Research Paper
This paper is based on Global 2017 presentation.

https://doi.org/10.7733/jnfcwt.2018.16.3.369

Systems Analyses of Alternative Technologies for the Recovery of Seawater Uranium

Margaret Flicker Byers*, Erich Schneider, and Sheldon Landsberger
University of Texas, 10100 Burnet Rd. Bldg 159, Austin, TX 78758, USA

(Received February 7, 2018 / Revised April 9, 2018 / Approved September 3, 2018)

The ability to recover the nearly limitless supply of uranium contained within the world's oceans would provide supply security to uranium based fuel cycles. Therefore, in addition to U.S. national laboratories conducting R&D on a system capable of harvesting seawater uranium, a number of collaborative university partners have developed alternative technologies to complement the national laboratory scheme. This works summarizes the systems analysis of such novel uranium recovery technologies along with their potential impacts on seawater uranium recovery. While implementation of some recent developments can reduce the cost of seawater uranium by up to 30%, other researchers have sought to address a weakness while maintaining cost competitiveness.

Keywords: Seawater uranium, Front end nuclear fuel cycle, Actinide chemistry, Systems analyses

*Corresponding Author.
Margaret Flicker Byers, University of Texas, E-mail: Margaret.Byers@austin.utexas.edu, Tel: +1-714-478-4766

ORCID
Margaret Flicker Byers http://orcid.org/0000-0001-7610-2300
Erich Schneider http://orcid.org/0000-0003-1346-9134
Sheldon Landsberger http://orcid.org/0000-0002-1438-0775

1. Introduction

Economically recovered uranium from seawater can have a transformative effect on the way policy makers view the long-term viability of nuclear fuel cycles. Seawater uranium, even when estimated to cost more than uranium from conventional terrestrial mines, is integral in establishing an economic backstop, thus reducing uncertainty in future nuclear power costs.

While a passive recovery scheme relying on a field of polymer adsorbents prepared via radiation induced grafting has long been considered the leading technology for full scale deployment, non-trivial cost and logistical barriers persist. Therefore, in addition to U.S. national laboratories conducting R&D on a systems capable of harvesting seawater uranium, a number of collaborative university partners have developed alternative technologies to complement the national laboratory scheme or address a perceived weakness. This work summarizes the systems analysis of such novel uranium recovery technologies along with their potential economic impacts on seawater uranium recovery.

2. Methodology

All of the following alternative technologies will be considered in reference to adsorbent fibers prepared by Oak Ridge National Laboratory (ORNL), which have consistently shown strong performance and are thus considered representative of material that would ultimately be deployed on a large scale [1]. These adsorbents consist of a high-density polyethylene backbone modified via irradiation induced grafting to contain an amidoxime ligand affording uranium affinity along with a hydrophilic functional group to encourage water diffusion into the material. After the necessary chemical processing [2] the adsorbents are braided into 60-meter long strands so they may be deployed on the bottom of the ocean in a kelp-field like structure. The braids are allowed to passively collect uranium for a period ranging from weeks to months before they are winched up to the surface by work boats. The uranium is retrieved using a chemical elution process, allowing the braids to be redeployed for multiple soaking campaigns [3, 4].

The industrial scale-up and cost of the proven bench-top technologies incorporated into the reference national laboratory recovery process has been modeled using discounted cash flow methodologies with subsequent publications continuing to improve and develop the model to reflect changes in the constantly evolving adsorbent technology [5-7]. These same techniques will be used to evaluate all of the technology variants discussed here by following a unit mass of adsorbent over its lifetime. The cost associated with each of the three major process steps, adsorbent production, mooring and deployment, and elution, along with the mass of recovered uranium are all discounted to a reference time so that the cost associated with all units of adsorbent can be summed appropriately.

Given the evolving nature and uncertainty surrounding even the reference technology it is difficult to define a single set of design and deployment parameters that would ultimately be implemented on an industrial scale. Therefore, the uranium production cost is often presented as a range bounded by the best and worst case adsorbent performance parameters. Adsorbent performance in a true marine environment is believed to be dominated by the effects of marine biofouling along with the realized adsorbent durability rates [6]. The deployment parameters associated with each of these scenarios is determined using a previously published optimization framework, which minimized the uranium production cost by manipulating the length of each exposure cycle and number of adsorbent recycles. The governing adsorbent performance parameters, implemented deployment strategy, and resulting uranium production cost for the two bounding base cases can be seen in Table 1 [6].

