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-14OR0310012

Title: Preparation of most promising braided and/or textile-based uranium adsorbents for seawater testing.

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Objective

Prepare the most promising braided and/or textile-based adsorbents for uranium uptake from seawater.

Progress

The focus of this project is to develop adsorbents for uranium uptake from seawater. Here, it is reported that ORNL, in collaboration with Steeger USA and Philadelphia University, has manufactured a wide range of braided and textile-based fabric candidates that included 20 braids, 12 knit and leno woven fabrics and 5 high surface area polyethylene fibers. Down-selection of several promising fabric candidates was completed for manufacturing adsorbent samples. Irradiation and grafting of over 40 braided and leno woven adsorbent samples were completed with % degree of grafting values ranging from 250 to 430%. The adsorbent samples included 24 braids, 18 leno woven fabrics, 3 high surface area polyethylene fibers and 3 grafting formulations. Amidoximation, potassium hydroxide (KOH) conditioning and laboratory screening studies were completed on 12 of the most promising braided and leno woven adsorbent samples. Uranium adsorption capacities, measured by using inductively coupled plasma-optical emission spectroscopy (ICP-OES), were found to be in the range of 125 to 180 g-U/kg adsorbent, using the standard ORNL screening solution. Four braided adsorbent samples were prepared and sent to PNNL for seawater flume testing. Detailed information on the preparation of the most promising braided and textile-based adsorbents for seawater testing is described below.

Experimental

Braids

Twenty braided fabrics were manufactured at Steeger USA that comprised a variety of fibers, fiber densities, widths, unidirectional triaxial fibers and hollow cores. Four different high-surface-area polyethylene fibers were melt-spun at Hills, Inc. using polylactic acid (PLA 6202) as the second polymer including:

- #15 caterpillar shaped fibers (Dow Aspun 6850);
- #16 hollow gear shaped fibers (Equistar H6018);
- #17 hollow gear shaped fibers (Dow Aspun 6835);
- #18 solid gear shaped fibers (Dow Aspun 6850)

The braided fiber densities ranged from 5 to 75 picks per inch (ppi) and the braid widths ranged from narrow (3-6 inches) to wide (8-11 inches). Although some of the braids were made without unidirectional triaxial fibers, it was quickly realized that triaxial fibers were necessary to provide mechanical integrity. In addition, some of the braids were made with hollow polyethylene cores in the center of the braid in order to provide buoyancy for future seawater deployment scenarios. Table 1 is a summary of the braids manufactured at Steeger.

Table 1. Braids Manufactured at Steeger, USA

Fiber #	Picks/inch (ppi)	# of triaxials (unidirectional)	Width	Hollow Core PE tubing
	25	4	Wide	No
	35	4	Wide	No
	45	4	Wide	No
	75	4	Wide	No
	5	4	Wide	No
	15	4	Wide	No
	25	4	Wide	No
	5	0 (braid pulls out w/o triaxials)	Wide	No
	15	0 (braid pulls out w/o triaxials)	Wide	No
	5	4	Wide	No
	15	4	Wide	No
	25	4	Wide	No
	5	0	Wide	No
	15	0	Wide	No
	25	0	Wide	No
	5	0	Narrow	No
	5	6	Narrow	3/8"OD ¼" ID
	15	6	Narrow	No
	25	6	Narrow	No
	5	0	Narrow	1/8" OD

After the braids were made, they were ranked in terms of mechanical integrity and their similarity in appearance to the Japanese braid. Based on these results, the #16 and #17 fiber braids (5 and 25 ppi) were down-selected for further processing into adsorbents. Figures 1-2 show the braiding machine and a representative braid that was made by Steeger USA. The Steeger braiding machine has produced braids that are similar in appearance to the Japanese braids and can be used to produce braids with various loop lengths and loop densities. The Japanese braiding machine and a representative braid that was made by the Japan Atomic Energy Agency (JAEA) are shown in Figures 3-4.

