.
AF1L2R1 (1 hr. 80°C)	Half Leno	#8	18	410	3X24 hrs. (tl. 72 hrs.)
AF1L2R2 (1 hr. 80°C)	Half Leno	#8	19	319	3X24 hrs. (tl. 72 hrs.)
AF1B17-5ppi (1 hr. 80°C)	Braid-5ppi	#17	20	250	3X24 hrs. (tl. 72 hrs.)
AF1B17-25ppi (1 hr. 80°C)	Braid-25ppi	#17	20	271	3X24 hrs. (tl. 72 hrs.)

The adsorbents were composed of high surface area polyethylene fibers that were melt-spun 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 four unidirectional tri-axial fibers and had fiber densities of 5 or 25 picks per inch (ppi) and were approximately 8-11 inches wide. A representative example of the braids made at Steeger is shown in Figure 8.

Figure 8. Representative Steeger braid.

The leno woven fabrics were made in a single cloth, half leno version with two leno pairs in the center (4 tow yarns total) and a plain weave on the outer edges of the fabric (removed) and were approximately 12-inches wide. Figure 9 is an example of the leno woven fabric.

Figure 9. L2 half leno single cloth.

Prior to irradiation of the braids and the leno woven fabrics the PLA was removed by submerging them in excess tetrahydrofuran (THF) at 60°C overnight. This process was repeated three times, and the fibers were filtered and dried at 50°C under vacuum. After drying the fabrics were secured on each end with polypropylene plastic ties to prevent unravelling and 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 and 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 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 10 shows the electron beam setup 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 underneath the 4-ft-wide scan horn of the electron beam machine that is contained within a concrete vault. The speed of LMS3 translating table was approximately 0.54 in/s.

Figure 10. Electron beam set-up used for irradiating braids and leno woven fabrics.

After irradiation, the fabrics were immersed in a flask containing a previously de-gassed AF1 grafting solution. The flasks were then placed in an oven at 60–70°C for about 1.5 to 20 hours for grafting. The braids were grafted in 1000 ml Erlenmeyer reaction flasks whereas the leno 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 at 50–60°C under vacuum. The grafted fabrics were weighed to determine the % degree of grafting (DOG).

Amidoximation and KOH Conditioning of PNNL Tested Braid Adsorbents

Amidoximation of the braid adsorbents prior to testing at PNNL, including the AF1B17-2-5ppi and AF1B17-2-25ppi adsorbents, was conducted in 1000 ml Erlenmeyer reaction flasks using 10 wt% hydroxylamine hydrochloride in 50/50 wt/wt water/methanol (previously neutralized with KOH) at 80°C for less than or equal to 52 hours (Note: the flask containing the AF1B17-2-5ppi adsorbent broke during the reaction). The samples were then washed under vacuum filtration with deionized water followed by a methanol rinse and allowed to dry at 50°C under vacuum. Table 3 provides summary information on the amidoximation conditions.

Table 3. Amidoximation conditions of PNNL tested braid adsorbents.

AF1 Braid Adsorbents	Dry weight of braid before AO (g)	Volume of AO solution (ml)	AO reaction time (hr)	mg adsorbent/ml AO solution (1X)
AF1B17-2-5ppi	10.9	600	< 52	18.2
AF1B17-2-25ppi	14.2	600	52	23.7

After drying, both braid adsorbents measured about 6-inches in width and were then cut into two samples each of approximately 3-3.5-inches long and secured on each end with polypropylene plastic ties, then shipped to PNNL for KOH conditioning. Prior to flume testing PNNL conditioned each braid adsorbent in a flask that contained 2000 ml of 2.5 wt % KOH and heated for 1 hour at 60 or 80°C, then washed with 18.2 mega-ohm water until the pH of the excess water was neutral. The braids were kept wet until placement in the flume. Table 4 summarizes the KOH conditioning of the braid adsorbents.

Table 4. KOH conditions of PNNL tested braid adsorbents.

