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Recovery of Uranium from Seawater: Modified Polyacrylonitrile Fibers as Selective Extractants

Fuel Cycle Research and Development

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Summary

A new bifunctional fiber has been prepared and found to have a significant loading capacity of uranium from real seawater. The fiber support is polyacrylonitrile and bifunctionality is provided by amidoxime and either diethylenetriamine (DETA) or ethylenediamine (EDA) ligands. The key feature is adjusting the hydrophilic /lipophilic balance within the fiber and this was best accomplished by partially acetylating or carboxylating EDA ligands. The bifunctional carboxylated EDA /AO fiber had a loading capacity of 3.83 mg U/g fiber at the Pacific Northwest National Laboratory with a 21 day contact time in real seawater. Key results are tabulated below of the modified fibers prepared at Hunter College and the U(VI) loadings from real seawater determined at the Pacific Northwest National Laboratory:

Date presented	fiber	U(VI) loading (mg/g)
March 2015[1]	PAN-DETA-AO	0.53 @ 21 days
August 2015[2]	PAN-DETA-AO	1.60 @ 42 days
January 2016[3]	PAN-DETA-AO	2.71 @ 42 days
July 2016[4]	PAN-EDA-AO	- - - - - - - - - -
December 2016[5]	PAN-EDA-AO	2.05 @ 21 days
	PAN-Ac[6]	3.16 @ 21 days
	PAN-Am[7]	3.83 @ 21 days

[1] ACS meeting at Denver

[2] review meeting at the Univ. of Maryland

[3] review at ORNL

[4] review at Univ. of Maryland: improvements reported but PNNL seawater results were still pending at the time of the review

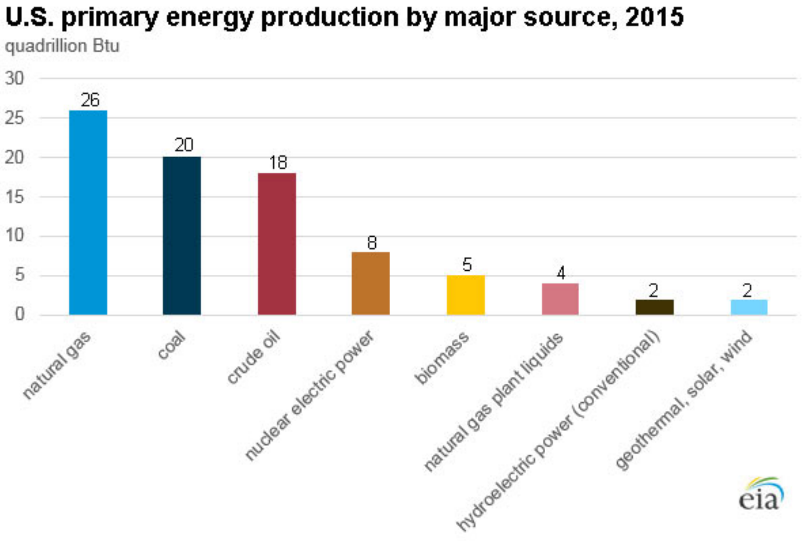
[5] review at Univ. of South Florida (Jan. 2017))

[6] bifunctional acetylated ethylenediamine /amidoxime

[7] bifunctional aminomethylcarboxylated EDA /amidoxime; it has a V/U ratio of 1.5

NOTE: ORNL AF-1 @ 21 days gives 2.6 mg U/g fiber

Introduction

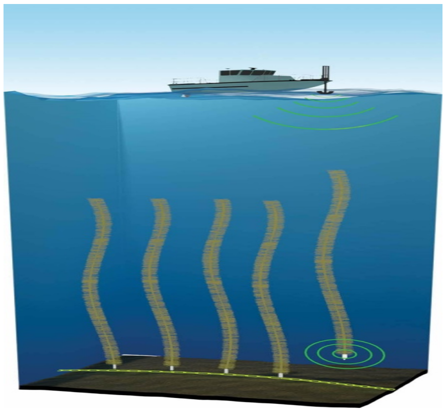


Source: U.S. Energy Information Administration, *Monthly Energy Review* (April 2016), preliminary data

