Advances in the Recovery of Uranium from Seawater: Studies Under Real Ocean Conditions

Fuel Cycle Research and Development

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Studies under real ocean conditions

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Abstract & Executive Summary

The objective of this project was to move the testing of uranium adsorbents from the laboratory to the field. We were successfully able to test fibers in both a flume and ocean environment under varying conditions to quantify the adsorptive properties and uranium uptake of adsorbents under coastal ocean conditions. Through this testing we have identified numerous challenges to be overcome prior to large-scale deployment of these fibers.

This project began in Phase I with laboratory experiments examining the effects of flow rates and water filtration on the absorption of uranium to fibers in flow-through columns. In this experiment we found that fibers adsorb most efficiently at a flow rate of 250 ml/min, on a per liter basis. However faster flow rates increase exposure volume and allowed for slightly greater total U absorption. Therefore a balance between current speeds that are too fast and potentially break down fibers and those that are slower will be important to consider, alongside bio-fouling and exposure time, when deciding which current regimes are best to place fibers in the ocean.

Phase II examined biofouling, comparing exposure of fibers in filtered flume water to that in a coastal ocean environment. Results from the dock and flume parallel experiment indicate a strong effect of biofouling on the capacity of the adsorbent fibers to adsorb uranium towards the very end of the experiment. Dock and flume samples showed comparable adsorption rates with the flume maximum achieved at day 49 with an adsorbance of 3.4 g U/kg-ads while the dock maximum was reached at day 42 with an adsorbance of 2.7 g U/kg-ads.

Biofouling mitigation techniques were also examined. A comparison of 5 m and 12 m samples showed less growth at 12 meters where there is less light as well as less growth on the copper cages, which are toxic to many marine organisms. Overall despite biofouling, particles and other elements present, the fibers adsorbed uranium up to 2.7 g U/kg-ads in our open water dock experiments. This is lower than the maximum achieved in the flume of 3.4 g U/kg-ads and much lower than rates observed with synthetic seawater in laboratory experiments.

Phase III involved two parts: working at Woods Hole Oceanographic Institution (WHOI) we examined the feasibility of reusing fibers after ocean deployment. Fiber reuse is an important consideration for operational costs associated with deployment. At present our data implies that reuse after open ocean exposure may not be significantly more effective than a single long deployment of fibers. The second part of Phase III involved collaboration with A. Slocum and M. Haji at MIT to examine the effects of various enclosures for fibers. This also involved testing a rotating system, designed to be deployed as part of an offshore wind turbine.
# Table of Contents

ABSTRACT & EXECUTIVE SUMMARY ........................................................................................................... II
TABLE OF CONTENTS ...................................................................................................................................... III
OBJECTIVES .................................................................................................................................................... 1
SCOPE ............................................................................................................................................................. 1
PHASE I ........................................................................................................................................................... 2
  EFFECTS OF FLOW RATE ............................................................................................................................... 2
  BIOFOULING IN FLOW-THROUGH COLUMNS ................................................................................................. 2
  SUMMARY ..................................................................................................................................................... 3
PHASE II ......................................................................................................................................................... 4
  PURPOSE .................................................................................................................................................... 4
  EXPERIMENTAL SET-UP ................................................................................................................................. 4
  RESULTS ..................................................................................................................................................... 5
PHASE III ....................................................................................................................................................... 6
  FIBER REUSE STUDY .................................................................................................................................... 6
  ADSORBENT ENCLOSURE FLUME STUDY ....................................................................................................... 7
  OCEAN TRIAL OF THE SYMBIOTIC MACHINE FOR URANIUM EXTRACTION .............................................. 9
PUBLICATIONS & OUTREACH ....................................................................................................................... 11
  PUBLICATIONS ........................................................................................................................................ 11
  CONFERENCE PRESENTATIONS & POSTERS ............................................................................................... 11
  PROJECT MEETING PARTICIPATION AND PRESENTATIONS ................................................................. 12
  WEBSITE .................................................................................................................................................. 12
REFERENCES ............................................................................................................................................... 12
FINAL QUAD CHART .................................................................................................................................... 14
Objectives

The objective of this project was to move the testing of uranium adsorbents from the laboratory to the field: to quantify the adsorptive properties and uranium uptake of adsorbents under coastal ocean conditions. There is a large gap between the detailed laboratory studies and the potential large scale ocean deployment of uranium adsorbing fibers. This study successfully examined fibers deployed under a variety of conditions with filtered and unfiltered seawater on the Atlantic coast. As an outcome of this effort the Department of Energy has gained vital field data on the behavior of uranium adsorbing materials being developed under this program. Such information will have a major impact on the direction of the program and feasibility of this approach being scaled up in the future.