AF1 Braid Adsorbents	KOH Conditioning	~ dry weight of braid before KOH (g)	~ mg adsorbent/ml KOH solution
AF1B17-2-25ppi	1 hr. 60°C	8.5	4.2
AF1B17-2-5ppi	1 hr. 80°C	6.55	3.3
AF1B17-2-5ppi	1 hr. 60°C	6.55	3.3
AF1B17-2-25ppi	1 hr. 80°C	8.5	4.2

Amidoximation and KOH Conditioning of the New Braid and Leno Woven Adsorbents

Prior to amidoximation of the new braid and leno woven adsorbents, they were cut into samples and secured on each end with polypropylene plastic ties. Amidoximation of the adsorbents was conducted using 10 wt% hydroxylamine hydrochloride in 50:50 wt/wt water/methanol that was previously neutralized with KOH, at 80℃ for 72 hours in an oven. 950 ml or 1800 ml Ace-Glass® pressure bottles (rated at 60 psi max. pressure at RT) with PTFE closures were used as reaction vessels. Care was taken to prevent floating of the samples (due to gradual built-up of inside pressure) by wrapping several hollow cylindrically shaped Teflon spacers (i.e., 6 x 0.5-inch dia. x 0.75-inch long) around the braided samples using one fiber tow of UHMWPE fiber. The hydroxylamine solution was replaced with fresh solution every 24 hours. The amidoximated samples were then washed using vacuum filtration with water and methanol to remove any trapped reactant chemicals, and dried at 50℃ in a vacuum oven. Table 5 provides a summary of the amidoximation conditions and Figures 11 and 12 show the adsorbents after the amidoximation reaction.

Table 5. Summary of amidoximation (AO) conditions of new braid and leno woven adsorbents.

Sample ID	Dry weight before AO (g)	Vol. of AO soln. every 24 hours (ml)	Weight after AO (g)	% weight gain after AO	mg adsorbent/ml AO solution (3X)
AF1L2R1-Flume #1	10.1	1400	12.7	25.7	7.2
AF1L2R2 - Flume #2	12.7	1400	16.0	25.9	9.1
AF1B17-5PPI – Flume #2	3.2	800	4.1	28.1	4.0
AF1B17-25PPI – Flume #1	4.7	800	6.0	27.7	5.9

Figure 11. Leno woven adsorbents after amidoximation reaction.

Figure 12. Braided adsorbents after amidoximation reaction.

After drying, the new braided and leno woven adsorbent samples (Figures 13-16) were shipped to PNNL on 3/5/2014 for subsequent KOH conditioning (1 hour/80^{o}C) and marine testing in two different flumes of seawater. The adsorbent samples were positioned in the high turbulent regions of each flume. During the course of exposure, snips of the feather portions will be collected for uranium adsorption capacity determination. In addition, small amounts of the same braided and leno woven adsorbents were placed in glass vials for flow-through column seawater testing at PNNL and laboratory screening studies at ORNL.

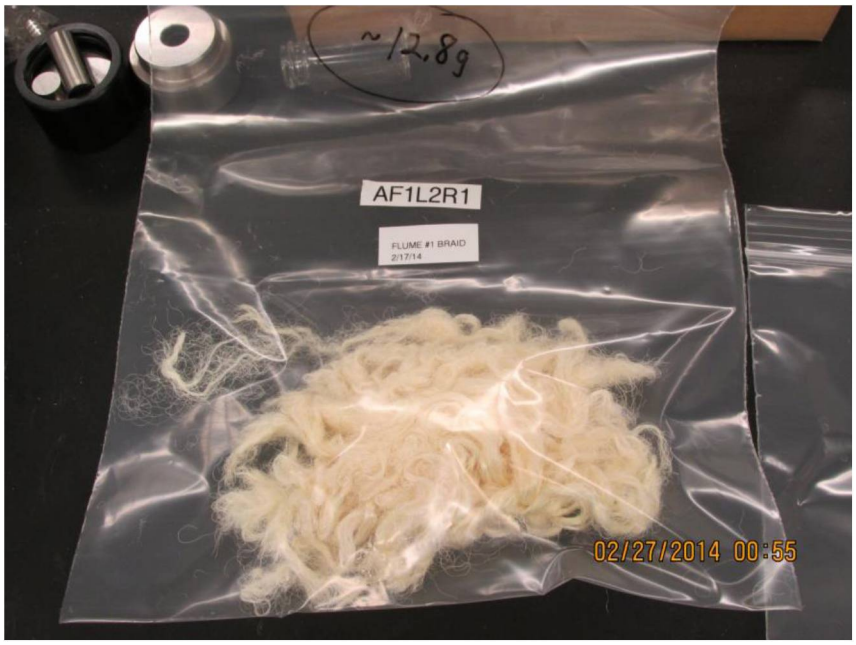


Figure 13. Leno woven fabric adsorbent (AF1L2R1) after AO and washing/drying.

