Milestone Report - Complete New Adsorbent Materials for Marine Testing to Demonstrate 4.5 g-U/kg Adsorbent

(Milestone M2FT-14OR03100115 – 8/20/2014)

Fuel Cycle Research & Development

Prepared for

U.S. Department of Energy

Fuel Cycle Research & Development

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August 20, 2014

FCRD-SWF-2014-000595

SUMMARY

This report describes work on the successful completion of Milestone M2FT-14OR03100115 (8/20/2014) entitled, "Complete new adsorbent materials for marine testing to demonstrate 4.5 g-U/kg adsorbent". 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 materials at the Oak Ridge National Laboratory (ORNL) and marine testing at the Pacific Northwest National Laboratory (PNNL). ORNL has recently developed two new families of fiber adsorbents that have demonstrated uranium adsorption capacities greater than 4.5 g-U/kg adsorbent after marine testing at PNNL. One adsorbent was synthesized by radiation-induced graft polymerization of itaconic acid and acrylonitrile onto high surface area polyethylene fibers followed by amidoximation and base conditioning. This fiber showed a capacity of 4.6 g-U/kg adsorbent in marine testing at PNNL. The second adsorbent was prepared by atom-transfer radical polymerization of *t*-butyl acrylate and acrylonitrile onto halide-functionalized round fibers followed by amidoximation and base hydrolysis. This fiber demonstrated uranium adsorption capacity of 5.4 g-U/kg adsorbent in marine testing at PNNL.

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ACRONYMS

AA	Acrylic acid
AN	Acrylonitrile
ATRP	Atom-transfer Radical Polymerization
%COV	Percent coefficient of variation
DMSO	Dimethyl sulfoxide
DOG	Degree of grafting
EB	Electron Beam
HDPE	High density polyethylene
ICP-AES	Inductively coupled plasma atomic emission spectrometry
ICP-MS	Inductively coupled plasma mass spectrometry
ITA	Itaconic acid
JAEA	Japan Atomic Energy Agency
JAERI	Japan Atomic Energy Research Institute
KOH	Potassium hydroxide
MAA	Methacrylic acid
Me_6-TREN	tris(2-(dimethylamino)ethyl)amine
ORNL	Oak Ridge National Laboratory
PNNL	Pacific Northwest National Laboratory
PAA	poly(acrylic acid)
PLA	Polylactic acid
Poly(TFE-E)	poly(tetrafluoroethylene-*co*-ethylene)
PVC	poly(vinyl chloride)
CPVC	chlorinated poly(vinyl chloride)
PSU	practical salinity units
RIGP	Radiation-induced graft polymerization
*t*BA	*t*-butyl acrylate
THF	Tetrahydrofuran

FUEL CYCLE RESEARCH & DEVELOPMENT

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1. INTRODUCTION

This report describes the manufacture, synthesis, and laboratory screening of ORNL's two new families of fiber adsorbents and the marine testing activities conducted at PNNL. The purpose of this document is to report on the successful completion of Milestone M2FT-14OR03100115 (8/20/2014) entitled, "Complete new adsorbent materials for marine testing to demonstrate 4.5 g-U/kg adsorbent".

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 a conservative element in seawater and its concentration varies in direct proportion to changes in salinity. Since seawater is slightly basic (pH 8.0±0.4), uranium exists primarily as $[UO_2(CO_3)_3]^{4-}$. 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. BACKGROUND INFORMATION

An extensive study conducted by German researchers in the 1980s concluded that the amidoxime ligand was the most effective functionality for the recovery of uranium from seawater.[11, 16] The amidoxime structure was first elucidated in 1884 by Tiemann; however, the first amidoxime was prepared in 1873 by Lossen and Schifferdecker from the reaction of hydrogen cyanide with hydroxylamine.[17] Despite the dozen existing methods to generate amidoxime, the exclusive approach for polymeric adsorbent synthesis still is the original preparation from 1873, the functional group interconversion of nitriles with hydroxylamine (Figure 1).

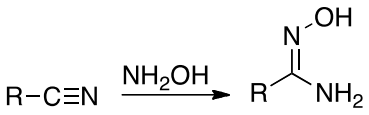

Figure 1. Functional group interconversion of nitriles with hydroxylamine.

Initial research efforts on polymeric adsorbents focused on those containing the amidoxime group including polyacrylamidoxime fibers and polymeric beads; however, these approaches were later abandoned due to their low mechanical properties, poor durability, and practical handling issues.[18-23] To improve the durability and tensile properties of amidoxime-based fiber adsorbents, researchers at the Japan Atomic Energy Research Institute (JAERI), which is

now part of the Japan Atomic Energy Agency (JAEA), studied the irradiation-induced graft polymerization (RIGP) of gaseous acrylonitrile (AN) on various trunk polymers, including tetrafluoroethylene-ethylene copolymer, polypropylene, polyamide, polyethylene, polyester, and carbon fiber.[24] By irradiating the materials, radicals were generated throughout the trunk polymer, which can initiate the graft polymerization. The grafting yield of the product was controlled by the irradiation dose, or in other words by the number of initial radicals and the length of the graft chains. The efficiency for adsorption of transition metal ions was improved either by adding small amounts of acrylic acid (AA) or 4-vinylpyridine, or by restricting the distribution of amidoxime groups at the tetrafluoroethylene ethylene copolymer fiber surface.[25] The hydrophilicity increased the exchange rate between the external hydrated metal ions and the internal polymer hydrating water, allowing the interaction of the functional groups throughout the polymer, and induced the diffusion of hydrated metal ions. The co-grafting with hydrophilic monomers was effective in improving the adsorption rate of the uranium onto the resulting amidoximated adsorbent in seawater.

