Ocean Testing of a Symbiotic Device to Harvest Uranium from Seawater through the Use of Shell Enclosures

Maha N. Haji, Jessica Drysdale†, Ken Buesseler†, and Alexander H. Slocum**
* Department of Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, MA, USA
† Department of Marine Chemistry & Geochemistry, Woods Hole Oceanographic Institution, Woods Hole, MA, USA

ABSTRACT

With conventional sources of uranium forecasted to be depleted within the century, research into the harvesting of uranium from seawater, which is estimated to contain 1000 times more uranium than land, is crucial to determining the continued viability of nuclear power generation. Recent studies have shown that the cost of harvesting uranium from seawater can be reduced by coupling the harvesting system with an existing offshore structure, such as a wind turbine, to eliminate the need for additional moorings and increase the overall energy-gathering ability of the wind farm system. This paper presents the design, fabrication, and ocean testing of 1/10th physical scale prototypes of two such systems. Both designs utilize adsorbent filament that is enclosed in a hard permeable shell to decouple the mechanical and chemical requirements of the device.

KEY WORDS: Seawater uranium; offshore wind turbine; uranium adsorption; design; ocean testing; prototype.

INTRODUCTION

The expanded use of nuclear power has the potential to significantly reduce carbon dioxide emissions from power generation, given that one gram of ^{235}U can theoretically produce as much energy as burning 1.5 million grams of coal (Emsley 2001). However, at the current consumption rate, global conventional reserves of terrestrial uranium (approximately 7.6 million tonnes) could be depleted in a little over a century (OECD, 2014). As these reserves decrease, uranium is expected to come from lower quality sites leading to higher extraction costs and greater environmental impacts. Fortunately, the ocean contains approximately 4.5 billion tonnes of uranium, present as uranyl ions in concentrations of approximately 3 ppb (Oguma et al., 2011). A sustainable way to harvest uranium from seawater will provide a source of nuclear fuel for generations to come. It will also give all countries with ocean access a stable supply of uranium, thereby eliminating the need to store spent fuel for potential reprocessing, and helping to address nuclear proliferation issues.

Kim et al. 2013 found uranium adsorption by chelating polymers to be the most viable uranium recovery technology in terms of adsorption capacity, environmental footprint, and cost (Zhang et al., 2003, Seko et al., 2003, Anirudhan et al., 2011). In this technology, chelating polymers allow for the passive extraction of uranium from seawater by adsorption. They are deployed in the ocean and remain submerged until the amount of captured uranium approaches the adsorption capacity. From there, the metal ions, including uranium, are stripped from the polymer through an elution process. Current experimental data indicates that uranium is best eluted from the polymer in a highly alkaline bath if the polymer is to be reused. Following elution it is regenerated with an alkaline wash to remove any adhered organic matter. The output is transformed into yellowcake through a purification and precipitation process similar to that for mined uranium.

Past work focused on systems in which the adsorbent was brought back to shore for the elution process and redeployed afterward. The adsorbent production and mooring costs of these systems were found to be the most expensive components of the recovery process (Schneider and Sachde, 2013, Byers and Schneider, 2016). Designs proposed by Picard et al. (2014), shown in Fig. 1, aimed to reduce costs associated with the deployment, mooring, and recovery of the adsorbent by coupling the uranium harvester with an existing offshore structure, such as an offshore wind turbine. In this design, a platform at the base of the wind tower supports a belt of adsorbent that loops in and out of the water. This belt cycles through the seawater beneath the tower and through an elution plant located on the platform, thereby allowing for an autonomous elution procedure that can be precisely timed depending on the type of adsorbent used. The system was sized to collect 1.2 tonnes of uranium per year, a sufficient amount to supply a 5 MW nuclear power plant. A recent independent cost-analysis compared this type of symbiotic deployment to a reference scheme in which the adsorbent polymer was braided into a buoyant net and deployed like a kelp-field across the ocean floor, serviced by boats for deployment, retrieval for onshore elution, and redeployment (Tamada, 2006, Schneider and Linder, 2014). It was found that the symbiotic deployment proposed by Picard et al. (2014) could reduce the cost in 2015 dollars of harvesting uranium from seawater by up to 11%, from \$450-890/kg-U for the reference scheme to \$400-850/kg-U (Byers et al., 2016).