Scope

This project was divided into three phases as shown in figure 1. It began with laboratory experiments examining the effects of flow rates and water filtration on the absorption of uranium to fibers in flow-through columns. Phase II examined biofouling, comparing exposure of fibers in filtered flume water to that in a coastal ocean environment. Biofouling mitigation techniques were also examined. Phase III involved two parts: working at Woods Hole Oceanographic Institution (WHOI) we examined the feasibility of reusing fibers after ocean deployment, as well we collaborated with A. Slocum and M. Haji at MIT to examine the effects of various enclosures for fibers. This also involved testing a rotating deployment system designed to be deployed as part of an offshore wind turbine.

**Figure 1.** Experimental phases of the project.
Phase I

**Effects of Flow Rate**

Our first experiment set out to determine how water flow rate (250, 500, 1000 ml min\(^{-1}\)) affects the adsorption of uranium onto fibers. Adsorbents were placed in columns separated by glass beads and water was held at a constant temperature of 20.7 °C +/− 0.3 (Figure 2). Fresh seawater was obtained using a piped system directly from the coastal Atlantic Ocean. Flow rates were controlled at desired rates with variable flow controllers and monitored via flow meter. Total U adsorbed (ug U/g adsorbent/day) was as follows: 150+/-5 at 250 ml min\(^{-1}\), 159 +/− 15 at 500 ml min\(^{-1}\) and 176 +/−15 at 1,000 ml min\(^{-1}\). Adsorption on a per-liter basis (ug U/g ads/L) was as follows: 0.41 +/− 0.01 at 250 ml min\(^{-1}\), 0.23 +/− 0.02 at 500 ml min\(^{-1}\) and 0.15+/- 0.13 at 1,000 ml min\(^{-1}\) (figure 3).

In this experiment we found that fibers adsorb most efficiently at a flow rate of 250 ml min\(^{-1}\), on a per liter basis. However, faster flow rates increase exposure volume and therefore allow for slightly greater total U absorption. This will be important to consider, alongside bio-fouling and exposure time, when deciding which current regimes are ideal for placing sorbents in the field.

![Flow-rate experimental set up](image)

**Figure 2.** Flow-rate experimental set up. Fibers were placed in clear columns between glass beads. Seawater was run through the columns at varying flow rates and monitored using in-line flow meters.

**Biofouling in Flow-Through Columns**

To investigate the effects of bio-fouling on uranium adsorbing fibers we ran two separate 1 month long experiments, one with seawater filtered to 0.45 μm (to eliminate most biological matter) and one with seawater filtered to 100 μm (to
eliminate sediment and fish only). Three columns of adsorbent fibers per experiment were exposed to the above seawater filtration conditions at a constant flow rate of 500 ml min\(^{-1}\) and constant temperature of 20 °C (+/- 1.1). The flume box was closed and dark 24 hrs/day. Flow was monitored by flow meter.

Results showed that samples exposed to unfiltered seawater yielded adsorption of approximately 2.4 g U/kg ads. Samples exposed to filtered seawater yielded only 0.8 g U/kg. This unexpected result may be the result of differing concentrations of other metals in the seawater during the experiments. The unfiltered experiment run in October 2014, showed much lower ratios of V:U and Fe:U on the fibers when compared to the filtered experiment which was run in December 2014. This may be due to changing concentrations of vanadium and iron in seawater over different seasons and/or due to the complexation of uranium with iron-oxides or organic carbon in the seawater. Uranium concentrations in seawater are conservative with salinity and only varied from 30.2 psu in the unfiltered experiment to 30.3 in the filtered experiment. The uranium concentrations extracted from fibers were also corrected for any salinity differences.

**Summary**

In our flow rate experiment, we found that U fibers adsorb most efficiently at a flow rate of 250 ml/min, *on a per liter basis*. However faster flow rates increase exposure volume and allowed for slightly greater *total* U absorption. Therefore a balance between current speeds that are too fast and potentially break down fibers and those that are slower will be important to consider, alongside bio-fouling and exposure time, when deciding which current regimes are best to place fibers in the ocean.
We found that in our second set of experiments uranium adsorbance was reduced when using water filtered to 0.45 microns despite adsorbent material being from the same batch as the flow rate experiments. An examination of other metal ion adsorbed to the fibers may be impeding uranium adsorption by competition of other ions for sites on the fiber. Greater competition for sites could be due either to changes in concentrations of these ions in seawater, such as higher V or Fe, or from complexation of Fe oxides with U in seawater.