One of the challenges in RIGP is to maximize the grafting yields, i.e., the percent degree of grafting (DOG) determined gravimetrically from pre-irradiation and post-grafting weights, of functional groups onto the trunk polymer (Eq 1). The Japanese obtained a DOG of 130% by grafting AN to hollow fiber adsorbents. The material was reacted with hydroxylamine to convert the nitrile groups to the amidoxime, and was then conditioned with alkali (2.5 wt% KOH). It was determined that the optimum alkaline treatment time was 1 hr.[26, 27] We have demonstrated that alkaline conditioning swells the adsorbent and converts some of the amidoxime groups to carboxylic acid groups, which increases its hydrophilicity and uranium adsorption capacity.

$$\%DOG = \frac{\left(wt_{AG} - wt_{BG}\right)}{wt_{BG}} x100 \qquad (1)$$

wt_{AG} = dry weight after grafting;
wt_{BG} = dry weight before grafting

Other studies utilizing grafting mixtures of AN and AA or methacrylic acid (MAA) onto polyethylene films demonstrated that hydrophilic groups increased the uranium adsorption. On polyethylene a maximum adsorption of uranyl ions on polyethylene was obtained when a 50:50 mixture of AN:AA was randomly co-grafted onto the fibers.[28] For polypropylene fibers, an optimum adsorption of uranium and a DOG of 200% and 150% was obtained with a starting mixture of 80:20 AN:MAA or 70:30 AN:MAA, respectively.[29, 30]

To synthesize a more durable deployable adsorbent, researchers from the JAEA attempted to use nonwoven polymeric fibers made from approximately 50/50 wt % of high-density polyethylene (sheath)/polypropylene (core).[30-34] These nonwoven fabrics were investigated for many years and are constructed using short, discontinuous, thermally spun-bonded fibers that have relatively poor mechanical strength compared with continuous fiber forms. Nonwoven fabrics were evaluated in several seawater experiments; however, due to their low mechanical properties, these materials had to be sandwiched into bulky stacks composed of nonwoven adsorbents, spacer nets, and stack holders that were placed on large, heavy floating frames which eventually proved too costly for deployment in the sea. In addition, the sandwich stacks that contained the nonwoven adsorbents prevented good accessibility to the seawater, resulting in much lower

adsorption capacities compared with braided adsorbents.[35, 36] Due to the high cost of the floating frames and the poor accessibility of the seawater for the nonwoven adsorbents, research efforts transitioned to braided fiber adsorbents.

The braided adsorbents were composed of continuous high-density polyethylene (HDPE) fibers that were braided around a porous polypropylene float that can be made into long lengths. The braided adsorbent was made from round, approximately 20-micron-diameter HDPE fibers. It is currently considered the material of choice for uranium adsorbents due to its outstanding balance of properties, including high mechanical properties, durability, low cost, chemical resistance (i.e., acids, bases, solvents) as well as ease of placement and retrieval from the sea.

A recent economic analysis performed by Schneider and Sachde assessed the current braid adsorbent process described by Tamada.[6, 37] This analysis concluded that the uranium adsorption capacity, the recyclability of the adsorbent, and the cost of the chemicals used in the adsorbent manufacturing process were the most important cost drivers for extracting uranium from seawater. Possible options for increasing the recyclability and durability of the adsorbent include using a less damaging chemical process for the elution and reconditioning steps. In addition, the adsorbent manufacturing cost can be reduced by minimizing or recycling the various chemicals used in the process. The uranium adsorption capacity for Japan's most advanced braid adsorbent and its nonwoven adsorbent (non-sandwich stack configuration) has been reported to be 1.5 g U/kg adsorbent after 30 days of immersion in seawater (M. Tamada; N. Seko, personal communication). However, these results could not be verified by ORNL or Pacific Northwest National Laboratory (PNNL) after conducting several seawater experiments using two different sets of nonwoven adsorbents that were provided by the JAEA, and the capacity results for these adsorbents ranged from 0.74–1.1 g U/kg adsorbent for 30 days exposure. Nevertheless, the capacity value of 1.5 g U/kg-adsorbent is still considered to be too low to be cost-effective for implementation; therefore, we began our development efforts to advance the existing Japanese technology and increase the adsorption capacity of fiber-based adsorbents.

2.1 High-surface-area polyethylene fibers

The current Japanese braided adsorbents are made from round, 20-micron-diameter HDPE fibers.[33] These fibers have relatively low surface area and cannot be made with fiber diameters less than approximately 15–20 microns due to inherent limitations in the melt-spinning process of polyethylene. However, we determined that one of the most effective methods to increase the uranium adsorption capacity is to increase the surface area of the adsorbent fibers. By using unique fiber technology developed and patented by Hills, Inc.,[38-44] we have achieved higher-surface-area fibers that show higher uranium adsorption capacities compared with commercially available 20-micron-diameter round fibers. This unique technology effectively increases the surface area of polyethylene fibers by reducing the diameter of the fibers and/or changing the shape of the fibers (see below). It has been determined that the surface area–to–weight ratio for adsorbent fibers can be increased substantially by reducing the diameter of the fiber or changing the cross-sectional shape of the fiber, or a combination of both. Figure 2 below shows the increase in surface area as the fiber diameter is reduced.

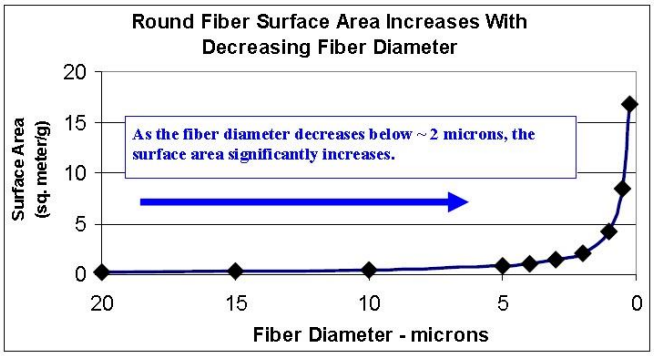

Figure 2. Increase in surface area as fiber diameter is reduced.

One feature of Hills, Inc. technology is called the islands-in-the-sea (I-S) method, wherein fibers as small as 0.25 micron in diameter can be made, resulting in a 6000% increase in surface area compared with commercially available 20-micron-diameter round fibers. In the I-S method, polyethylene nanofibers, i.e. the islands, are embedded inside a larger diameter fiber made of a dissolvable polymer like polylactic acid (PLA), i.e. the sea. After the fibers are spun, the sea polymer is dissolved away to expose the nanofibers. Using this manufacturing process, fibers with as many as 156,000 islands can be made.

Another unique aspect of this technology involves melt-spinning fibers that have non-round shapes. Round or circular cross-sectional shaped fibers have much lower surface areas than non-round shaped fibers of the same diameter. Fiber shapes that we have studied include solid or hollow flower shape, solid or hollow gear shape, solid or hollow trilobal shape, solid trilobal gear shape, and others (Fig. 4.2). In our research, we have evaluated several high-surface-area fibers including a range of small-diameter, round fibers (0.24–15 microns in diameter) and many non-round-shaped fibers that had surface areas from 0.36 to 11.5 m^2/g, about 2–60 times higher than the standard 20-micron-diameter round fiber (0.18 m^2/g). Figure 3 shows some selected cross-sectional shapes of high-surface-area polyethylene fibers used to make our adsorbents, including the hollow gear-shaped fibers, which constitute one of our better adsorbents (38H).