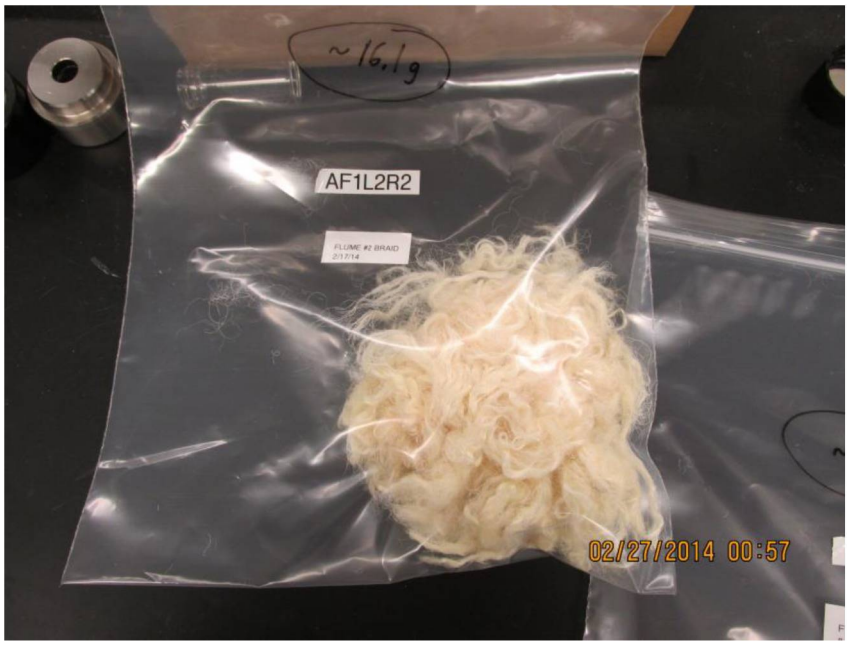


Figure 14. Leno woven fabric adsorbent (AF1L2R2) after AO and washing/drying.

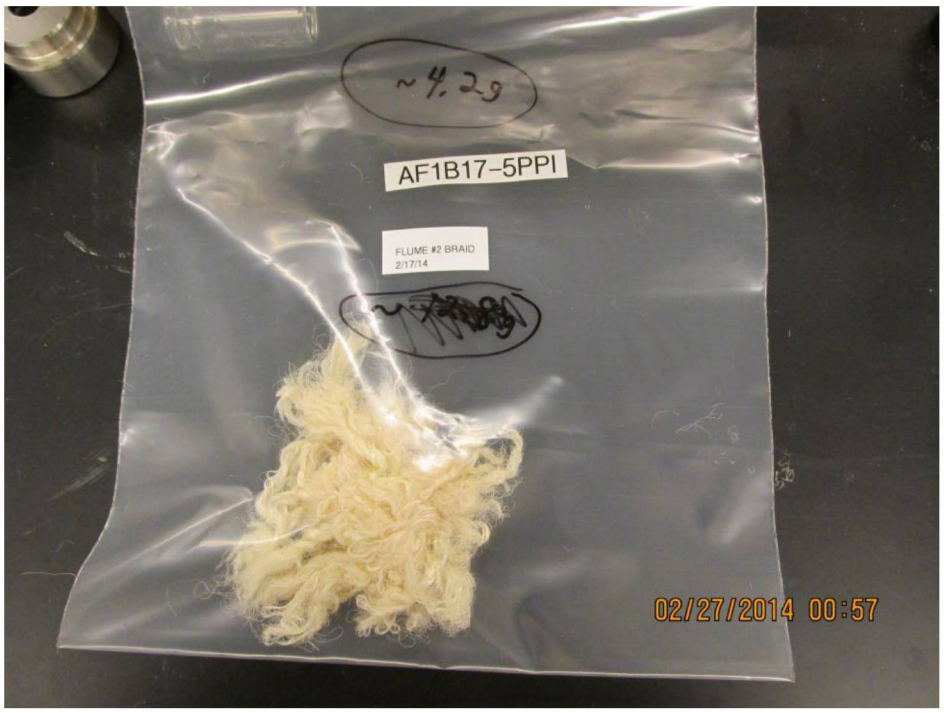


Figure 15. Braided adsorbent (AF1B17-5ppi) after AO and washing/drying.