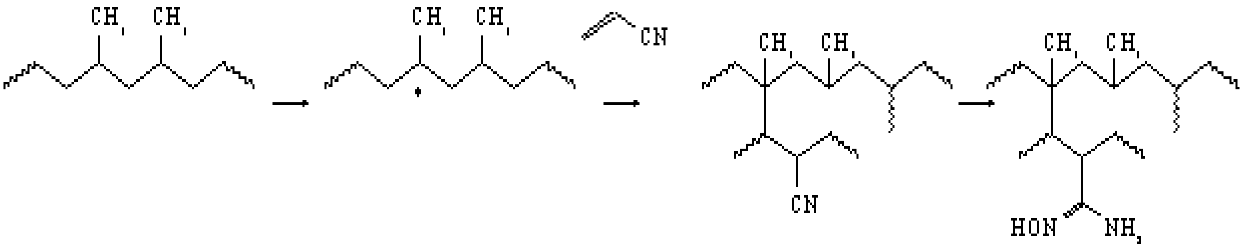
Energy production in the United States relies overwhelmingly on the burning of fossil fuels. The energy is utilized in industry, construction, transport, lights, heating, etc. – all of what we take for granted in modern life. The combustion reaction is an efficient means of delivering heat and electricity to homes but also results in the inevitable emission of CO_2. This has led to an increase in atmospheric CO_2 levels from 280 ppm to 400 ppm and has most significant environmental implications in increasing the average global temperature and resulting climate change. Another consequence is acidification of the oceans which, though not discussed as much as climate change, is at least as dire since this decreases the survivability of organisms low on the food chain on which those higher (i.e., fish and humans) depend.

Solar energy seems to be the ideal replacement to fossil fuels, but it is not ready on the scale required for powering cities. The only alternative that is ready now to replace fossil fuels is nuclear energy. Though hard to love, given its origin and the issue of nuclear waste, it is better to understand it, control it, and use it to buy time to go solar. The principal advantage to nuclear energy is that one tonne of U yields 44 million kilowatt-hours of electricity. Terrestrial sources of uranium require mining operations, either open-pit or underground *in-situ* leaching. Mill tailings remain a persistent problem.

From this situation, an innovation was proposed: to recover uranium from seawater. It is known that the four billion tons of uranium dissolved in seawater is an attractive alternative resource for nuclear power but that the challenge is its very low concentration (3.3 μg/L) in a matrix of numerous competing ions.[1] The strategy is thus to develop sorbents with high U capacity, selectivity, kinetics and durability at low recovery cost. Most importantly, the recovery method must be environmentally compatible (i.e., non-polluting). The preferred form is a fiber that can be anchored to the seabed, as illustrated below from a diagram published in *ORNL Review* (available at www.ornl.gov). As a result, the U.S. Department of Energy formed a team of national laboratories (e.g., Pacific Northwest and Oak Ridge), universities (e.g., California, Chicago, MIT, Texas, Alabama, South Florida, Hunter College) and institutes (e.g., Woods Hole) to identify ways of extracting U(VI) as a sustainable resource from the oceans.



Efficient recovery methods have been studied in numerous laboratories around the world and significant progress has been made.[2] The amidoxime (AO) ligand is promising for uranium recovery because of its relatively high affinity for U(VI) and its facile preparation from the –CN group as precursor, having been first identified by Egawa and Harada in a publication entitled *Recovery of Uranium from Sea-water by Using Chelating Resins Containing Amidoxime Groups* in 1979.[3] Early work utilized polypropylene which is irradiated to create free radicals, contacted with acrylonitrile (AN) for graft polymerization, then converted to AO with hydroxylamine.