Hollow gear shape | Solid gear shape | Flower shape | Caterpillar shape

Figure 3. Selected cross-sectional shapes of some high-surface-area polyethylene fibers used to make ORNL adsorbents.

3. NEW ADSORBENT DEVELOPMENT

In 2013 we successfully achieved the 3-year goal of this project by building off the Japan Atomic Energy Agency (JAEA) technology, and developed an amidoxime fiber adsorbent that has an adsorption capacity at least double (3 g-U/kg adsorbent) that of the best Japanese nonwoven fiber adsorbent. Our approach focused on increasing the uranium adsorption capacity by increasing the surface area of fiber adsorbents and optimizing the radiation-induced graft polymerization (RIGP) conditions and degree of grafting of AN and MAA. Based on this work we successfully developed and optimized the 38H adsorbent which demonstrated a capacity of about 3.3 g U/kg adsorbent after 56 days of marine testing at PNNL.[45]

During 2013-2014 we developed a new family of adsorbents that have demonstrated capacities up to 4.6 g U/kg adsorbent (AF8RMCJ adsorbent) after only 49 days of marine testing at PNNL. These new adsorbents, referred to as "AF type" adsorbents are synthesized by RIGP of itaconic acid and AN onto high surface area polyethylene fibers instead of MAA and AN. The hypothesis was that the uranium adsorption capacity could be increased by increasing the hydrophilicity of the polymers. Thus, different carboxylic acids were polymerized into the polymer adsorbents including itaconic acid, which has two carboxylic acid groups per molecule as opposed to one for methacrylic acid (Figure 4). The polar (δP) and hydrogen bonding (δH) for itaconic acid are 8.4 (calculated) and 18.1 (calculated) compared to 2.8 and 10.2 for MAA indicating higher hydrophilicity for itaconic acid versus MAA.[46] [47] The series of AF type adsorbents were prepared by RIGP using different ratios of AN to itaconic acid co-monomers onto high surface area polyethylene fibers, designated as AF1 through AF9.

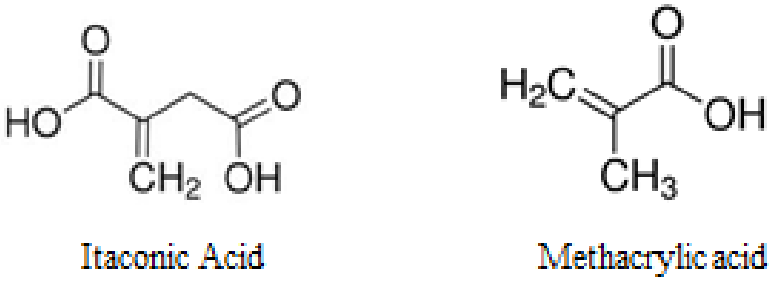

Figure 4. Chemical structures of itaconic acid and methacrylic acid.

In addition to RIGP technology for growing functional polymers from chemically and mechanically robust trunk polymer fibers, we explored an alternative method to graft uranium-adsorbing polymer chains on fiber substrates using atom-transfer radical polymerization (ATRP). In comparison with RIGP, ATRP allows for the control of molecular weight, molecular weight distribution, end groups, and polymer architecture, such as block and graft copolymers. Moreover, ATRP achieves a high-DOG due to its controlled polymerization mechanism. In our study, ATRP of AN and *tert*-butyl acrylate (*t*BA), a precursor for polyacrylic acid (PAA), was performed on a fibrous copolymer of poly(vinyl chloride) and chlorinated poly(vinyl chloride), PVC-*co*-CPVC, followed by amidoximation and KOH treatment, similarly to the RIGP method.

3.1 Overview of Adsorbent Preparation

3.1.1 Manufacture and Synthesis of Adsorbents

ORNL's adsorbent fibers were prepared by RIGP, as illustrated in Figure 5, and involve four processing steps: electron beam irradiation of high-surface-area polyethylene fibers; co-grafting polymerizable monomers containing nitrile groups and hydrophilic groups to form grafted side chains throughout the fiber; conversion of nitrile groups to amidoxime groups; and alkaline conditioning of the grafted fibers. The resulting adsorbents are then tested for their capacity to bind uranium from seawater.

Each of the four processing steps discussed above has many parameters that can greatly influence the uranium adsorption capacity; therefore, much of our efforts were focused on systematically investigating the large number of experimental variables and preparing hundreds of adsorbent samples to determine which of these parameters were the most important. These parameters included trunk polymer fiber type, fiber diameter, fiber morphology, fiber surface area, and crystallinity. Irradiation conditions included dose, dose rate, irradiation time, atmosphere, and temperature. Graft conditions included solvent, co-monomers, concentration, co-monomer ratio, additives, and reaction temperature and time. Amidoximation conditions included solvent, solvent concentration, hydroxylamine concentration, and reaction temperature and time. Alkaline conditions included alkaline concentration and reaction temperature and time. Based on these results, additional experiments were conducted to better understand and optimize the key parameters in order to continuously improve the uranium adsorption capacity.

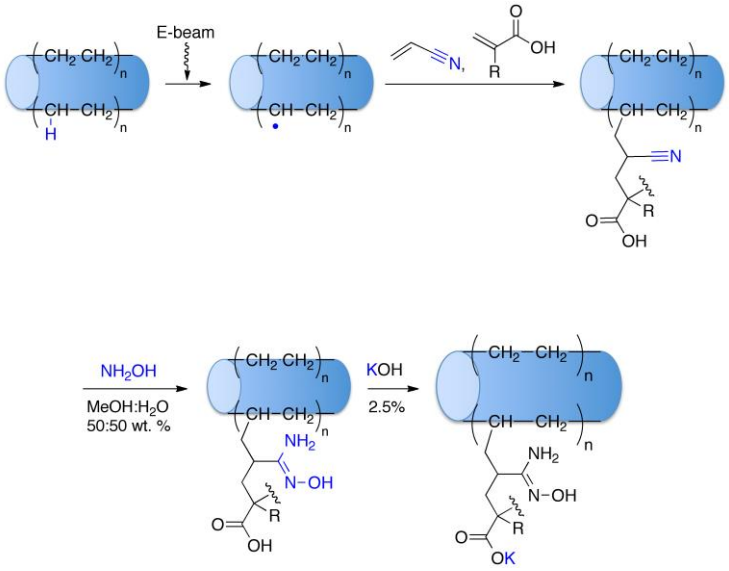

Figure 5. Reaction scheme for ORNL's adsorbent fibers**.**

3.1.2 Irradiation of High-Surface-Area Polyethylene Fibers

ORNL's adsorbents were composed of hollow-gear (see Figure 3), high surface area polyethylene fibers (Dow Aspun 6850/6202DPLA - #8 fibers) that were melt-spun at Hills, Inc. using polylactic acid (PLA) as the second polymer. Prior to irradiation the PLA was removed by

submerging the fibers 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 fiber samples (~0.75g) 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 6 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 underneath a 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 6. Electron beam set-up for irradiating adsorbent fibers.