The worst case adsorbent performance scenario with respect to marine microorganism growth comes from observations made by Pacific Northwest National Laboratory (PNNL) [8]. Given the warm bright laboratory conditions

Table 1. Reference Uranium Production Cost Range

Parameter	Best Case	Worst Case	Units
Marine Biofouling	0%	30%	loss in uptake
Average Degradation upon Reuse	5%	7%	loss in uptake
Number of Uses	17	13	
Length of Campaign	46	12	days
Uranium Production Cost	$460	$840	$/kg U

under which these experiments were conducted, this is believed to be a conservative upper bound. The lower bound comes from the potential to fully mitigate the effects of marine microorganism colonization, which may be possible simply by deploying below the photic zone or other less passive measures. The worst case regarding durability of adsorbent performance likewise comes from PNNL experiments where the degradation upon reuse was seen to be a function of cumulative length of marine exposure. The model derived in the previous publication for the reference ORNL adsorbent types can be seen in Fig. 1 [4]. Given that the use of this model results in a unique degradation rate for each re-use, the average loss in capacity suffered upon each recycle was listed in Table 1.

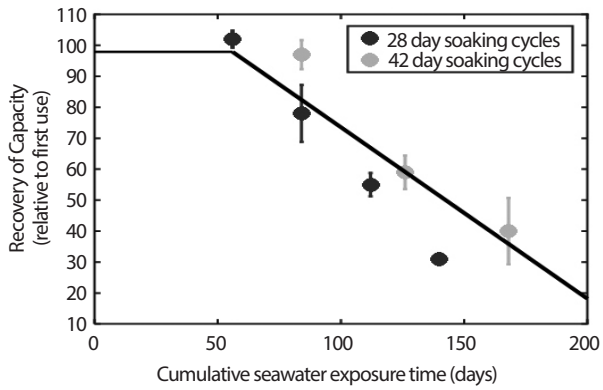

Fig. 1. Upper bound model for loss of adsorbent capacity upon reuse as pictured in [4]. Unlike the lower bound model, characterized by a constant degradation rate, recent observations suggest uranium capacity may decrease with increasing seawater exposure.

The best case adsorbent durability comes from observations made on chemically similar adsorbents deployed in real seawater and is thus believed to be attainable [9]. These adsorbent performance possibilities and the optimization of deployment parameters will likewise be applied to the novel technologies described in the rest of this analysis.

2.1 Additional Ligand (CUNY)

The uranium capacity of adsorbent fibers has been shown to be a significant driver of the final uranium production cost [1, 6]. Partners at Hunter College of the City University of New York (CUNY) have therefore attempted to increase capacity by enhancing the uranium affinity of the amidoxime ligand used in reference fibers [10]. In addition to amidoxime, these novel fibers contain a second amine ligand that offers two mechanisms of facilitating amidoxime-uranium interaction.

The adsorbent synthesis of the CUNY material differs from that of the reference scenario beginning with the fibrous backbone. Commercially available polyacrylonitirle fiber is used in lieu of the high-density polyethylene, where existing functional groups are converted to amidoxime rather than having to graft on the amidoxime precursor as in the ORNL adsorbents. Additionally, a second ligand, diethylenetriamine (DETA), is added with the hopes of enhancing the affinity of amidoxime for uranium. It is suspected that DETA can provide two possible mechanisms for increasing uranium uptake: direct action upon the existing

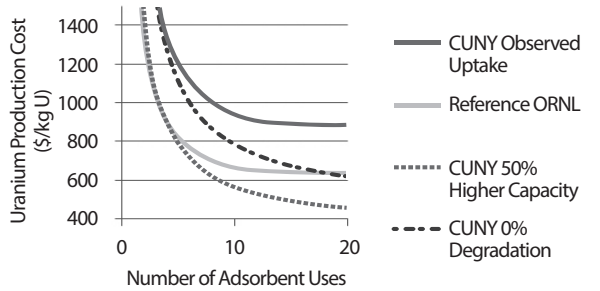

Fig. 2. Uranium production cost for CUNY adsorbent material. In addition to the observed adsorbent performance, the results of sensitivity analyses exploring the cost impact of increased capacity and robustness upon reuse are pictured. The base case is also pictured to provide context.