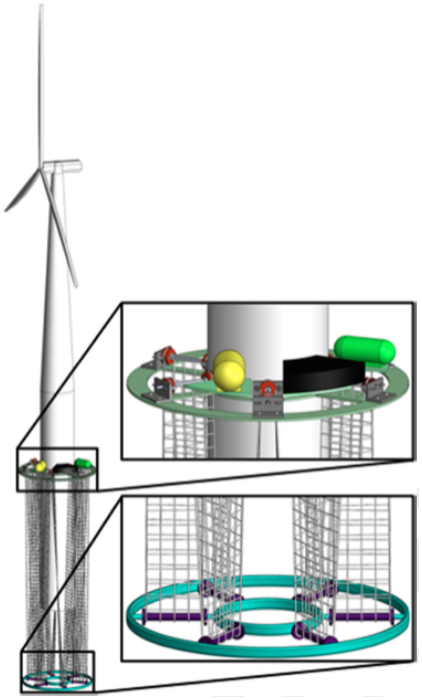

Fig. 1 Three-dimensional model of continuous uranium recovery system with adsorbent belt looped around the mast of an offshore turbine proposed by Picard et al. (2014).

ADSORBENT BEHAVIOR

In general, materials with the optimal chemical properties for high uranium adsorption have inherently low tensile strength and durability (Mayes, personal communication). Therefore, designs requiring the adsorbent fibers to be woven into a belt, like those previously investigated and prototyped by Picard et al. (2014), will likely face significant challenges given that current adsorbents do not have the durability and tensile strength to withstand an ocean environment. The prototypes presented in this paper decouple the mechanical and chemical requirements of the seawater uranium harvesting device using a two-part system in which a hard permeable outer shell encapsulates the adsorbent fibers (Fig. 2). The outer shell is designed with sufficient mechanical strength and durability for use in an offshore environment and chemical resilience against elution treatments, thereby serving as a protective enclosure for uranium adsorbing material with high adsorbent capacity in its interior (Haji et al., 2015).

The designs described in this paper utilized the AI8 adsorbent developed at Oak Ridge National Laboratory (Gill et al., 2016). For these systems,

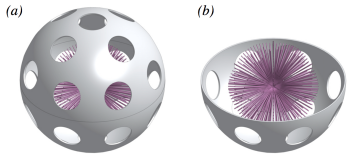

Fig. 2 Decoupling of mechanical and chemical requirements through the use of a a tough, outer protective sphere encapsulating a soft, inner adsorbent. The outer sphere features holes to allow adequate seawater flow to the adsorbent interior (Haji et al., 2015).

the uranium uptake was predicted using the one-site ligand-saturation model. In this model, the uranium uptake, y, after a certain exposure time in days, t, is given by

$$y = \frac{\beta_{max} t}{K_D + t}, \tag{1}$$

where β_{max} is the saturation capacity in kg-U/t-ads, and K_D is the half-saturation time in days, both properties of the adsorbent used from Gill et al. 2016. The amount of uranium adsorbed in kg-U/t-ads after n elution cycles is given by Γ_n as follows

$$\Gamma_n = C_{ratio} \frac{\beta_{max} t}{K_D + t} \left[\frac{1 - (1 - d)^n}{d} \right] \tag{2}$$

where C_{ratio} is the ratio of adsorbent capacity after initial conditioning pre-deployment to theoretical capacity (taken to be 90% for this study), and d is the degradation of the polymer per elution cycle (Haji et al., 2016).

FUNCTIONAL REQUIREMENTS

The functional requirements of the continuous seawater uranium harvester are as follows:

1. Use the amidoxime-based polymeric adsorbent developed by Oak Ridge National Laboratory known as AI8 (Gill et al., 2016).
2. Recover 1.2 tonnes of uranium from seawater per year, enough annual fuel for a 5-MW nuclear power plant.
3. Bring the cost of uranium extraction from seawater as close as possible to terrestrial uranium mining.