3.1.3 Grafting of Polymerizable Monomers Containing Nitrile Groups and Hydrophilic Groups

After irradiation, the fibers were immersed in 250 mL flasks containing previously de-gassed grafting solutions. The 38H grafting solution contained AN, MAA and dimethylsulfoxide (DMSO) and the AF1-AF9 grafting solutions contained different amounts of AN and itaconic acid (ITA) in DMSO. The flasks were then placed in an oven at 60–70 °C for 17-20 h for grafting. After the grafting reaction was complete, the fibers 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 °C under vacuum. The grafted fibers were weighed to determine the % degree of grafting (DOG). Tables 1-3 provide information on the grafting formulations that were used to prepare the 38H and AF type adsorbents.

Table 1. Weight and volume composition of grafting formulations for AF type adsorbents.

Adsorbent	DMSO, mL	AN, mL	ITA, g	DMSO, wt.%	AN+ITA wt. %	AN/ITA, wt.%
AF4	56.7	129.7	68.6	26.4	73.6	44.5/29.1
AF5	56.7	140.5	59.9	26.4	73.6	48.2/25.4
AF6	56.7	151.3	51.2	26.4	73.6	51.9/21.7
AF2	51.7	147.7	42.5	26.0	74.0	54.6/19.4
AF3 or AF1	56.8	162.0	42.5	26.4	73.6	55.6/18.0
AF7	56.7	172.7	33.8	26.4	73.6	59.3/14.3
AF8 (AF8RMCJ)	56.7	183.4	25.1	26.4	73.6	62.93/10.64
AF9	56.7	194.1	16.5	26.4	73.6	66.6/7.0

Table 2. Weight and volume composition of grafting formulation for 38H adsorbent.

Adsorbent	DMSO, mL	AN, mL	MAA, g	DMSO, wt.%	AN+MAA wt. %	AN/MAA, wt.%
38H	49.9	142.4	48.7	25.0	75.0	52.5/22.5

Table 3. Molar composition of grafting formulations and % DOG for 38H and AF type adsorbents.

Adsorbent	Grafting solution AN:MAA (mol/mol) DMSO 25 wt. %	Grafting solution AN:ITA (mol/mol) DMSO ~ 26 wt. %	% DOG
38H	3.78		250-600
AF4		3.76	154
AF5		4.66	170
AF6		5.87	187
AF2		6.90	266
AF3 (AF1)		7.57	354
AF7		10.14	213
AF8 (AF8RMCJ)		14.50	348
AF9		23.36	282

Figures 7-11 are pictures from NEO Beam facility during the irradiation and grafting experiments conducted on the adsorbent fibers.

Figure 7. NEO Beam Laboratory – adsorbent sample preparation and grafting.

Figure 8. Degassing graft solutions.

Figure 9. Glove bag containing pressure bottles and grafting solutions.

Figure 10. Grafting oven.

Figure 11. Adsorbent fibers after grafting reaction**.**

3.1.4 Conversion of Nitrile Groups to Amidoxime Groups – Amidoximation

Approximately 40 mg of each grafted fiber 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) and heated at 80 °C for 24 hours on a heating block. The samples were then filtered, and the process was repeated two more times for a total of 72 h (note: the AF8RMCJ sample was also amidoximated for a total of 72 h by heating once for 24 h followed by 48 h. 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.

3.1.5 Alkaline Conditioning of Grafted Fibers

Approximately 15 mg of each amidoximated fiber sample was added to a flask containing 15 mL of 2.5 wt % KOH and heated for 1-3 h at 80 °C on a heating block. 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.

3.1.6 Preparation of Fiber Adsorbents via ATRP

Synthesis of fibrous uranium adsorbents on PVC-*co*-CPVC fiber by ATRP was performed in three steps: 1) ATRP of AN and *t*BA from labile chlorides on PVC-*co*-CPVC fiber, 2) amidoximation with NH_2OH, and 3) KOH conditioning (Figure 12). Step 1 produces a brush architecture of grafted functional polymers, PAN-*co*-P*t*BA. Amidoximation converted PAN to polyacrylamidoxime (PAO), which has high affinitiy in binding to uranyl ions. The last step, KOH conditioning, hydrolyzed P*t*BA to poly(acrylic acid), PAA, and any unreacted nitriles to

carboxylate groups, thereby, increasing hydrophilicity and the swelling of fibrous adsorbents in seawater.

The PVC-*co*-CPVC fiber used in this study is Rhovyl^{TM}'s ZCS tow fiber. It is a copolymer between PVC and CPVC, processed without any plasticizer, to the round fiber form (average diameter: 15.4±2.8 μm). The measured wt % Cl from elemental analysis (EA) is 49.16%, which is lower than expected even for pure PVC (theoretical, 56.73%). This experimental value, 49.16%, was used in the calculation for moles of "alkyl chlorides" (RCl) that could potentially react. For example, for each 150-mg Rhovyl^{TM}'s fiber, (0.150 g × 0.4916)/(35.453 g/mol of Cl) = 2.08×10^{-3} mol RCl were present.

Due to the solubility of PVC fiber in various solvents and monomers, especially at elevated temperatures, ATRP conditions were limited to reactions in ethylene carbonate (EC) at 65 °C, which allowed reasonable growth rates of polymers. The copper catalyst for the ATRP reaction was complexed with tris(2-(dimethylamino)ethyl)amine (Me_6-TREN), since Cu complexes with Me_6-TREN form one of the most active and most reducing catalysts, which lead to high DOG.

In these studies, a fixed amount of catalyst was used while the [*t*BA]/[AN] feed ratio was varied in the copolymerization (Table 4). From [*t*BA]/[AN] feed ratios, mole fractions of AN in the feed, F_{AN}, were calculated (3rd column). The elemental analysis (EA) of grafted fibers permitted the calculation of P*t*BA/PAN molar ratios, i.e. mole fractions of PAN in grafted fibers, F_{PAN} (4th column). Overall, F_{PAN} in the fiber decreased with the decreasing F_{AN} in the feed. The successful preparation of fibers with varied composition of PAN and PtBA was accomplished and the effect of the composition was investigated. The nitrile group on PAN was subsequently amidoximated with hydroxylamine, while *t*BA group on PtBA was hydrolyzed via KOH treatment, which were described above.