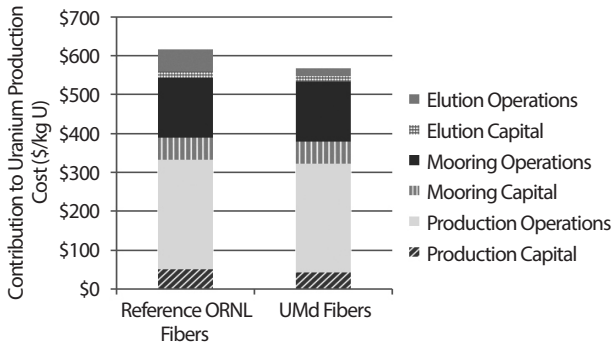

Fig. 3. Uranium production cost for UMd technology, and the base case, broken down by process step. Although the UMd technology involves a simpler fabrication process, much like the base case the material inputs required by adsorbent synthesis are a major cost driver.

amidoxime to increase ion exchange ability, or contribution of additional coordination sites for the uranyl ion.

The cost to recover uranium using this adsorbent is calculated, for clarity using a single intermediate adsorbent performance scenario, as can be seen in Fig. 2. This intermediate case, also applied to the reference ORNL adsorbents assumes the best case adsorbent durability while losing 30% of adsorbent capacity due to biofouling. Although initial experimental data has indicated these novel adsorbents have lower uranium uptake, our study shows that if the uranium capacity can be increased 50% above observed levels, a 16% savings could result. This sensitivity, along with other adsorbent performance parameters, are also displayed in Fig. 2.

2.2 Green Fabrication (University of Maryland)

Recognizing the adsorbent production process as the most expensive step, researchers at the University of Maryland (UMd) have created a novel adsorbent variety via a much simpler synthesis process [11]. In addition to reducing equipment requirements, the UMd team aimed to offer a "greener" production process by replacing organic solvents with simple water.

This particular adsorbent technology deviates quite significantly from the reference fibers with respect to the chemical composition of both the substrate and the uranium chelating agent, as well as the chemical elution process. The fibrous backbone is made of a high surface area winged nylon fabric. An X-ray irradiation process is used to graft the ligand, bis(2-methacryloxyethyl) phosphate, onto the fibers in an aqueous environment. This novel direct grafting procedure resulted in degrees of ligand grafting on the order of 100wt%, similar to that of the reference fibers.

Given limited data regarding adsorbent performance in true marine conditions, the economic analysis considers adsorbent uptake capacity and kinetics similar to that of the reference fibers. Results of uptake experiments conducted using simulated seawater were notable in suggesting higher durability achieved by these adsorbents. Capacity losses on the order of 1% per re-use were observed and are thus used in the cost calculation in lieu of the 5% or higher degradation rate suffered by the reference fibers.

The cost breakdown for these fibers, as compared to that of the reference fibers can be seen in Fig. 3. It is clear that these adsorbents can be considered a competitive alternative to the amidoxime based fibers. In addition to the benefit of utilizing green chemistry, these adsorbents have the potential to offer a 10% cost savings if similar uptake performance can be achieved.

2.3 Natural Fibers (University of Alabama)

The team at University of Alabama has set out to address

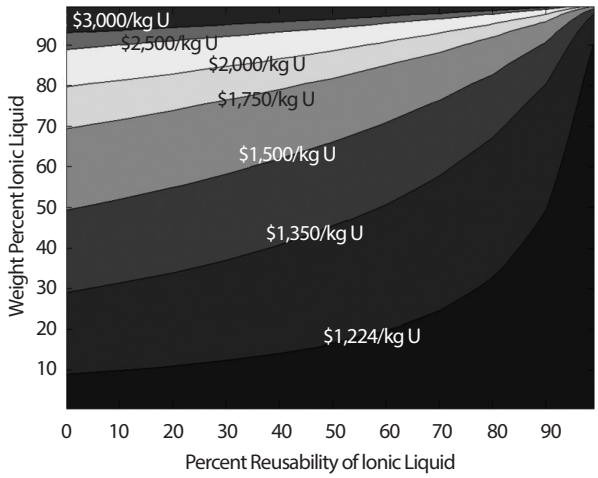

Fig. 4. Uranium production cost of the Alabama technology. The cost prohibitive nature of the initial fabrication process renders sensitivity analyses the most insightful way to consider this technology. Given the high cost and consumption rate of the ionic liquid the economic impact of reducing the net ionic liquid use are explored via the possibility of chemical recycle and/or dilution.

environmental concerns regarding the introduction of large quantities of plastic to marine ecosystems. In doing so they are attempting to eliminate the use of plastic altogether by pursuing an adsorbent synthesis method that replaces the synthetic fiber backbone with a natural waste product. Chitin nanomats suitable for ligand grafting have been prepared from shrimp shell waste.