SYMBIOTIC MACHINE FOR OCEAN URANIUM EXTRACTION DESIGN

The designs for the Symbiotic Machine for Ocean uRanium Extraction (SMORE) presented in this paper build upon the previous design and testing of a 1/50th scale system (Haji et al., 2016). The initial design calculations for SMORE at a full-scale are detailed in a previous publication (Haji and Slocum, 2016). SMORE utilizes adsorbent shells that are incrementally spaced along high strength mooring rope, resembling conventional ball-chain belts. However, unlike those utilized by the design of Haji et al. (2016), the ball-chains are then strung together to create a net using incrementally spaced cross-members which add rigidity and reduce the likelihood of tangling of individual lengths.

Previous design analysis and prototype testing from Haji et al. (2016) found that a higher device uptime could be achieved by a machine that used multiple subsystems for harvesting uranium. This is because there is a lower probability that all subsystems will fail at the same time due to unforeseen circumstances or complications.

1/10TH SCALE PROTOTYPE

In the full-scale design, described by Haji and Slocum (2016), large rollers are used to move ball-chain nets down the entire length of the turbine. One question that arose in the development of the design was whether the ball-chain nets should be continuously moving through the ocean or completely stationary (i.e. should the rollers continuously cycle the ball-chain net like a conveyor belt through the ocean?). The additional movement of the ball-chain net might induce more seawater flow to the fiber adsorbents within the shells and hence increase the uranium

adsorbed. However, the additional complexity of a continuously moving system as opposed to a stationary system would likely result in higher capital and operational costs for the machine. The question remains as to whether the value of the additional uranium adsorbed by a system continuously moving the adsorbent fibers would offset the increased cost of the system due to its increased complexity. For this reason, two modules were prototyped at a 1/10th physical scale for prolonged ocean testing: one system in which the net remained stationary and another in which the net was continuously moving.

Ocean test site

The prototypes were tested at the Massachusetts Maritime Academy (MMA) in Buzzards Bay, MA. They were located at the end of the MMA dock where the water depth was approximately 23 feet at low-tide. Although fairly close to shore, the tides in this location vary up to 6 feet and the currents can be extremely strong due to the proximity to the Cape Cod Canal, which frequently has currents of about 5 knots (2.6 m/s). Additionally, the wind often generates waves of approximately 1-2 feet in height at this location. For these reasons, this site was deemed to have conditions that could provide valuable results from the prolonged ocean testing of the 1/10th scale SMORE prototypes.

Both systems were mounted to a single wooden float measuring 24 ft long and 7 ft wide which was moored to the end of the MMA concrete dock. A variety of ocean sensors were also deployed along with the prototypes. These were mounted at various depths along a piling located at the end of the concrete dock within 3 ft of the wooden float, where the ocean depth was approximately 19 ft at low tide.

Shell enclosure net

In the prototypes designed and tested in this paper, the adsorbent shells were incrementally spaced along high strength mooring rope, and then strung together to create a net using cross-members of the same rope to increase the net's rigidity and reduce the likelihood of tangling. Both prototypes used the same type of net, with four lengths of shells combined to make a single net. The vast majority of the shells for the ocean test did not contain uranium adsorbing fibers and were used primarily to test the mechanical components of the system. The net for the stationary system was approximately 20 ft long and used a total of 430 shells. The net for the continuous system was about 42 ft in length and required 960 shells.

The net was constructed by stringing placeholder 1.6 in diameter shells along 3/16 in diameter rope. The rope comprised of a braided cover and a braided core made from high-performance aramid, also known as Technora, resulting in a high-temperature (rated up to 300^{o}F), wear-resistant rope meant for lifting (rated for 550 lbs capacity). The shells were spaced approximately 0.45 in apart lengthwise such that 13 shells fit around the circumference of a 8.625 in diameter roller, and approximately 2.23 in apart widthwise, so that four lengths fit along the length of the 11 in roller. The shells were kept in place along the rope by 16 gauge steel c-ring staples.

To test the uranium uptake of the AI8 adsorbent fibers used on the prototypes, two shell designs were investigated, shown in Fig. 5. The first used slotted holes while the second used circular holes. Each net included nine of each type of design, for a total of 18 shells per net that would include AI8 fibers (see Fig. 6). The shells were 3D printed out of ABS in two halves with a series of tabs and corresponding slots to ensure the two halves were aligned each time they were connected. The two halves were kept together using a 1/4 in threaded acetal rod placed through the middle and two nylon hex nuts on either end. On the stationary net, the shells were placed approximately 10 ft below the ocean surface so that they were about mid-depth in the water column when deployed. In the case of the net for the continuously moving system, two narrow cable ties were also used to secure each half of the shell together to ensure the shells would not come apart unintentionally. The shells were made water-proof using three coats of polyurethane to reduce the amount of water absorbed by the shells which could cause unwanted deformation during the experiment.