Figure 1. Steeger Braiding Machine

Figure 2. Representative Steeger Braid

Figure 3. Japanese Braiding Machine

Figure 4. Representative Japanese Braid

Knitted and Leno Woven Fabrics

Philadelphia University (Kanbar College of Design, Engineering and Commerce) has recently manufactured several textile loop fabrics that are potentially suitable for use as adsorbents including leno woven and knitted fabrics. These fabrics are similar in appearance to the Steeger and Japanese braids and they offer advantages with respect to the braids including: lower fiber density (less compaction) in middle section of fabric; easier machine set-up (only a few spools needed); fabric widths of at least four feet wide are possible and; leno fabrics can potentially be made in double, triple or quadruple cloth versions (4, 6 and 8 sets of loops) if greater density of fiber is needed.

Twelve different knitted and leno woven loop fabrics were made at Philadelphia University using the same types of high-surface-area polyethylene fibers that were used for making the Steeger braids. The knitted fabrics were made using #17 hollow gear fibers (Dow Aspun 6835/PLA6202), and the leno woven fabrics were made using either #17 hollow gear fibers or #8 hollow gear fibers (Dow Aspun 6850/PLA6202). A range of loop densities were used during the manufacture of the fabrics, and the fabric widths ranged from 4 to 12 inches. In addition, different amounts of reinforcing tow fibers were used in the center of the leno fabrics to increase mechanical stability. Table 2 summarizes the knitted and leno woven fabrics manufactured at Philadelphia University.

Table 2. Knitted and Leno Woven Fabrics Manufactured at Philadelphia University

Loop Fabric type	Fiber#	Specific Features
Knitted	17	Intargia knit
Knitted net	17	Large intersecting loops
Knitted net	17	Small intersecting loops
Half leno woven	17	Single cloth, low density
Full leno woven	17	Single cloth, low density
Full leno woven	17	Double cloth, medium density
Full leno woven	8	Single cloth; 4 leno pairs in center; plain weave on outer edges removed
Full leno woven	8	Single cloth; 2 leno pairs in center & 1 leno pair on each end
Half leno woven	8	Single cloth; 2 leno pairs in center; plain weave on outer edges removed
Half leno woven	8	Single cloth; high density; 2 leno pairs in center; plain weave on outer edges removed
L1 - Full leno woven	8	Single cloth; medium density; 2 leno pairs in center (4 tow yarns total); plain weave on outer edges removed (~ 12" wide)
L2 – Half leno woven	8	Single cloth; medium density; 2 leno pairs in center (4 tow yarns total); plain weave on outer edges removed (~ 12" wide)

The knitted and leno woven fabrics were then ranked in a similar method to that of the braids and based on these results the L1 and L2 leno fabrics made with #8 hollow gear fibers were down-selected for further processing into adsorbents. Figures 5-7 show the weaving loom that was used to manufacture the leno fabrics and the down-selected L1 and L2 fabrics.

Figure 5. Leno Weaving Loom

Figure 6. L1 - Full Leno Single Cloth

Figure 7. L2 - Half Leno Single Cloth

Irradiation and Grafting of Braids and Leno Woven Fabrics – NEO Beam

Prior to irradiation the PLA was removed from the braided and leno woven fabrics 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. The fabrics 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 then irradiated for 16 passes under the 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. Due to the high reactivity of the free radical species that are generated during the irradiation of the polyethylene fibers, it is very important to irradiate them under low temperatures and inert conditions, and then add them as quickly as possible to the grafting solution. Irradiation in the presence of the monomers provides low grafting yields.

All irradiation and grafting activities were conducted off-site at NEO Beam— Mercury Plastics, Inc. in Middlefield, Ohio. Figure 8 shows the electron beam setup for irradiating the fabrics, which shows the sealed Styrofoam insulated box, containing dry ice and several fabric samples, 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 8. 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 grafting solution of either 38H (acrylonitrile (AN), methacrylic acid (MAA) and dimethylsulfoxide (DMSO)), AF1 (AN, itaconic acid (ITA) and DMSO) or AI8 (AN, vinylphosphonic acid (VPA) and DMSO). The flasks were then placed in an oven at 60–70 °C for about 1.5–20 hours for grafting. 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). In addition, the same fibers that comprised the braids and leno woven fabrics were also irradiated and grafted at the same time in order to compare with the fabric samples.