The adsorbent synthesis process used in the economic model follows the chemistry described by the developers [12]. In its raw waste form, chitin exists simply as wet shucked crab and shrimp shells which must be converted into usable powder. Wet shells are pressed with a screw press, dried, and ground to result in a powder composed of chitin and proteins. The shell-derived powder is then dissolved in an ionic liquid, 1-ethyl-3-methylimidazolium acetate, to separate the chitin from proteins via an electrospinning process. The resulting fibers consist of high molecular weight chitin chains, providing ample binding sites for amidoxime ligands. Although the amidoxime ligand used for the chitin-based adsorbents is chemically identical to that of the reference fibers, the process of attaching it to the chitin nanomats is unique. Instead of relying on irradiation induced graft polymerization, the University of Alabama method is a strictly chemical grafting process, where the degree of ligand grafting achieved with the chitin substrate was seen to be on the order of 10% of the initial fiber weight. Given the boutique-nature of some chemicals, the ionic liquid in particular, a market analysis was conducted to quantify the change in price, resulting from increased demand for use in chitin nanomat production.

Much like other adsorbent varieties, production is the most expensive step in the lifecycle. Unique to this adsorbent however is the degree to which a single chemical, the ionic liquid contributes to the adsorbent production cost. While the ionic liquid is not in itself prohibitively expensive, once adjusted for future economies of scale, the extremely large quantity required per unit mass of chitin drives up the cost significantly. Therefore it is worth exploring the cost savings that would result if the required mass of ionic liquid could be reduced via chemical recycle or if the weight percent of ionic liquid required to dissolve each unit mass of chitin were reduced. Fig. 4 shows the effects of varying these two parameters.

Clearly, in order to offer the significant environmental benefits of replacing plastic with a natural substrate, considerable improvements in the adsorbent production process or resulting performance must be achieved.

2.4 Symbiotic Deployment

Although the adsorbent fabrication makes the most significant contribution to the seawater uranium production cost, the mooring and deployment cost effectively establishes a cost floor by governing the maximum number of economical adsorbent recycles. Therefore, researchers at the Massachusetts Institute of Technology (MIT) designed a symbiotic deployment structure where uranium adsorbing braids are moored on marine structures for wind-based electricity generation, named the Wind and Uranium from Seawater Acquisition symBiotic Infrastructure (WUSABI).

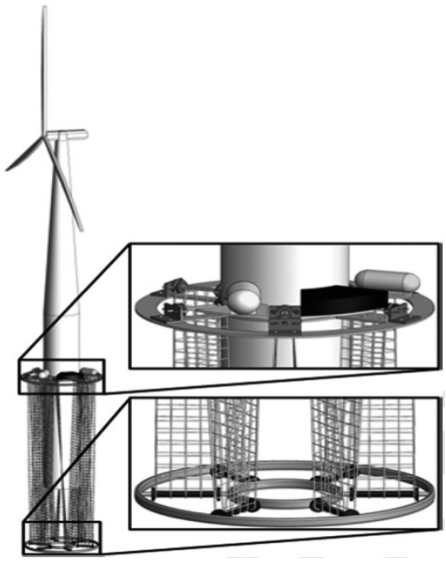

Fig. 5. WUSABI deployment structure by MIT [13]. In this deployment scheme adsorbent fibers are fabricated into nets that are in constant motion, traversing the length of the submerged portion of an off-shore wind turbine. A motor driven pulley system allows the adsorbent net to travel through tank reactors containing the elution chemicals, allowing for autonomous recycle.

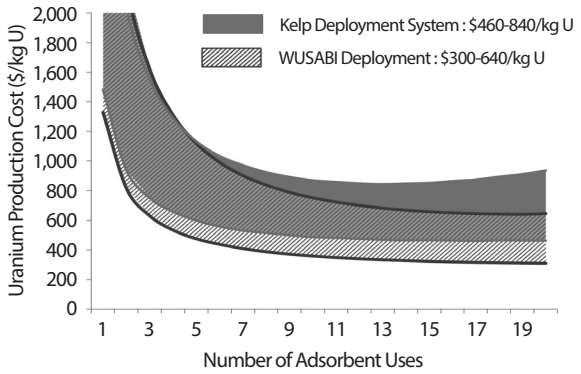

Fig. 6. A comparison of the uranium production cost as a function of number of adsorbent recycles for the MIT and base case technology shows that cost savings can be achieved by utilizing this novel deployment scheme.