More detail of methods and results from Phase I may be found in the publication Gill et al., 2016 listed under the Publications and Outreach section of this document.

**Phase II**

**Purpose**

The objective of Phase II of this NEUP project was to move from testing of uranium adsorbents from the lab to the field to quantify the sorptive properties of uranium uptake in real ocean conditions. For this experiment we used in-situ ocean testing and parallel laboratory flume experiments to test fibers for uranium adsorption. Due to evidence that biofouling may impact adsorption in non-filtered water we also further tested enclosures for the fibers to try to mitigate biofouling of the fibers in the ocean. Details regarding methods and experimental design can be found in the Milestone II report number M2NU-13-MA-WHOI-0601-0323.

**Experimental Set-up**

The first experiment of Phase II was a parallel exposure study comparing uranium fiber adsorption rates in filtered seawater and in coastal ocean conditions (referred to hereafter as Experiment I). This experiment ran from May to August 2015. This 49 day dock and flume study compared fibers deployed in a flume receiving filtered seawater with a dock deployment of fibers inside a large mesh bag. Water was filtered to 0.45 microns, which removes organisms in the water. The growth of these organisms on a substrate is referred to as biofouling.

Experiment I which compared open ocean exposure to the flume (filtered water) exposure highlighted the importance of quantifying the amount of biological growth on the fibers over time. Does the growth impede the adsorption of uranium to the fibers? Experiment II was therefore designed to test fibers deployed at two depths and in enclosures made of nylon, copper and steel. Nylon was chosen to replicate conditions from Experiment I. Copper is a known antimicrobial and is toxic to many marine organisms. It is commonly used to prevent algal growth and adherence by being mixed in boat paints and on fishing nets. Steel was chosen as it is relatively resistant to corrosion in the ocean and would provide a ridged enclosure of identical nature to the copper one.
Results

Results from the dock and flume parallel experiment indicate a strong effect of biofouling on the capacity of the adsorbent fibers to adsorb uranium towards the very end of the experiment (after day 42). Dock and flume samples showed comparable adsorption rates with the flume maximum achieved at day 49 with an adsorbance of 3.4 g U/kg-ads while the dock maximum was reached at day 42 with an adsorbance of 2.7 g U/kg-ads (figure 4).

The second dock experiment used pre-weighed braids to better quantify the amount of biological growth on the fibers over time. A comparison of 5 m and 12 m samples showed less growth at 12 meters as well as less growth on the copper cages, which are toxic to many marine organisms (figure 5).

Overall despite biofouling, particles and other elements present the fibers adsorbed uranium up to 2.7 g U/kg-ads in our open water dock experiments. This is lower than the maximum achieved in the flume of 3.4 g U/kg-ads and much lower than rates observed with synthetic seawater in laboratory experiments. Previous flume experiments at WHOI found adsorption rates of 3.3 g U/kg-ads in a column study and 3.2 g U/kg-ads in a flume study both using the AF1 braid. At PNNL column flow through tests the AI8 braid achieved 3.5 g U/kg-ads after 56 days. The modeled saturation capacity of this braid type was 5.9 g U/kg-ads. The lower rate of adsorbance in the second WHOI dock experiment (max. 2.4 g/kg) may be due to the reduced temperature at that time, averaging 15.3 over the course of the experiment at both depths.

![U concentrations from dock and flume](image)

**Figure 4.** Uranium adsorption on fibers exposed to filtered seawater in a flume (grey squares) and to coastal seawater (white triangles). Dock temperature is also shown on the right-hand axis.
Phase III

Fiber Reuse Study

One of the largest costs associated with the use of amidoxine based acrylic fibers is the capital production cost (Byers & Schneider, 2016). All cost analyses of the use of these fibers have considered them for multiple use, up to 10 times however this has not been tested in the ocean environment. We therefore set up an experiment to test fiber reuse after ocean exposure similar to the second part of phase II described above. Fibers were placed at two depths and sampled weekly from August to November of 2016. Following exposures of either 28 or 42 days the uranium was extracted from the fibers using a method described by Pan et al. (2017) which involves using a 3M KHCO₃ solution to strip the fibers of some metals without damaging them.