Table 3 provides information on the irradiation and grafting test matrix that was conducted on the braids and tow fibers. A total of 24 braids and 12 tow fiber samples were irradiated, then grafted with either 38H, AF1 or AI8 formulations (8 braids and 4 tows per graft formulation) in 1000 ml Erlenmeyer reaction flasks. The grafting time was 17-20 hours for most samples, however for the EB Run #4 samples the oven was turned off after about 1.5 hours due to an abnormal event.

Table 3. Irradiation and Graft Test Matrix for Braids and Tow Fibers

1st set of experiments was conducted on #16 and #17 braided fibers (5 & 25 ppi; 4 triaxials; wide width) and continuous fiber tows. Grafting formulations included **38H** (acrylonitrile(AN)/methacrylic acid/DMSO), **AF1** (AN/itaconic acid/DMSO) and **AI8** (AN/vinylphosphonic acid/DMSO).							
EB Run#	Sample ID	Graft Formulation	Fiber #	Wt. of braids & continuous tow fibers before grafting, g			Graft Time, hrs.
				5ppi	25ppi	tows	
1	38HB16	38H	16	3.1	3.0	0.6	17
2	AF1B16	AF1	16	3.7	4.9	1.2	20
3	AI8B16	AI8	16	3.0	3.8	1.2	20
1	38HB17	38H	17	2.2	2.7	1.1	17
2	AF1B17	AF1	17	2.8	3.4	1.2	20
3	AI8B17	AI8	17	2.8	3.4	1.0	20

2nd (replicate) set of experiments was also conducted on #16 and #17 braided fibers (5 & 25 ppi; 4 triaxials; wide width) and continuous fiber tows. Grafting formulations included 38H, AF1 and AI8.							
EB Run#	Sample ID	Graft Formulation	Fiber #	Wt. of braids & continuous tow fibers before grafting, g			Graft Time, hrs.
				5ppi	25ppi	tows	
4	38HB16-2	38H	16	3.1	3.3	0.6	1.5
4	AF1B16-2	AF1	16	4.5	3.9	1.0	1.5
4	AI8B16-2	AI8	16	3.4	4.1	1.1	1.5
4	38HB17-2	38H	17	2.9	1.9	0.9	1.5
4	AF1B17-2	AF1	17	3.1	3.8	1.5	1.5
4	AI8B17-2	AI8	17	3.7	2.2	1.2	1.5

A large number of braids and tow fiber samples were made for conducting laboratory screening, optimization studies and seawater evaluations. The sample weights for the braids and tow fibers after grafting ranged from about 8-20g and 3-6g, respectively. Table 4 summarizes the inventory of the braid and tow fiber samples and their respective %DOG. A plot of the %DOG for the braids and fiber tows are shown in Figure 9 and they ranged from about 250-600% and were generally higher for the #16 fiber samples compared to the #17 fiber samples.

Table 4. Sample Inventory of Braids and Tow Fibers and %DOG

1st set of experiments conducted on #16 and #17 braided fibers (5 & 25 ppi; 4 triaxials; wide width) and continuous fiber tows. Grafting formulations included 38H (acrylonitrile(AN)/methacrylic acid/DMSO), AF1 (AN/itaconic acid/DMSO) and AI8 (AN/vinylphosphonic acid/DMSO).									
EB Run#	Sample ID	Graft Formulation	Fiber #	Wt. of braids & continuous tow fibers after grafting, g			% Degree of grafting		
				5ppi	25ppi	tows	5ppi	25ppi	tows
1	38HB16	38H	16	15.6	13.7	4.0	403	357	567
2	AF1B16	AF1	16	16.0	20.6	6.5	332	320	442
3	AI8B16	AI8	16	13.8	17.2	5.4	360	353	350
1	38HB17	38H	17	9.0	10.7	4.4	309	296	300
2	AF1B17	AF1	17	9.8	12.6	5.1	250	271	325
3	AI8B17	AI8	17	10.3	12.6	3.4	268	271	240