Recovery of U(VI) from seawater remains problematic as sorption by amidoxime-grafted fiber needs improvement. In one example, uranium loading on amidoxime polyethylene fibers was 1.0 g U(VI) /kg fiber after seawater contact for 30 days, while calcium and magnesium loading reached 40 g Ca^{2+} /kg and 20 g Mg^{2+} /kg, even though the concentration factor of uranium was as high as 280000.[4] Co-grafting amidoxime with hydrophilic monomers and alkaline treatment of the fiber have been applied to improve seawater uranium loading.[5,6] Pretreatment of amidoxime fiber with KOH at 80°C for 1h increased seawater uranium recovery but without continuous alkaline treatments, uranium loading decreased significantly.[7] The increase in uranyl loading was ascribed to increasing the fiber hydrophilicity: Alkaline treatment resulted in a water uptake capacity by the amidoxime fiber of 200 wt %.[8] The best results at the start of this project were from ORNL, in a process indicated below with polyethylene fiber. This fiber had a loading of 2.6 mg U/g fiber (seawater contact time of 21 days), and was the benchmark against which other results were measured. (All results reported below are with a 21 day contact time.)

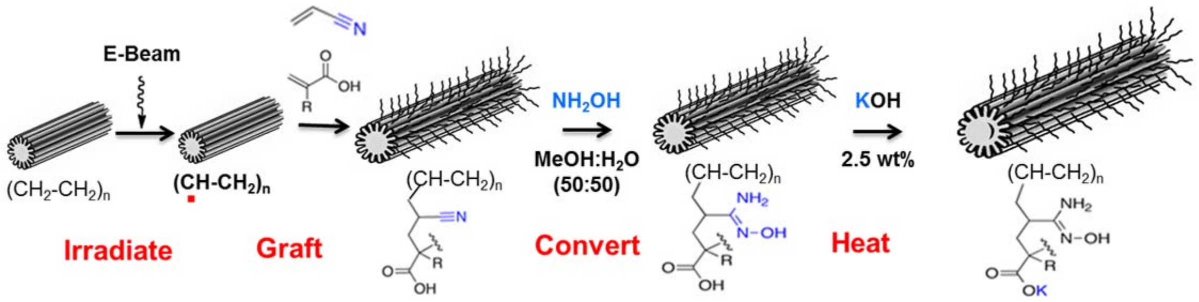
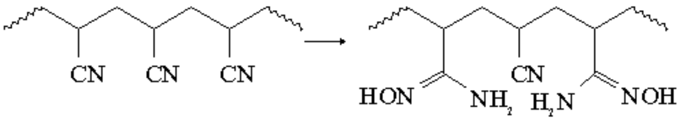


Figure 1 courtesy of Dr. Costas Tsouris (ORNL)

The objective of our part of the project was to develop a fiber with improved U(VI) loading without graft polymerization. For that, we began with polyacrylonitrile fiber (PAN) available from Sterling Fibers.



We thus developed a three-phase research plan:

Phase I: Evaluate PAN-AO; propose a hypothesis for the
mechanism; identify a method to increase AO affinity

Phase II: Identify critical variables in the synthesis

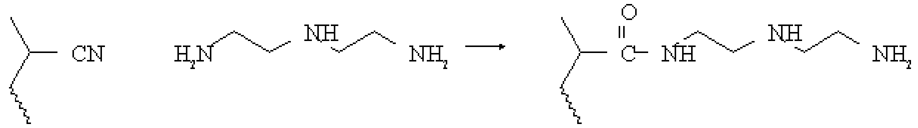
Phase III: Improve synthesis + prepare optimum fiber

Results and Discussion

We began by immobilizing AO on the Sterling PAN fiber and evaluating the PAN-AO for its ability to load the uranyl ion from actual seawater. The loading was determined at PNNL to be 0.12 mg U/g at a 21 day contact time. The issue now became to propose a hypothesis for why loading was so much lower than the ORNL fiber. The amidoxime ligand itself should be very hydrophilic given its polar and weakly acidic nature. However, those same properties could allow the formation of strong inter-ligand hydrogen bonding and this would limit its uptake of metal ions. In a related example, phosphorus acids form inter-ligand interactions hydrogen bonds to give dimers and polymers, and even diphosphonic acids form dimers with only one exchangeable proton.[9] Hydrogen bonding among amidoxime groups could thus be an important factor in limiting uranyl sorption from seawater and, if so, weakening inter-ligand AO hydrogen bonding could increase uranyl sorption from seawater.