This experiment found that on average only 55% of the uranium on fibers was able to be eluded using the 3M KHCO₃ solution versus a total acid digestion. This has important implications for cost analysis and production when reusing fibers. As well the sum of three 28-day exposures (total 84 days) extracted by KHCO₃ at 5 & 12 m was 2.30 g U/kg-ads and 2.07 g U/kg-ads respectively, whereas a single 56 day deployment with acid digestion showed 2.78 g U/kg and 2.65 g U/kg at 5 m and 12 m (Figure 6). This result suggests that the effort involved in stripping and collecting the fibers may not be cost effective.

Figure 5. Growth on the fiber enclosures over time on the copper (top) and steel (bottom) cages at 5 meters depth. Day 49 for 12 meters is also shown with nearly no growth on the copper cage.
In collaboration with PhD student Maha Haji, undergraduate Jorge Gonzalez and Dr. Slocum at MIT a flume study was conducted to evaluate the impact of shell enclosures on uranium uptake onto acrylic fibers during the summer of 2016. This study used an opaque flume with filtered seawater located at WHOI in which fibers were placed inside plastic spheres with varying sized openings (figure 7). Fibers were exposed to seawater at a flow rate greater than previous experiments (4.8 cm/s) for 56 days. Small samples (approx. 100 mg) were taken each week and analyzed for uranium and other element adsorption.

Water flow measurement was determined using a novel technique involving the use of radium-adsorbing MnO₂ impregnated acrylic fibers. In brief MnO₂ fibers adsorb radium which is naturally occurring in coastal seawater. Fibers were placed in the enclosures following the uranium exposure experiment. At the same time a known

**Figure 6.** Uranium adsorption on fibers deployed at 5 meters for 56 days continuously, three exposures of 28 days or two exposures of 42 days. Uranium was extracted from fibers deployed for 56 days via total acid digestion. Uranium from fibers that were reused was extracted using 3M KHCO₃ to enable their reuse.

**Adsorbent Enclosure Flume Study**
volume of water was sampled and passed through a column containing the MnO₂ fibers. By pre-weighing the fiber amounts and comparing the fibers exposed to a known volume of water, we were able to calculate the volume of water seen by the fibers in the different enclosures.

Results show that water flow in the varying enclosures differs greatly depending on placement in the flume, orientation of the openings or lack of enclosure. The fiber closest to the pump showed the highest water seen comparable to the furthest fiber which had no enclosure. Despite these differences however overall uranium uptake averaged 3.5 g U/kg-ads ranging from 3.2 g U/kg to 3.7 g U/kg-ads in the enclosure with the largest openings. This result indicates that the enclosure is likely not constraining uranium adsorption and that the linear velocity of the water is great enough that the reaction is not mass limited. This has important implications for choosing deployment locations in the future.

More detail of methods and results from the Adsorbent Enclosure Flume Study may be found in the publication Haji et al., 2018 (Submitted) listed under the Publications and Outreach section of this document. Details may also be found in the PhD thesis of Maha Haji entitled: Extraction of uranium from seawater: Design and Testing of a symbiotic system, Massachusetts Institute of Technology, 2017.
Ocean Trial of the Symbiotic Machine for Uranium Extraction

A second collaboration with MIT in the fall of 2016 examined the use of fiber shell enclosures in a coastal ocean environment. These were tested off a dock at the Massachusetts Maritime Academy in Bourne, MA. This 9-week trial involved testing fibers in two different enclosure types woven in a net on both moving and stationary systems, as well as control fibers in nylon enclosures (identical to those deployed at WHOI in earlier experiments) (Figure 8).

This experiment showed much lower uranium adsorption than previous experiments which we attribute to the low average water temperature (11.5°C versus 18°C-21°C over WHOI dock experiments). Total uranium uptake was 1.21 g U/kg-ads in a slotted enclosure design that was stationary and 1.06 g U/kg-ads in the equivalent rotating system. A control in nylon identical to WHOI deployments had 1.16 g U/kg-ads. The stationary systems had more biofouling but this does not appear to have affected uranium adsorption. Results indicate that the systems rely more on water current velocities, which are much faster than the rotation of the machine.