2nd (replicate) set of experiments also conducted on #16 and #17 braided fibers (5 & 25 ppi; 4 triaxials; wide width) and continuous fiber tows. Grafting formulations included 38H, AF1 and AI8.									
EB Run#	Sample ID	Graft Formulation	Fiber #	Wt. of braids & continuous tow fibers after grafting, g			% Degree of grafting		
				5ppi	25ppi	tows	5ppi	25ppi	tows
4	38HB16-2	38H	16	14.4	14.4	4.1	365	336	583
4	AF1B16-2	AF1	16	19.4	16.7	5.3	331	328	430
4	AI8B16-2	AI8	16	12.0	14.5	6.1	253	254	455
4	38HB17-2	38H	17	11.1	7.6	3.4	283	300	278
4	AF1B17-2	AF1	17	10.9	14.2	6.3	253	275	317
4	AI8B17-2	AI8	17	12.9	7.7	5.5	249	250	358

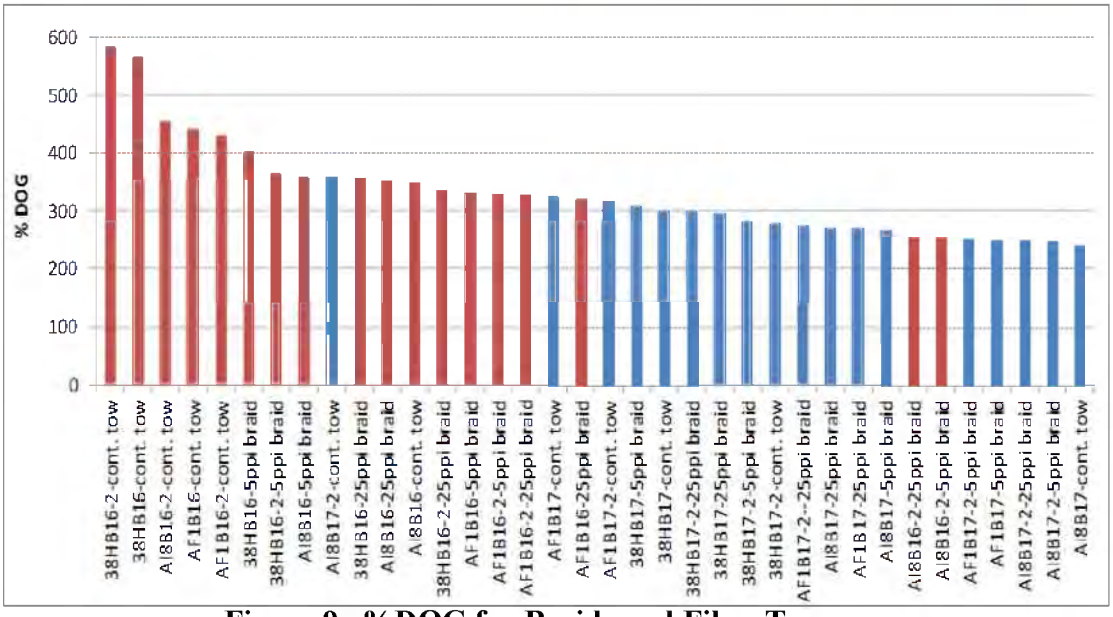

Figure 9. %DOG for Braids and Fiber Tows

Table 5 provides information on the irradiation and grafting test matrix for the leno woven fabrics and tow fibers. A total of 18 leno fabrics and 6 tow fiber samples, all comprised of #8 hollow gear fibers, were irradiated and then grafted with either 38H, AF1 or AI8 formulations. Three identical sets of L1 and L2 leno fabrics were grafted per formulation and 2 identical sets of tow fiber samples were grafted per formulation. A large number of leno fabrics and tow fiber samples were made for conducting laboratory screening, optimization studies and seawater evaluations. Grafting for the leno fabrics and their tow fibers were conducted in 950 ml Ace-

Glass pressure bottles. The grafting time ranged from 18-19 hours and the graft temperature was 64°C. Weights for the leno fabrics and tow fibers after grafting ranged from about 14-40g and 16-19g, respectively. The %DOG for the leno fabrics and tow fibers ranged from about 300-400% and the data were comparable for all 3 identical sets of samples. The AF1 formulations generally yielded the highest %DOG followed by 38H and AI8. The %DOG for the leno woven fabrics and tow fibers are shown in Figure 10.