If hydrophilicity increases hydrogen bonding and lipophilicity decreases it, the objective became to prepare modified fibers with a varying hydrophilic – lipophilic balance, a concept that is associated with surfactants. Building on earlier results, the method chosen in this research was to introduce an auxiliary ligand proximate to the AO. Amines were chosen as the class of auxiliary ligands since their lack of an acidic hydrogen would decrease the tendency to hydrogen bond but they would not be too lipophilic, given their polarity, since that would decrease accessibility of hydrophilic metal ions into the fiber. Syntheses were thus initiated with diethylenetriamine (DETA) since it offered polarity with minimal steric interference to access of the AO site by the uranyl ion.

Bifunctional fiber synthesis occurs in two steps. The first step is immobilization of DETA onto PAN with water as solvent. Functionalization is followed with FTIR spectra at different temperatures with optimum levels at 70 – 80°C; at 90°C, the –CN band at 2250 cm^{-1} vanishes, making impossible the second step of AO immobilization in aqueous solution.



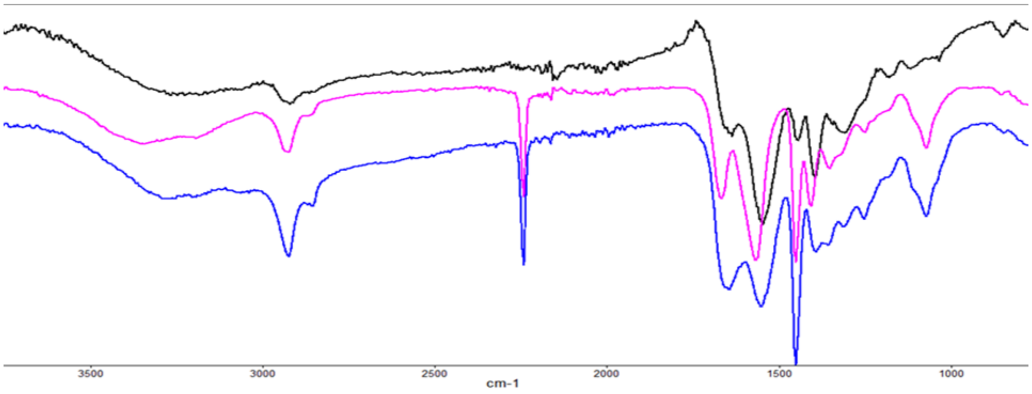


Figure 2. Blue 70°; Pink 80°, Black 90°C

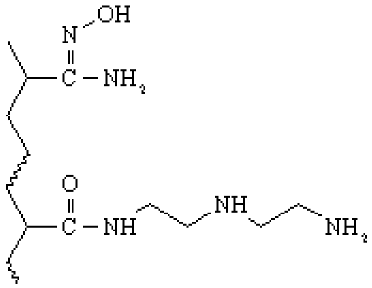
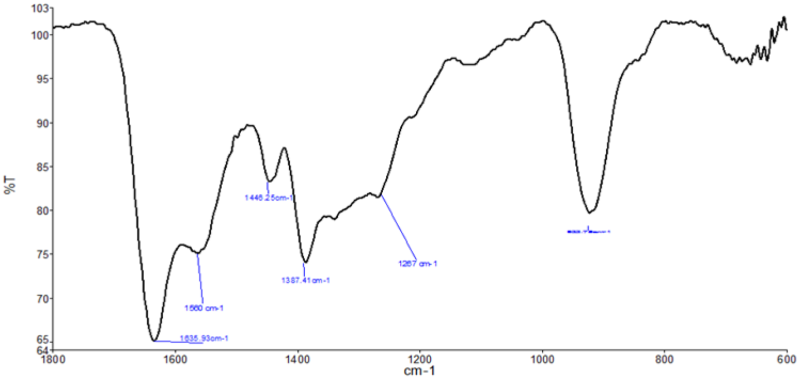


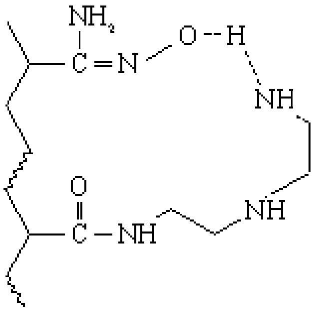
Figure 3. PAN-DETA-AO

The fiber was evaluated at PNNL and found to load 0.54 mg U /g, a marginally improved amount over PAN-AO. However, higher loading in AO-DETA was evident with other seawater ions monitored at PNNL (e.g., Ca^{2+} and Mg^{2+}) indicating that a weaker overall hydrogen bonding may be increasing accessibility. This concluded Phase I.