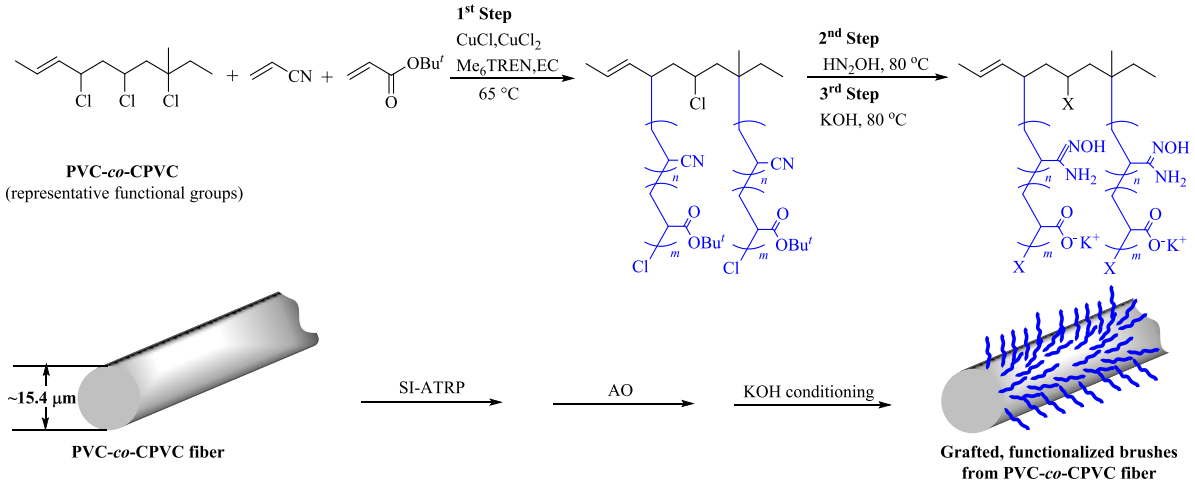

Figure 12. Synthesis of fibrous uranium adsorbents from PVC-*co*-CPVC.

Table 4. Simultaneous copolymerization of *t*BA and AN and U uptake in 750-mL U-spiked simulated seawater.

no.	[*t*BA]/[AN][a]	F_{AN} from feed [b]	F_{PAN} from EA[c]	d.g.,	adsorption capacity,[d] mg U/g	K_d L/g
1.2	0:993	1.00	1.0	437	116.5	30.7
2.1	50:494	0.908	0.858	162	90.0	20.0
2.2	124:494	0.799	0.796	256	81.6	17.6
2.3	249:494	0.665	0.738	1390	174.7	75.1
2.4	371:494	0.571	0.679	1012	150.5	48.7
2.5	496:494	0.499	0.608	754	154.0	52.8
2.6	624:494	0.442	0.516	1527	118.0	32.7

[a] [*t*BA]/[AN]/[RCl]/[CuCl]/[Me_6TREN]/[$CuCl_2$] = the above monomer ratios:5.4:1.0:1.2:0.05, in 50 vol % EC, 65 °C, 24 h.
[b] mole fraction of AN = (moles of AN in the feed)/(total moles of monomers in the feed)
[c] mole fraction of PAN = (moles of PAN from EA)/(moles of PAN from EA + moles of P*t*BA from EA)
[d] Testing conditions: 15 mg adsorbent in 750 mL of 6-ppm U, 10123 ppm Na^+, 15529 ppm Cl^-, 140 ppm HCO_3^-, pH 8, 20–25 °C, 24 h; ICP-OES at λ_U 367.007 nm.

3.2 Laboratory Screening of Adsorbents

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 analyzed prior to adsorbent addition to determine the initial uranium concentration before the adsorption experiment. Each of the KOH conditioned adsorbent samples were then equilibrated with 750 mL test solutions for 24 h 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 h. 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 (Perkin Elmer Optima 2100DV ICP-OES). Using the difference in uranium concentration of the initial and final solutions, the uranium adsorption capacity is determined, using Eq. (2).

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

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 13 below.

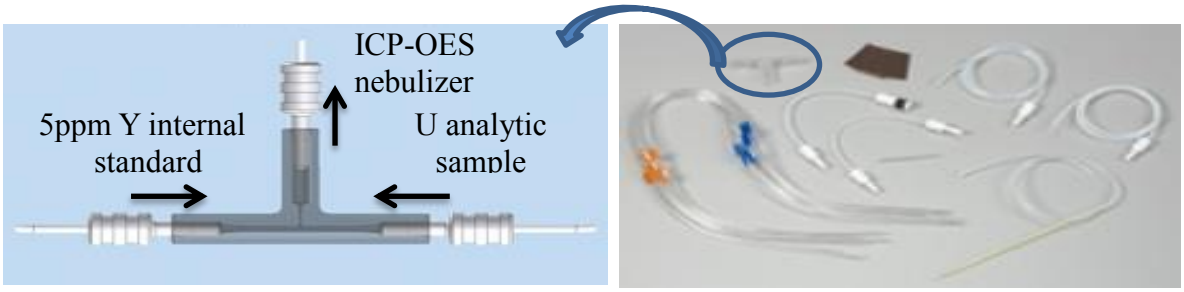

Figure 13. Internal Standard Addition Kit for ICP-OES (Perkin-Elmer).

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 sample solutions were 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 ATRP, 38H and AF type adsorbent samples from the laboratory screening process are shown in Tables 4 and 5. The capacity values ranged from about 80-175 g-U/kg adsorbent for the ATRP adsorbents, 150-190 g-U/kg adsorbent for the 38H adsorbent and from 170 to 200 g-U/kg adsorbent for the AF type adsorbents.

Table 5. Uranium adsorption capacity results of ORNL adsorbents.

Adsorbent	Grafting solution AN:MAA (mol/mol) DMSO 25 wt. %	Grafting solution AN:ITA (mol/mol) DMSO ~26 wt. %	%DOG	Uranium Adsorption Capacity, g-U/kg ads.
38H	3.78		250-600	150-190
AF4		3.76	154	185
AF5		4.66	170	179
AF6		5.87	187	184
AF2		6.90	266	182
AF3 (or AF1)		7.57	354	200
AF7		10.14	213	191
AF8		14.50	348	194
AF9		23.36	282	170

Figure 14 is a plot of the %DOG and uranium adsorption capacities for the AF type adsorbents. From this figure it is clear that the %DOG does not necessarily directly correlate with the adsorption capacity and that a high capacity can be achieved with adsorbents having lower %DOG (i.e., AF4, AF5, AF6).