Table 5. Irradiation and Grafting Test Matrix for Leno Woven Fabrics and Tow Fibers

EB run no.	Sample ID	Graft Formulation; Fabric Type	Graft Time, hrs.	Wt. before grafting, g	Wt. after grafting, g	% DOG
1	38HL1R1	38H; L1 fabric	18	3.2	14.3	347
1	38HL2R1	38H; L2 fabric	18	4.5	19.7	338
1	AF1L1R1	AF1; L1 fabric	18	3.2	15.7	391
1	AF1L2R1	AF1; L2 fabric	18	4.8	24.5	410
1	AI8L1R1	AI8; L1 fabric	18	3.6	14.8	311
1	AI8L2R1	AI8; L2 fabric	18	4.8	19.7	310
2	38HL1R2	38H; L1 fabric	19	4	17.9	348
2	38HL2R2	38H; L2 fabric	19	6.3	30.2	379
2	AF1L1R2	AF1; L1 fabric	19	4	17.7	343
2	AF1L2R2	AF1; L2 fabric	19	6.3	26.4	319
2	AI8L1R2	AI8; L1 fabric	19	4.5	18.8	318
2	AI8L2R2	AI8; L2 fabric	19	5.1	20.9	310
2	38HFR2	38H; #8 cut fiber	19	4	17.3	333
2	AF1FR2	AF1; #8 cut fiber	19	4	18.5	363
2	AI8FR2	AI8; #8 cut fiber	19	4	16.4	310
3	38HL1R3	38H; L1 fabric	18	4.9	22.5	359
3	38HL2R3	38H; L2 fabric	18	8.8	39.7	351
3	AF1L1R3	AF1; L1 fabric	18	4.8	20.4	325
3	AF1L2R3	AF1; L2 fabric	18	6.7	35.3	427
3	AI8L1R3	AI8; L1 fabric	18	4.6	19.2	317
3	AI8L2R3	AI8; L2 fabric	18	6.9	29.7	330
3	38HFR3	38H; #8 cut fiber	18	4	17.2	330
3	AF1FR3	AF1; #8 cut fiber	18	4	19.1	378
3	AI8FR3	AI8; #8 cut fiber	18	4	17.4	335