More detail of methods and results from the Ocean Trial of the Symbiotic Machine of Uranium Extraction may be found in the upcoming publication Haji et al., 2018 titled “Results of an Ocean Trial of the Symbiotic Machine for Uranium Extraction” listed...
under the *Publications and Outreach* section of this document. Details may also be found in the PhD thesis of Maha Haji entitled: Extraction of uranium from seawater: Design and Testing of a symbiotic system, Massachusetts Institute of Technology, 2017.

**Research Conclusions**

This project was successfully able to take uranium adsorbing fibers from laboratory testing to the open coastal environment. Through this testing we have identified numerous challenges to be overcome prior to large-scale deployment of these fibers.

The complex and continuously changing nature of seawater creates a unique environment. As seen in Phase I changing element composition within the water (i.e., iron and vanadium) can greatly affect the adsorption of uranium. Seasonal temperature changes also affect biofouling as well as adsorption kinetics. While increases in temperature cause increased uranium adsorption, increasing biofouling has the opposite effect. Experiments with the lowest temperatures and unfiltered environment show the lowest overall uranium adsorption.

![Figure 9](image)

**Figure 9.** Summary of uranium adsorbed to fibers in all experiments under this report. All uranium concentrations obtained by total acid digestion with the exception of the 3x28 day and 2x42 day reuse data shown in Phase III. Temperature average over the course of each experiment is shown with orange diamonds using the right-hand side axis.
The operating cost of large scale deployment of uranium adsorbing fibers is a consideration and fiber reuse is an important concern. At present our data implies that reuse after open ocean exposure may not be significantly more effective than a single long deployment of fibers. More research is needed to increase the adsorption rates as well as the elution method for reuse to be viable.

Lastly there are environmental considerations to deploying these fibers. In this study we were unable to quantify loss of fiber over time but fish, crabs and other marine organisms were observed on the fibers. As the fibers are small and plastic there is a consideration whether these should be deployed in an unenclosed area of the ocean. Further studies will be needed to determine material lost during a deployment and how to increase the strength of the fibers.

Publications & Outreach

Publications


Submitted


In Preparation


Conference Presentations & Posters


**Project Meeting Participation and presentations**

- Marine Sciences Laboratory, Pacific Northwest National Laboratory, Sequim, WA, August 2-4, 2017
- University of South Florida, Tampa, FL, January 12-14, 2017
- University of Maryland, College Park, MD. August 5-7, 2015.
- Marine Sciences Laboratory, Pacific Northwest National Laboratory, Sequim, WA, August 2014.
- Oak Ridge National Laboratory, Oak Ridge, TN, January 2014.

**Website**

http://uraniumfromseawater. engr.utexas.edu/partners/woods-hole-oceanographic-institution - Maintained by The University of Texas at Austin

**References**


Advances in the recovery of uranium from seawater: studies under real ocean conditions

OVERVIEW

**Purpose:** To take sorbent testing from controlled laboratory experiments to large scale natural ocean conditions over the course of three years. There is a big gap between detailed lab studies and potential large scale extraction of U from the ocean. We will begin with seawater laboratory studies, then move studies out to the dock and finally to a mooring in the coastal ocean where we can monitor the effect of environmental changes as well as bio-fouling on U sorbent uptake, extraction efficiency and re-usability.

**Objectives:**
- To test extraction efficiency of U adsorbents at different flow speeds and filtration
- To use dock tests to evaluate active pumping versus passive collection and assess the effects of natural environmental changes on the effectiveness of uranium adsorption using in situ monitoring systems
- To field test U adsorbents in offshore conditions and design a model for large deployment

DETAILS

**Principal Investigator:** Dr. Ken Buesseler

**Institution:** Woods Hole Oceanographic Institution

**Collaborators:** none

**Duration:** 3 years * 1 year no cost extension to 30/04/18 (01/05/14-30/04/17)

**Total Funding Level:** $398,882

**TPOC:** Gary Gill (PNNL)

**Federal Manager:** Stephen Kung

**Workscope:** MS-FC1

**PCS:NE Work Package #:** NU-13-MA-WHOI-0601-03

RESULTS

**Results:**
Final results of all studies are shown in the figure to the right. Overall fibers in warmer, filtered water performed best.

**Accomplishments:**
Overall we produced one completed publication, one that has been submitted, and two nearing submission to be reviewed in the next month. We were able to test fibers in the ocean following laboratory studies and confirm their ability to adsorb uranium under varying temperatures and with changing water composition as well as biological activity.