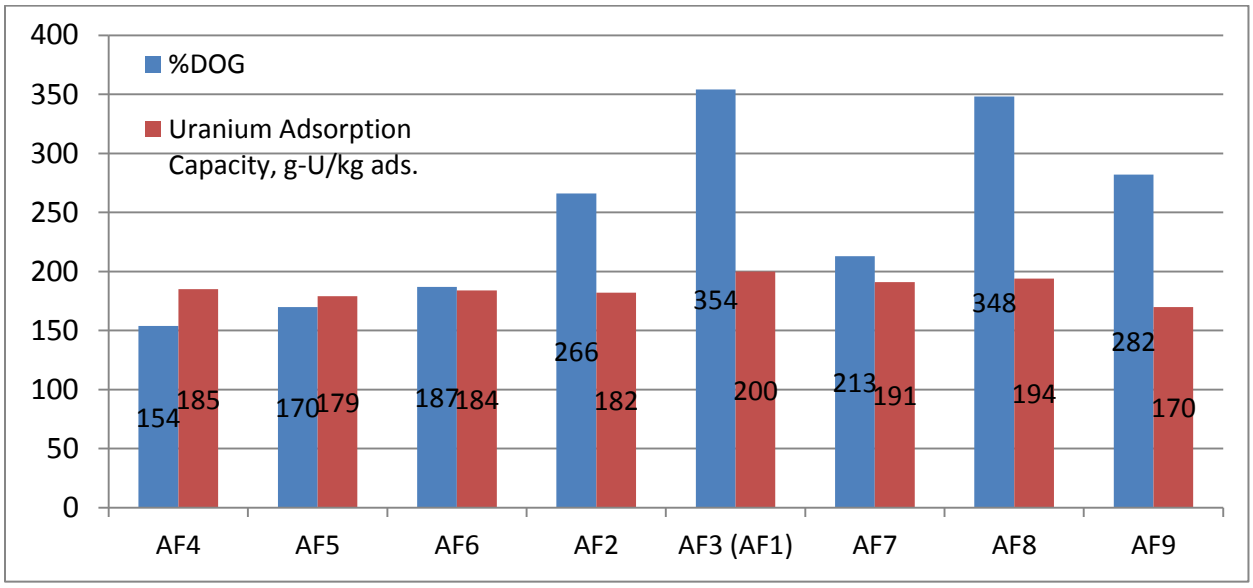

Figure 14. %DOG and uranium adsorption capacities for the AF type adsorbents.

4. Preparation and Setup for Field Adsorption Tests at PNNL

The adsorbent capacity was determined using natural seawater and flow-through columns at PNNL. The quality of seawater was quantitatively monitored for pH, temperature, salinity, and trace-metal concentrations over the experimental period. The average uranium concentration observed in this study was 2.85 ppb which is slightly lower than the uranium concentration in seawater of 3.3 ppb (for a salinity of 35 practical salinity units (psu)). Marine testing was performed using filtered (0.45 μm) seawater at a temperature of 20 ± 2 °C and at two different flow rates (250 and 500 mL/min) using actively pumping systems.

Adsorbent beds were prepared using a 1 in. internal diameter (i.d.) by 4 and 6 in. long columns fabricated from all plastic components, mostly PVC and polypropylene. The adsorbent was dispersed and packed in the column, where it was held in place by glass wool and/or 3 mm glass beads that were used to fill up the empty space of the columns. Schematic diagrams of the physical layout used for adsorption exposure experiments are presented in Figure 15. The exposures were conducted in a parallel configuration using a 12-port, all PVC manifold system. Water was drawn from a reservoir and forced through the manifold using a pump with all plastic components in the pump head and PVC tubing feed lines. Prior to initial use, the adsorbent exposure columns, feed lines, and fittings were cleaned with a laboratory soap and weak acid (10% hydrochloric acid) solution to minimize contamination. Samples of seawater delivered by the system were monitored for trace elements to document any contamination introduced by the exposure system. Natural seawater was continuously provided to each adsorbent bed from reservoirs of filtered (0.45 μm polypropylene membrane) seawater collected from Sequim Bay,

Sequim, WA. The temperature in the seawater reservoir was controlled with an all-titanium immersion-heating element.

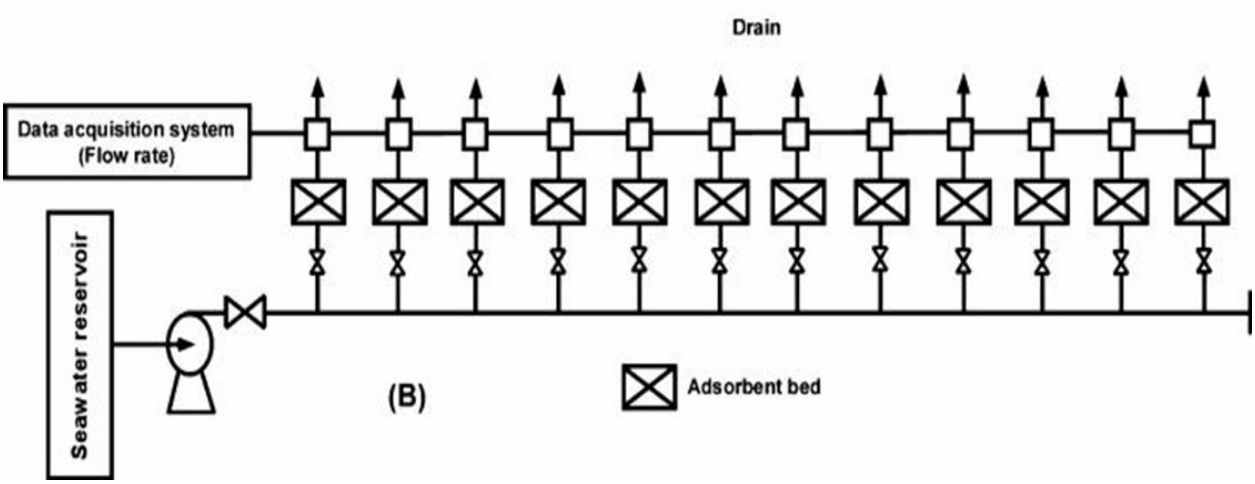

Figure 15. Schematic diagram of flow-through experiments using a parallel configuration at the Marine Sciences Laboratory of PNNL.