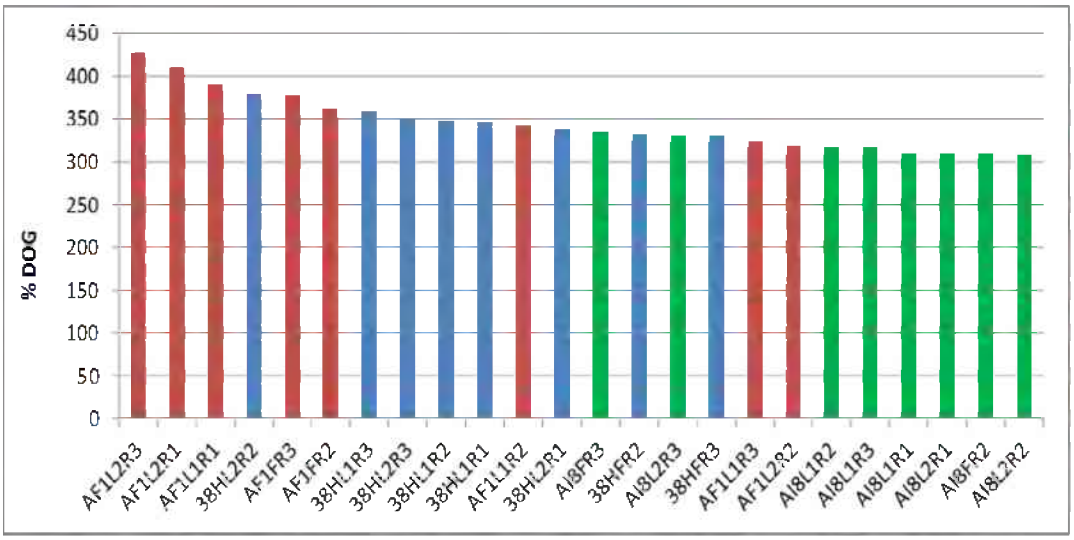

Figure 10. Plot of %DOG for Leno Woven Fabrics and Tow Fibers

Figures 11-15 are recent pictures from NEO Beam during the irradiation and grafting experiments conducted on the leno woven fabrics and tow fibers.

Figure 11. NEO Beam Laboratory – Sample Preparation and Grafting

Figure 12. Degassing Graft Solutions

Figure 13. Glove Bag Containing New Pressure Bottles

Figure 14. New Grafting Oven

Figure 15. Leno Woven Fabrics After Grafting

Amidoximation and KOH Conditioning of Braids and Leno Woven Fabric Samples

Amidoximation – Conversion of Nitrile Groups to Amidoxime Groups

A mass of approximately 40 mg of each grafted braid and leno woven fabric sample was placed in a glass vial containing approximately 20 mL of 10 wt% hydroxylamine hydrochloride in 50/50 (w/w) water/methanol (previously neutralized with KOH) at 80°C for 24 hours. The samples

were then filtered, and the process was repeated two more times for a total of 72 hours. 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.

KOH Conditioning

A mass of approximately 15 mg of each amidoximated braid and leno woven fabric sample was added to a flask containing 15 mL of 2.5 wt % KOH and heated for 3 hours at 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. It was found that if the fibers dried out, the capacity would significantly decrease.

Laboratory Screening of Braids and Leno Woven Fabric Samples – Uranium Adsorption Capacity

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 dioxide believed to be in tricarbonate complex $\{[UO_2(CO_3)_3]^{4-}\}$ at a pH of 7.5–8.4. The screening solution that is 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 6–7 ppm uranium ions from dissolving uranyl nitrate hexahydrate in 18.2 megohm water. The pH of this solution was approximately 8. A sample of the solution was collected prior to sorbent addition to determine the initial uranium concentration before the adsorption experiment. The KOH-conditioned braided adsorbent samples were then equilibrated with 750 ml of the screening solution 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 with the solution. After shaking was completed, an aliquot of the 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).

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

Equation 1. With the initial and final uranium concentrations determined for each sample, the uranium adsorption capacity (mg uranium/g adsorbent) was calculated.

The ICP-OES was calibrated using 6 standard solutions ranging from 0-10 ppm, which were prepared from a 1000-ppm uranium in 5% nitric acid stock solution, and a linear calibration curve was obtained. In addition, a blank solution of 2–3% nitric acid was prepared and washouts

were monitored between samples. 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 of several promising braided and leno woven adsorbent fabrics was determined by laboratory screening and, as shown in Table 6 and Figure 16, it ranged from 125 to 180 g-U/kg ads. These fabrics were made from 3 different fibers, including #16 and #17 hollow gear fibers for the braids and #8 hollow gear fibers for the leno woven fabrics, and 3 different grafting formulations including 38H, AF1 and AI8. The samples based on AF1 and AI8 grafting formulations appear very promising for achieving high adsorption capacity. Laboratory screening on additional braided and leno woven adsorbents is currently on-going.