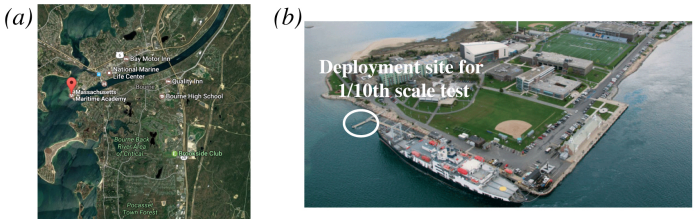

Fig. 3 Massachusetts Maritime Academy (MMA) (*a*) location in reference to Cape Cod Canal and Buzzards Bay, and (*b*) aerial view of MMA's campus with the location of the prototype test indicated by the white circle.

Fig. 4 Both prototypes mounted to the wooden float and moored to the end of the MMA dock during testing.

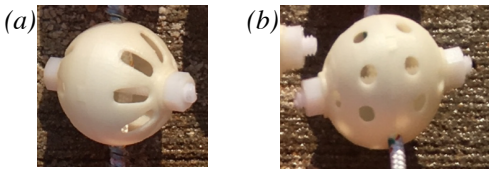

Fig. 5 Shell designs for the testing of uranium adsorption fibers using (*a*) slotted holes and (*b*) circular holes.

Fig. 6 Small section of net with white shells for adsorbent fibers. Adsorbent enclosure shells were alternated with orange placeholder shells used for mechanical testing.

System 1: Stationary net system

The stationary net system, shown in Fig. 7, comprised of a roller and wheel assembly, surface support structure, motor and gearbox, transmission system using a timing belt, battery, 18 ft long bottom support structure, and two guide wires. The roller was constructed from a 8.625 in outer diameter pipe, 0.322 in thick, with a length of 11 in and 1.6 in diameter circular holes to fit the shells of the adsorbent net. The roller was designed to fit 13 shells along its circumference and four shells along its length.

The roller was motorized in order to wind and unwind the shell enclosure net periodically to retrieve adsorbent samples. This motorization was accomplished using grooved wheels on a circular track welded to the interior of the roller on either end (Fig. 7(*c*)). The number of grooved wheels required was determined by using the maximum pressure of the contact for an ellipsoid Hertz contact between the wheels and the groove, as well as the friction required to provide sufficient torque to move the roller. Using a similar analysis to that described in Haji and Slocum (2016), it was found that three polyurethane wheels of approximately 1.77 in outer diameter along an 0.675 in diameter aluminum rail would be sufficient.