Flow rate, salinity, and temperature of the seawater were monitored at the outlet of the exposure columns at least twice daily for all experiments. Adjustments were made when the temperature was more than 2 °C outside of the target temperature and the flow rate was more than 10% above or below the target. The flow rate was determined using an in-line turbine-style flow sensor (Model DFS-2W) manufactured by Digiflow Systems connected to either a hand-held digital readout or a multiport data acquisition system (Measurement Computing, MicroDAQ, Contoocook, NH, USA). Flow rate adjustments were made by adjusting the flow by a 10-turn needle valve placed on the outlet of the columns in the manifold system (Figure 15). Salinity and temperature were determined using a hand-held salinometer (YSI, Model 30). In later experiments, the 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 30 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).

5. Sample Handling and Analytical Procedures at PNNL

Seawater exposed adsorbent fibers were collected from adsorbent beds, washed with deionized (DI) water to remove salts, and dried under vacuum filtration using a nylon membrane filter with a pore size of 200 nm (Pall Life Sciences, Port Washington, NY, USA).

The dried fibers (100−200 mg) were then digested with high-purity (Optima, Fisher Scientific) concentrated aqua regia acid mixture (3:1; i.e., 15 mL:5 mL hydrochloric acid:nitric acid) for 24 h at room temperature with 500 rpm shaking frequency. High-purity DI water (Optima, Fisher Scientific) was then added to make up a 100-mL dilute acid solution and to have the desired

concentration range of uranium for the analysis. The samples were shaken at 500 rpm for an additional 3 days at room temperature to complete the digestion process.

Inductively coupled plasma mass spectroscopy (ICP-MS, Thermo Scientific X-Series II) was used for quantitative analysis of the metals. The average of six replicate measurements per sample was used to quantify uranium-238 against a six-point calibration curve. Samples of spent glass wool and glass beads used for packing were also analyzed to investigate whether uranium was retained on these packing materials. No appreciable uranium was observed to be adsorbed on these materials.

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.,[48] Sella et al.,[49] and Skogerboe et al.[50]

6. Marine Testing Results

The uranium adsorption capacities on eleven different batches of AF1 adsorbents, conditioned with KOH for 1 hour at 80 ^{o}C and marine tested at PNNL for 56 days at 20 ^{o}C using flow-through columns, are shown in Table 6 and Figures 16-17. The capacities for the eleven

different batches of AF1 adsorbents were normalized to 35 practical salinitiy units (psu) and ranged from 3.8 to 4.3 g-U/kg adsorbent with an average capacity of 4.019 ± 0.159 g-U/kg adsorbent. It is important to note that the different batches of the AF1 adsorbents were all synthesized under the same processing conditions (i.e., irradiation, grafting, amidoximation and KOH conditioning), however they were manufactured and/or marine tested on different dates in order to assess the batch-to-batch variability of the AF1 adsorbents. The percent coefficient of variation (%COV) in Table 6 for the capacities from the various AF1 adsorbents was only 4.0%. This low %COV indicates that there is only a small batch-to-batch variability for the AF1 adsorbents and that the capacities are relatively insensitive to any changes that may have resulted during adsorbent manufacturing and marine testing.

The uranium adsorption capacities for the AF8RMCJ adsorbent and the ATRP 2.3 adsorbent, after KOH conditioning for 3 h at 80 ^{o}C and marine testing at PNNL at 20 ^{o}C using flow-through columns for 49 days, were 4.6 g-U/kg adsorbent and 5.4 g-U/kg adsorbent, respectively and are shown in Figure 18 along with the 38H and AF1 adsorbents (all capacity data was normalized to 35 psu). The increased capacity for the AF8RMCJ adsorbent compared to the AF1 adsorbents is believed to be due to the higher ratio of AN:ITA that is used in the grafting solution (14.5 versus 7.6) resulting in a higher concentration of amidoxime groups available for binding the uranyl.

Table 6. Uranium adsorption capacities of AF1 adsorbents (11 different batches).

AF1 Adsorbents (11 different batches)	%DOG	Uranium Adsorption Capacity, g-U/kg ads. (KOH conditioning -1 hr/80 ^{o}C; normalized to 35 psu; 56 days seawater; 20C)
AF1L2R1 (6/23/14)	410	4.243
AF1L2R1 (5/28/14)	410	3.949
AF160-2RMCJ (6/23/14)	347	4.129
AF1L1R1 (6/23/14)	391	4.314
AF1L1R2 (6/23/14)	343	3.918
AF1L2R2 (6/23/14)	319	3.938
AF1L2R2 (6/24/14)	319	3.997
AF1L1R3 (6/23/14)	325	4.120
AF1L2R3 (6/23/14)	427	3.873
AF1FR2 (6/23/14)	363	3.905
AF1FR3 (6/23/14)	378	3.828
Average	367	**4.019**
Std. dev.	39	**0.159**
% COV	10.6	**4.0**

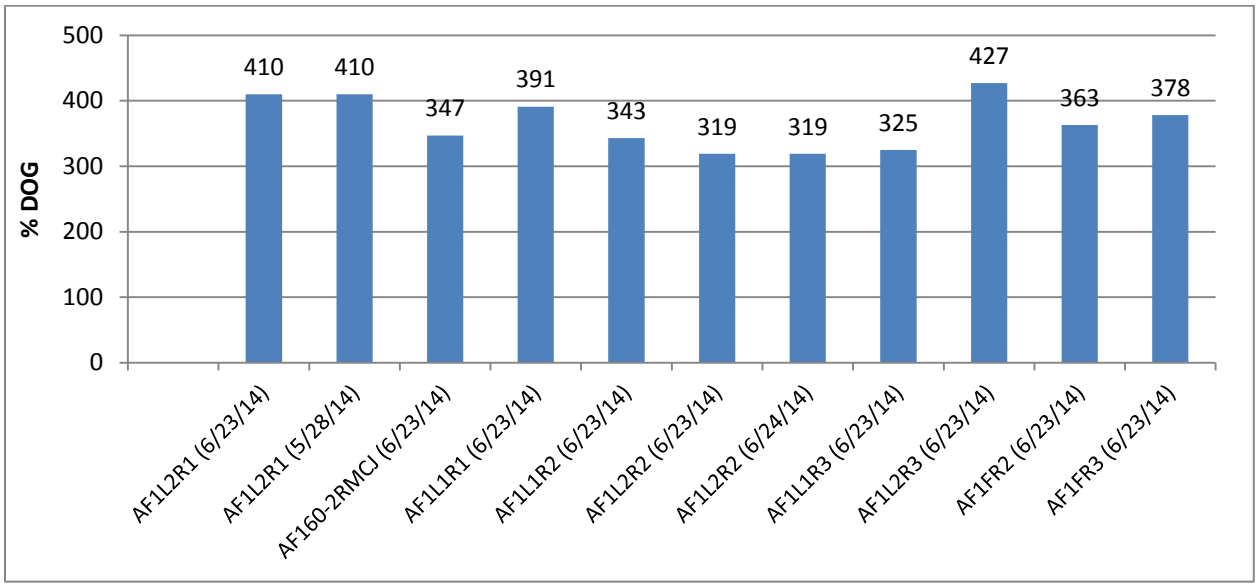

Figure 16. % Degree of grafting of AF1 adsorbents.