The system first proposed by Picard et al. [13] allows for continuous uranium recovery by attaching a mobile adsorbent belt along with the necessary elution equipment to the base of off-shore wind turbines. The WUSABI design can be seen in Fig. 5, taken from [13]. This system was first analyzed for economic feasibility in the original publication. This zeroth order estimate was later expanded for increased accuracy and robustness in an independent publication [14].

Independent economic analysis and associated incorporation of the WUSABI deployment scheme into the existing cost model also allowed for the conduction of sensitivity analyses in order to identify design parameters resulting in significant cost impacts. Therefore work has been conducted aimed at alleviating some of these cost burdens by altering various design parameters, namely the servicing frequency of the structures and optimizing the size of the required fleet [15].

The uranium production cost resulting from the use of the improved WUSABI deployment scheme as compared to the reference kelp-field can be seen in Fig. 6.

3. Conclusions

It is clear that the alternative technologies analyzed here offer great promise to improve the current leading chemical and deployment technology scheme. While some of these alternatives offer a cost savings to the ultimate uranium production cost, other technologies considered here seek to address a potential weakness.

The addition of another ligand, by CUNY, to assist amidoxime in the adsorption of uranium could lead to a 16% cost savings if a 50% increase in capacity can be achieved. If the novel adsorbent material under development via a green chemistry process by the University of Maryland can achieve an uptake similar to that of the reference material, then a 10% cost savings could result. The natural, chitin-based adsorbents proposed by the University of Alabama likewise address an environmental concern by avoiding the introduction of plastic in the ocean, which may come at an increased uranium production cost. Lastly, the implementation of a symbiotic deployment system as proposed by MIT could not only reduce the environmental footprint of

uranium recovery, but also offers a cost savings of 30%. Most importantly to conclude however is the notion that with continued future development of these adsorbent and deployment technologies it is likely that these projections will further improve to continue to reduce the cost of seawater uranium, thereby reducing economic uncertainty surrounding nuclear power. Future work will thus include the systems analysis of more recent design improvements made to the symbiotic wind turbine deployment method initially proposed and analyzed here [16]. Additionally, broader efforts aimed at improving seawater uranium recovery through biofouling mitigation [17] and selecting deployment location to take advantage of favorable ocean conditions such as temperature [18] and current flow rate [19] will be modeled in future analyses.

REFERENCES

[1] S. Das ,Y. Oyola, R, Mayes, C.J. Janke, L.-J. Kuo, G. Gill, J.R. Woods, and D.I. Dai., "Extracting Uranium from Seawater: Promising AF Series Adsorbents", Ind. Eng. Chem. Res., 55(15), 4110-4117 (2015).

[2] S. Das,W.P Liao, M. Flicker Byers, C. Tsouris, C.J. Janke, R.T. Mayes, E. Schenider, L.-J. Kuo, J.R. Wood, G.A. Gill, and S. Dai, "Alternative Alkaline Conditioning of Amidoxime Based Adsorbent for Uranium Extraction from Seawater", Ind. Eng. Chem. Res., 55(15), 4303-4312 (2015).

[3] H.B. Pan, C.M. Wai, L.-J. Kuo, G.A. Gill, G.X. Tian, L.F. Rao, S. Das, R.T. Mayes, and C.J. Janke, "Bicarbonate Elution of uranium from amidoxime-based polymer adsorbens for sequestering uranium from seawater", Chem. Sel., 2(13), 3769-3774 (2017).

[4] L.-J. Kuo, H-B. Pan, C.M. Wai, M.F. Byers, E. Schneider, J.E. Strivens, C.J. Janke. S. Das, R.T Mayes, J.R. Wood, N. Schlafer, and G.A. Gill, "Investigations into the reusability of amidoxime-based polymeric adsorbents for seawater uranium extraction", Ind. Eng. Chem. Res., 56(40), 11603-11611 (2017).

[5] E. Schneider and D. Sachde, "The Cost of Recovering Uranium from Seawater by a Braided Polymer Adsorbent System", Sci. Glob. Secur., 21(2), 134-163 (2013).