The focus of Phase II was to identify critical variables in the synthesis that would improve fiber stability and significantly improve uranyl loading. The synthesis conditions were made milder by replacing water with ethylene glycol and shortening the reaction time in the first step and replacing water with aqueous glycol as solvent in the second step. Analysis at PNNL found the loading doubled to 1.04 mg U/g, indicating that improved fiber rigidity enhanced uranyl uptake. Further studies of the DETA reaction temperature in order to adjust the DETA:AO ratio led to no significant improvement in loading (1.12 mg U/g).

It is important to note that in all cases reported above, the standard technique was to pre-treat the fiber with 1L elutions of 1M NaOH – H_2O – 1M HCl – H_2O prior to contact with seawater. It was then thought reasonable to omit the HCl elution and keep only 1M NaOH – H_2O as the pre-treatment so as to form the oximate and perhaps weaken the overall hydrogen bonding by removing the weakly acidic H^+ from N-OH. The PNNL result validated this suggestion: uranyl loading jumped to 1.76 mg U/g from the same fiber that had given 1.12 mg U/g. After NaOH – H_2O elution, N-OH deprotonates and the FTIR spectrum showed a new band at 1560 cm^{-1} consistent with an $-NH_2$ bend as the oximate formed a weak hydrogen bond to $-NH_2$.





The PNNL result for PAN-DETA-AO of 1.76 mg U/g thus marked the end of Phase II with the following conclusions being drawn:

*Hydrogen bonding limits U(VI) loading

*Lower H-bonding increases loading

*The $-NH_2$ in PAN-DETA-AO fibers decreases hydrogen bonding

*Elution of PAN-DETA-AO with 1 M NaOH increases U(VI) loading by forming an oximate with a weak hydrogen bond to $-NH_2$.

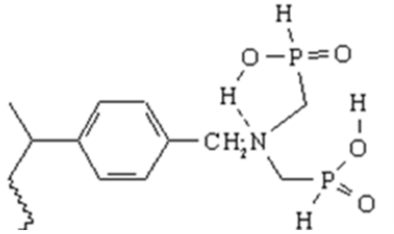
As Phase III began, the minimum target remained 2.6 mg U/g (ORNL fiber) with an emphasis on continuing to improve the synthesis. During the first half of Phase III, conclusions were made based on screening results using commercially available artificial seawater spiked with 50 ppm U(VI). The two most important results from those screening studies were that changing the amine from DETA to ethylenediamine (EDA, $H_2N-CH_2CH_2-NH_2$) would result in higher loadings at PNNL (this was later confirmed with a loading of 2.05 mg U/g) and that changing from EDA to $H_2N-CH_2CH_2-OH$ would sharply diminish loading, supporting that the terminal $-NH_2$ is important to the binding mechanism.

The second half of Phase III began with renewed emphasis on the question that was asked at the outset of the project: How can internal hydrogen bonding be affected? The answer now considered was to adjust the hydrophilic /lipophilic balance by capping some of the terminal –NH_2 sites and this was accomplished through partial acetylation:

$\text{PAN-NH-CH}_2\text{CH}_2\text{-NH}_2 \longrightarrow \text{PAN-NH-CH}_2\text{CH}_2\text{-NHC(O)CH}_3 \longrightarrow \text{PAN-AcEDA-AO}$

The loading of this fiber was determined to be 3.16 mg U/g, exceeding, for the first time, the ORNL value of 2.6 mg U/g.