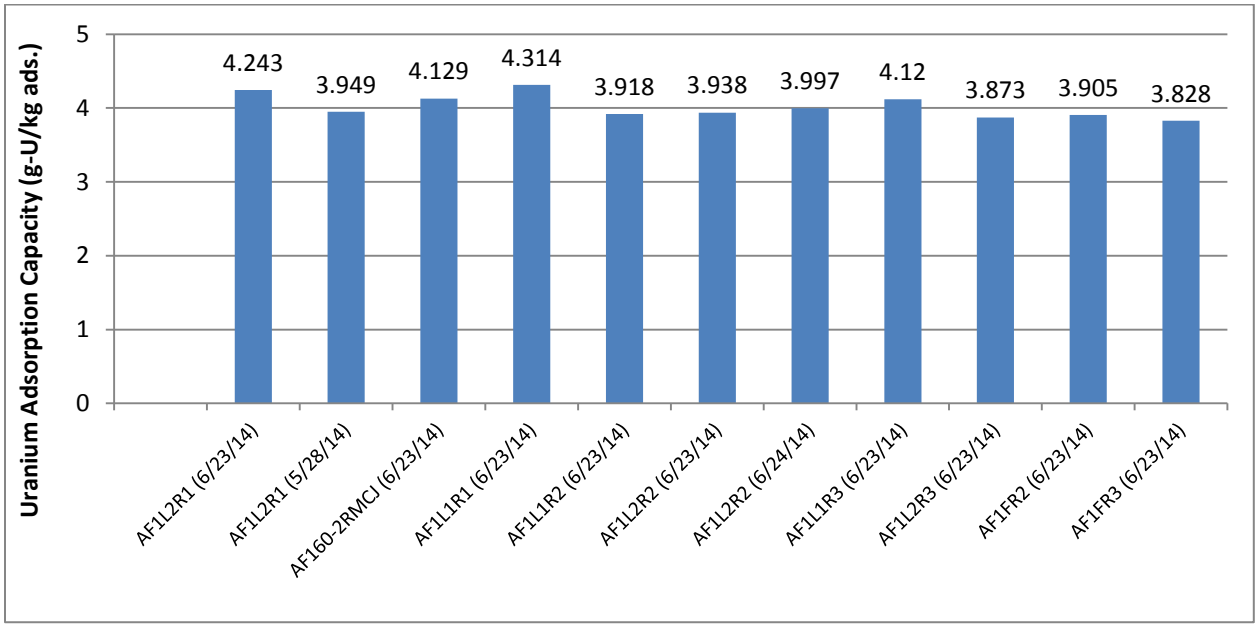

Figure 17. Uranium adsorption capacities of AF1 adsorbents (11 different batches).

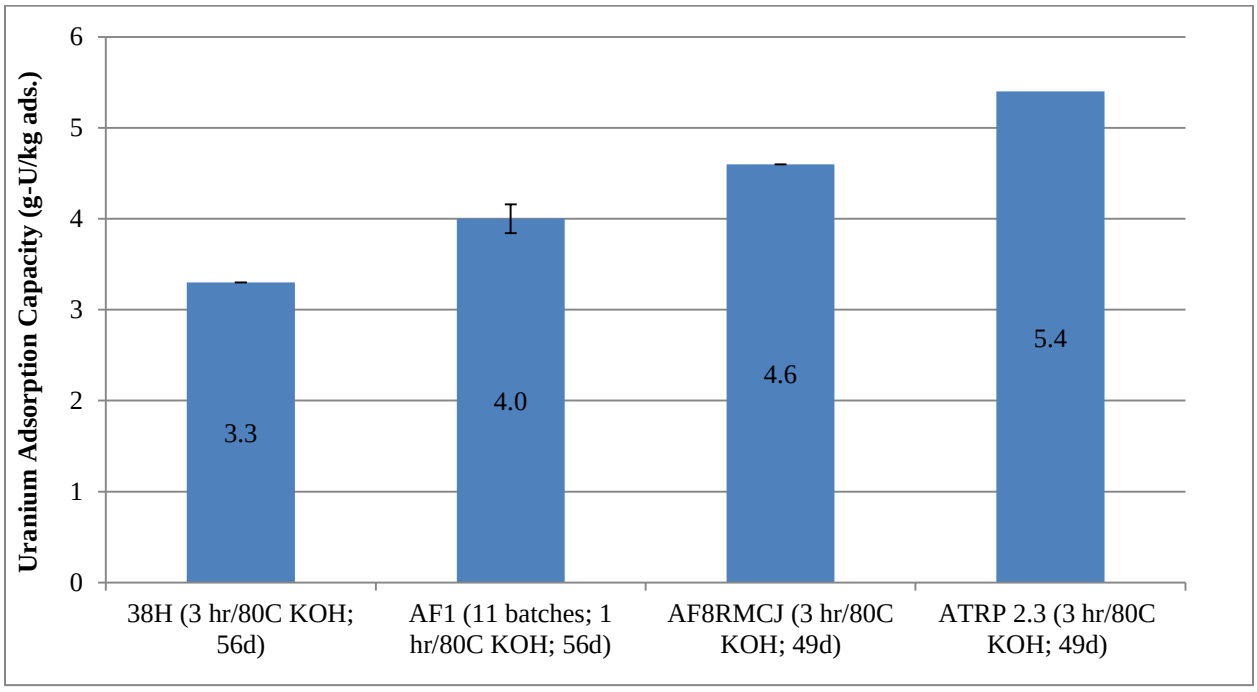

Figure 18. Uranium adsorption capacities of ORNL adsorbents after 49 or 56 days of marine testing at PNNL.

7. Acknowledgments:

This research was conducted at the Oak Ridge National Laboratory and the Marine Sciences Laboratory at Pacific Northwest Laboratory and supported by the U.S. DOE Office of Nuclear Energy, under Contract DE-AC05-00OR22725 with Oak Ridge National Laboratory, managed by UT-Battelle, LLC.

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