Table 6. Uranium Adsorption Capacities on Braids & Leno Woven Adsorbents; AN: Acrylonitrile; MAA: Methacrylic acid; ITA: Itaconic acid; VPA: Vinylphosphonic acid

Sample ID	Grafting formulation in DMSO	Fiber Type	% DOG	Uranium adsorption capacity (g-U/kg-ads)
38HB16-5ppi braid	AN-MAA	#16; hollow gear; PE	403	125
AF1B16-5ppi braid	AN-ITA		332	148
AI8B16-5ppi braid	AN-VPA		360	160
38HB17-5ppi braid	AN-MAA	#17; hollow gear; PE	309	131
AF1B17-5ppi braid	AN-ITA		250	180
AI8B17-5ppi braid	AN-VPA		268	173
AF1L1R1 leno	AN-ITA	#8; hollow gear; PE	391	154
AF1L2R1 leno	AN-ITA		410	147
AF1L1R2 leno	AN-ITA		343	156
AF1L2R2 leno	AN-ITA		319	151
AF1L1R3 leno	AN-ITA		325	151
AF1L2R3 leno	AN-ITA		427	158

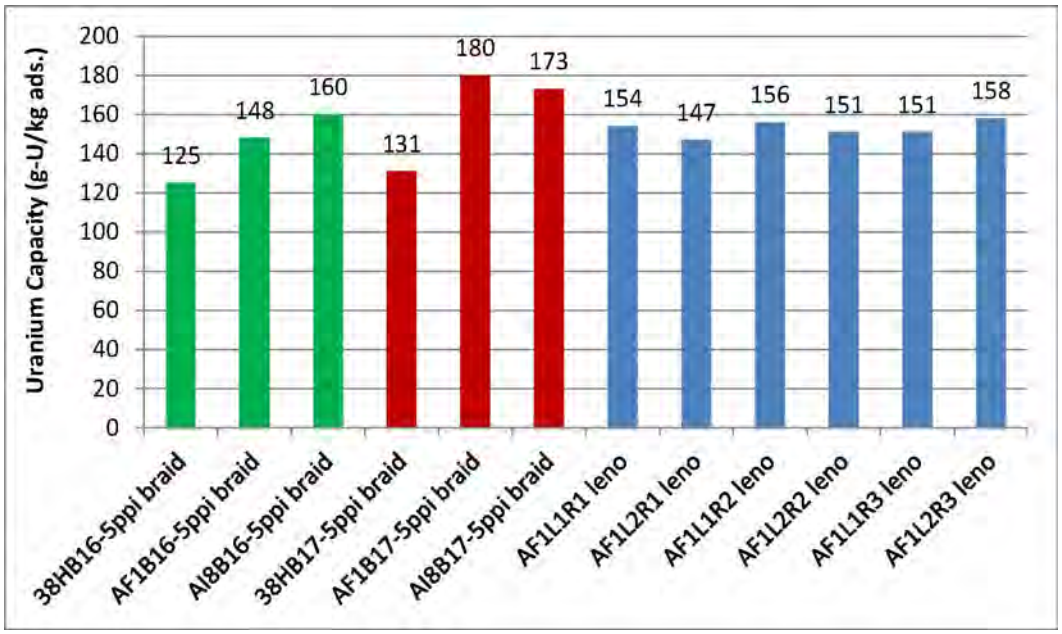

Figure 16. Uranium Adsorption Capacity Results on Braids and Leno Woven Adsorbents

Braid Adsorbents Prepared and Sent to PNNL

Four "practice" braid adsorbents underwent amidoximation at ORNL and were sent to PNNL for KOH conditioning and preliminary flume testing in seawater including 2 samples of AF1B17-2-5ppi and 2 samples of AF1B17-2-25ppi. Uranium adsorption capacities are currently being determined on these samples.

Summary

In summary, a wide variety of braids and other textile fabric candidates have been manufactured and several promising braided and leno woven fabrics were down-selected and underwent further processing including irradiation, grafting, amidoximation and KOH conditioning. Uranium adsorption capacities have been determined on 12 of these promising adsorbents using ORNL's Laboratory Screening Protocol and ranged from approximately 125 to 180 g-U/kg-adsorbent. Four braided adsorbent samples have been prepared and sent to PNNL for seawater flume testing. Additional braided and leno woven adsorbents are being prepared for shipment to PNNL for seawater testing.