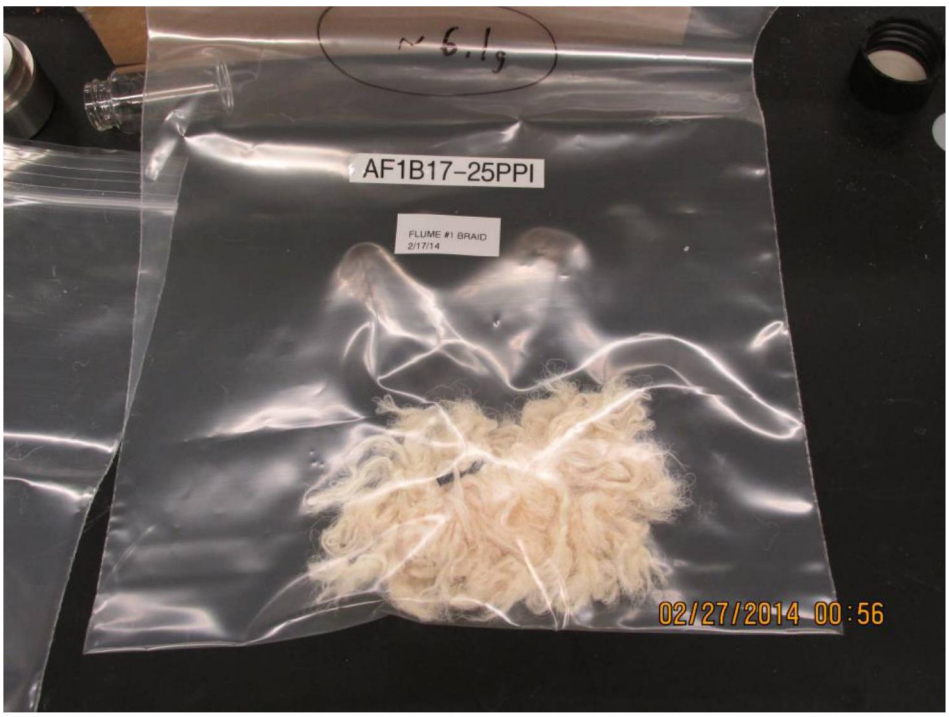


Figure 16. Braided adsorbent (AF1B17-25ppi) after AO and washing/drying.

KOH Conditioning and Laboratory Screening of Braids and Leno Woven Fabric Adsorbents at ORNL – Determination of Uranium Adsorption Capacity

Samples of each of the amidoximated braided and leno woven fabric adsorbents (described above) were KOH conditioned and tested at ORNL using the Laboratory Screening Protocol described below in order to determine their uranium adsorption capacity.

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.

Laboratory Screening Protocol of Braid and Leno Woven Adsorbents at ORNL

Since typical screening experiments with real seawater take 30–60 days to reach equilibrium, 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 tricarbonate complex $\{[UO_2(CO_3)_3]^{4-}\}$ 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 and 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 were then equilibrated with 750 ml test solutions for 24 hours at RT with constant shaking at 250-500 rpm. It was 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).

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

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 17 below.