A second method was then evaluated: to further decrease hydrogen bonding to AO by placing a group on the PAN-EDA-AO that would bind some of the –NH_2 sites. The genesis of this idea was in earlier BES-sponsored research on aminomethylphosphinic acid where that polymer's high affinity for U(VI) from 1 – 6 M H_3PO_4 was ascribed to one phosphinate being freed from a neighboring phosphinate through an –NH- and that decreased hydrogen bonding allowed a greater U(VI) capacity.[10]



PAN-EDA was thus partially carboxylated by controlling the time of reaction and a subsequent reaction with hydroxylamine gave the bifunctional polymer.[11]

$\text{PAN} \longrightarrow \text{PAN-NH-CH}_2\text{CH}_2\text{-NH}_2 \longrightarrow \text{PAN-NH-CH}_2\text{CH}_2\text{-NHCH}_2\text{C(O)OH} \longrightarrow \text{PAN-AmEDA-AO}$

The loading of this bifunctional polymer at PNNL with real seawater and a 21 day contact time was 3.83 mg U/g, significantly exceeding the target and supporting the importance of the hydrophilic /lipophilic balance within ion-binding polymers.

Conclusions

The final loading of 3.83 mgU/g at 21 days is very promising. It is important to note that the final form the material is not a gel but, rather, a solid fiber. It thus has the potential for being deployed in seawater in its woven form.

Future work should focus on contact angle measurements to quantify the hydrophilicity /lipophilicity, the kinetics of uptake by the fiber and varying percent modification by acetylation and aminomethylcarboxylation in the bifunctional fiber.

Acknowledgements

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References

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[1] R.V. Davies; J. Kennedy; R.W. McIlroy; R. Spence; K.M. Hill, Extraction of Uranium from Seawater, Nature 1964, 203, 1110-1115.

[2] T. Sugo, Status of development for recovery technology of uranium from seawater. Nippon Kaisui Gakkaishi 1997, 51, 20−27.

[3] K. Sugasaka, S. Katoh, N. Takai, H. Takahashi, Y. Umezawa, Recovery of uranium from seawater. Sep. Sci. Technol. 1981, 16, 971−985.

[4] T. Takeda, K. Saito, K. Uezu, S. Furusaki, T. Sugo, J. Okamoto, Adsorption and elution in hollow-fiber-packed bed for recovery of uranium from seawater, Ind. Eng. Chem. Res. 1991, 30, 185-190.

[5] H. Omichi, A. Katakai, T. Sugo, J. Okamoto, A new type of amidoxime-group-containing adsorbent for the recovery of uranium from seawater. II. Effect of grafting of hydrophilic monomers, Sep. Sci. Technol. 1986, 21, 299-313.

[6] S. Das, C. Tsouris, C. Zhang, J. Kim, S. Brown, Y. Oyola, C. J. Janke, R. T. Mayes, L.-J. Kuo, J. R. Wood, G. A. Gill, S. Dai. Enhancing uranium uptake by amidoxime adsorbent in seawater: An investigation for optimum alkaline conditioning parameters, Ind. Eng. Chem. Res., 2016, 55, 4294–4302.

[7] N. Kabay, A. Katakai, T. Sugo, Preparation of amidoxime-fiber adsorbents by radiation-induced grafting, Radiat. Phys. Chem. 1995, 46, 833-836.

[8] S. Das, A.K. Pandey, A. Athawalea, V. Kumar, Y. K. Bhardwaj, S. Sabharwal, V.K. Manchanda, Chemical aspects of uranium recovery from seawater by amidoximated electron-beam-grafted polypropylene membranes, Desalination 2008, 232, 243–253.

[9] R. Chiarizia, D.R. McAlister, A.W. Herlinger. Trivalent actinide and lanthanide separations by dialkyl-substituted diphosphonic acids. Sep. Sci. Technol. 2005, 40, 69-90.

[10] S.D. Alexandratos; X. Zhu, Polymer-Supported Aminomethylphosphinate as a Ligand with a High Affinity for U(VI) from Phosphoric Acid Solutions: Combining Variables to Optimize Ligand–Ion Communication, Solv. Extr. Ion Exch. 2016, 34, 290–295.

[11] S.D. Alexandratos; X. Zhu, High-Capacity Bifunctional Fibers for the Harvesting of Uranium from Seawater, Application Serial No. 62/459,193; Filed February 15, 2017.