[6] M.F. Byers and E. Schneider, "Optimization of the Passive Recovery of Uranium from Seawater", Ind. Eng. Chem. Res., 55(15), 4351-4361 (2015).

[7] M.F. Byers and E. Schneider, "Uranium from Seawater Cost Analysis: Recent Updates", Trans. Am. Nucl. Soc. 2016 Annu. Meet., 114(1), 161-164 (2016).

[8] J. Park, G.A. Gill, J.E. Strivens, L-J. Kuo, R.T. Jeters, A. Abila, J.R. Wood, N.J. Schlafer, C.J. Janke, E.A. Miller, M. Thomas, R.S. Addleman, and G.T. Bonheyo, "Effect of biofouling on the performance of amidoxime-based polymeric uranium adsorbents Effect Of Biofouling On The Performance Of Amidoxime-Based Pol- ymeric Uranium Adsorbents", Ind. Eng. Chem. Res., 55(15), 4328-4338 (2016).

[9] T. Sugo, M. Tamada, T. Seguchi, T. Shimizu, M. Uotani, and R. Kashima, "Recovery system for uranium from seawater with fibrous adsorbent and its preliminary cost estimation", J. At. Energy Soc. Japan, 43(10), 1010-1016 (2010).

[10] S.D. Alexandratos, X. Zhu, M. Florent, and R. Sellin, "Polymer-Supported Bifunctional Amidoximes for the Sorption of Uranium from Seawater", Ind. Eng. Chem. Res., 55(15), 4208-4216 (2016).

[11] T.C. Dietz, C.E. Tomaszewski, Z. Tsinas, D. Poster, A. Barkatt, M. Adel-hadadi, F.B. Bateman, L.T. Cumberland, E. Schnieder, K. Gaskell, J. Laverne, and M. Al-sheikhly, "Uranium Removal from Seawater by Means of Polyamide 6 Fibers Directly Grafted with Diallyl Oxalate through a Single-Step, Solvent- Free Irradiation Process", Ind. Eng. Chem. Res., 55(15), 4179-4186 (2016).

[12] P.S. Barber, C.S. Griggs, J.R. Bonner, and R.D. Rogers, "Electrospinning of chitin nanofibers directly from an ionic liquid extract of shrimp shells", Green Chem., 15(3), 601-607 (2013).

[13] M. Picard, C. Baelden, Y. Wu, L. Chang, and A.H. Slocum, "Extraction of Uranium from Seawater: Design and Testing of a Symbiotic System", Nucl. Technol., 188(2), 200-217 (2014).

[14] M. Byers, M.N. Haji, E. Schneider, and A.H. Slocum, "A Higher Fidelity Cost Analysis of Wind and Uranium from Seawater Acquisition SymBiotic Infrastructure", Trans. Am. Nucl. Soc. 2016 Annu. Meet., 115, 271-274 (2016).

[15] M.F. Byers, M.N. Haji, A.H. Slocum, and E.A. Schneider, "Cost Optimization of a Symbiotic System to Harvest Uranium from Seawater via an Offshore Wind Turbine", Ocean Eng. Accepted., 2017.

[16] M. Haji, C. Delmy, J. Gonzalez, and A.H. Slocum, "Uranium Extraction from Seawater using Adsorbent Shell Enclosures via a Symbiotic Offshore Wind Turbine Device", Proc. of the Twenty-sixth (2016) INt. Ocean and Polar Eng. Conf. (2016).

[17] M.F. Byers, S. Landsberger, and E. Schneider, "The use of silver nanoparticles for the recovery of uranium from seawater by means of biofouling mitigation", Sustainable Energy and Fuels (2018).

[18] L.-J. Kuo, G. Gill, C. Tsouris, L. Rao, H.-B. Pan, C. Wai, C. Janke, J. Strivens, J. Wood, N. Schlafer, and E. D'Alessandro, "Temperature Dependence of Uranium and Vanadium Adsorption on Amidoxime Based Adsorbents in Natural Seawater", Chem. Select, 2(2), 834-848 (2018).

[19] A. Ladshaw, L.-J. Kuo, J. Strivens, J. Wood, N. Schlafer, S. Yiacoumi, C. Tsouris, and G. Gill, "Influence of Current Velocity on Uranium Adsorption from Seawater Using an Amidoxime-Based Polymer Fiber Adsorbent", Ind. Eng. Chem. Res., 56(8), 2205-2211 (2017).