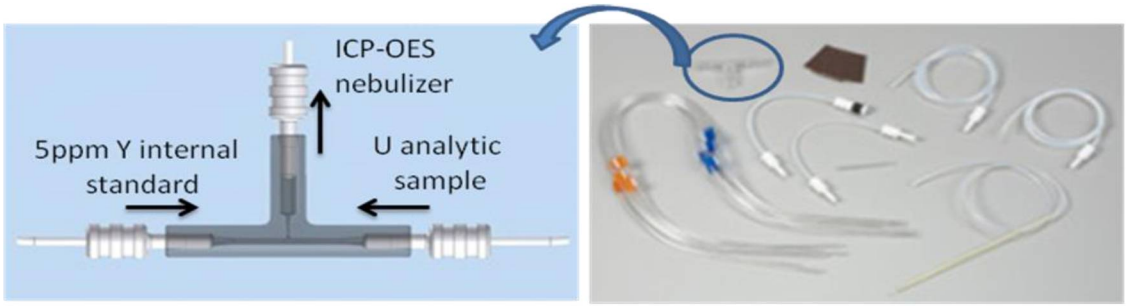


Figure 17. Internal Standard Addition Kit for ICP-OES (Perkin-Elmer).

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 were then 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 are shown in Figure 18 for the recently tested braided adsorbents at PNNL (AF1B17-2-5ppi and AF1B17-2-25ppi) and for the new braided and leno woven adsorbents. The capacity values ranged from 155 to 193 g-U/kg ads. 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) and work is currently on-going at ORNL and PNNL to optimize the KOH conditioning parameters.

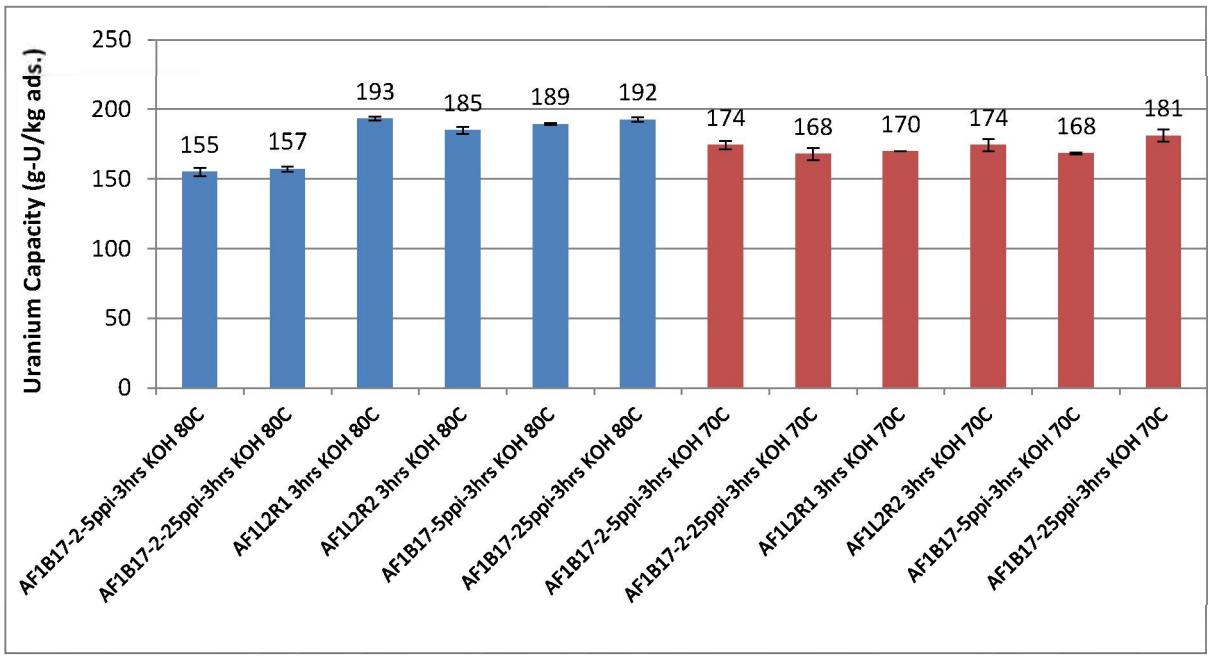


Figure 18. Uranium adsorption capacity results on braided and leno woven adsorbents from laboratory screening at ORNL.

Summary
ORNL has manufactured four braided adsorbents that successfully demonstrated uranium adsorption capacities ranging from 3.0-3.6 g-U/kg-adsorbent in marine testing at PNNL. Four new braided and leno woven fabric adsorbents have also been prepared by ORNL and are currently undergoing marine testing at PNNL.