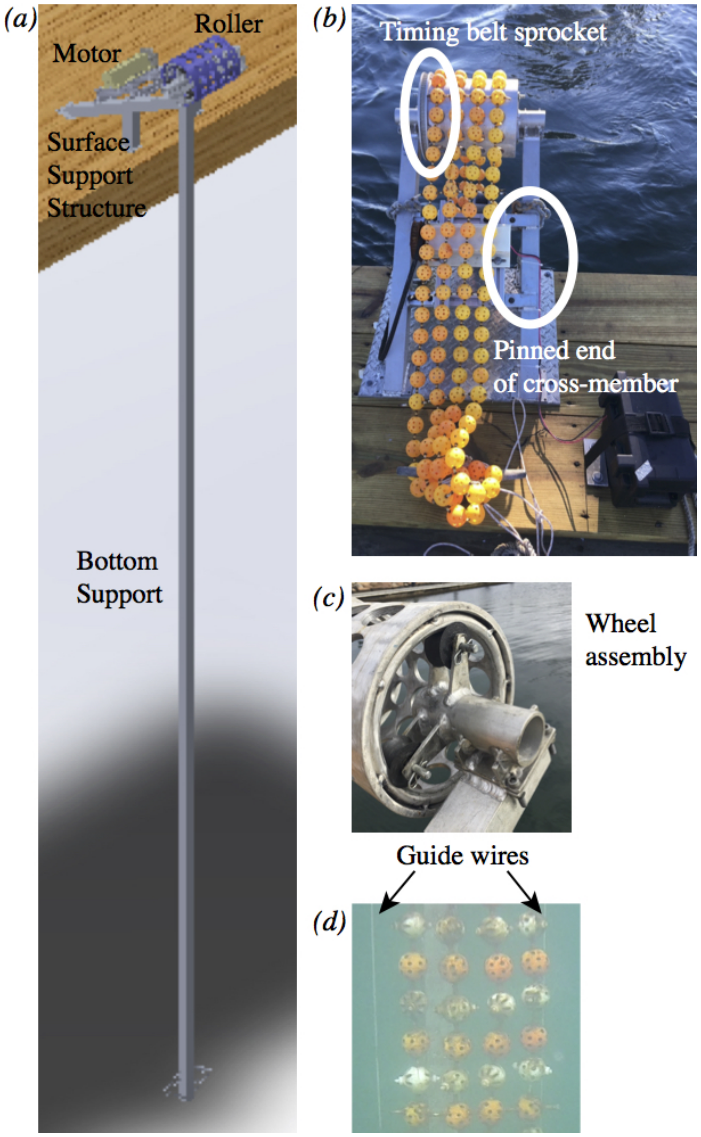

Fig. 7 Stationary system design as shown in (*a*) solid model, (*b*) fabricated surface structure, (*c*) fabricated wheel assemblies, and (*d*) fabricated net and guide wires.

A brushed DC motor with a torque rating of 345 oz-in was used to drive the roller. The motor was fitted with a 12:1 gearbox in order to reduce the speed. The power was transmitted using a timing belt from the motor to a fabricated sprocket welded to the exterior of the roller. The motor was powered using a 7 amp, rechargeable lead acid battery housed in a waterproof battery box mounted next to the surface structure of the stationary system.

A thrust bearing was used on one side of the top wheel on the belt side of the roller to counteract the force of the timing belt pulling the belt side of the roller and thereby causing the top wheel to fall out of alignment and possibly causing it to rub to one side resulting in premature failure due to friction. This bearing was able to take the radial load of the wheel pushing against the side support and push the wheel back towards the intended alignment. All other wheels would then move to compensate for the imperfections in the welded rails as needed, so as not to over-constrain the system.

The wheel assemblies were first connected to the roller and then bolted into surface support members. In order to ensure alignment between the roller and both wheel assemblies without over-constraining the system, the surface support structure was fabricated with a cross-member connecting the two sides. This cross-member was welded to one surface support and pinned to the other using carriage bolts to through a thin attachment plate. These cross-members also served as a mount for the motor subassembly. The entire surface assembly was then bolted into an aluminum plate to maintain alignment and this aluminum plate was then bolted into the wooden float.

In order to reduce the likelihood of the stationary adsorbent net tangling or being dragged away by strong currents, it was clipped in place to galvanized vinyl-coated wire rope that was attached on either side of the bottom support pole (Fig. 7(*d*)). Additionally, because the net was inherently buoyant, small dive weights were added to the bottom of the net to ensure it sank.

System 2: Continuous net system

Aside from the bottom support, net, and motor assembly, the continuous net system was analogous to the stationary net system. In the case of the continuous net system, the shell enclosure net was a complete loop, making a sort of a conveyor belt. Originally, a roller, similar to the one on the surface, was designed to be attached to the bottom of the 18 ft long bottom support.

Similar to the stationary system, a brushed DC motor with a torque rating of 345 oz-in was used to drive the roller. However, the speed was reduced much lower using a 256:1 gearbox. The motor was powered by a 12V AC to DC converter, rated for up to 25 amps. On average, the system drew approximately 8 amps, resulting in an output torque of approximately 15 oz-in. The resulting linear velocity of the adsorbent net was approximately 4.7 in/s (11.9 cm/s).

Adsorbent deployment and sampling

As mentioned previously, each system contained 18 shells in which the uranium adsorbent was placed, for a total of 36 shells with adsorbent fibers. The adsorbent was deployed as a “mini braid” (Fig. 9), a pre-weighed, small mass (80-100 mg) of adsorbent fiber that was cut from

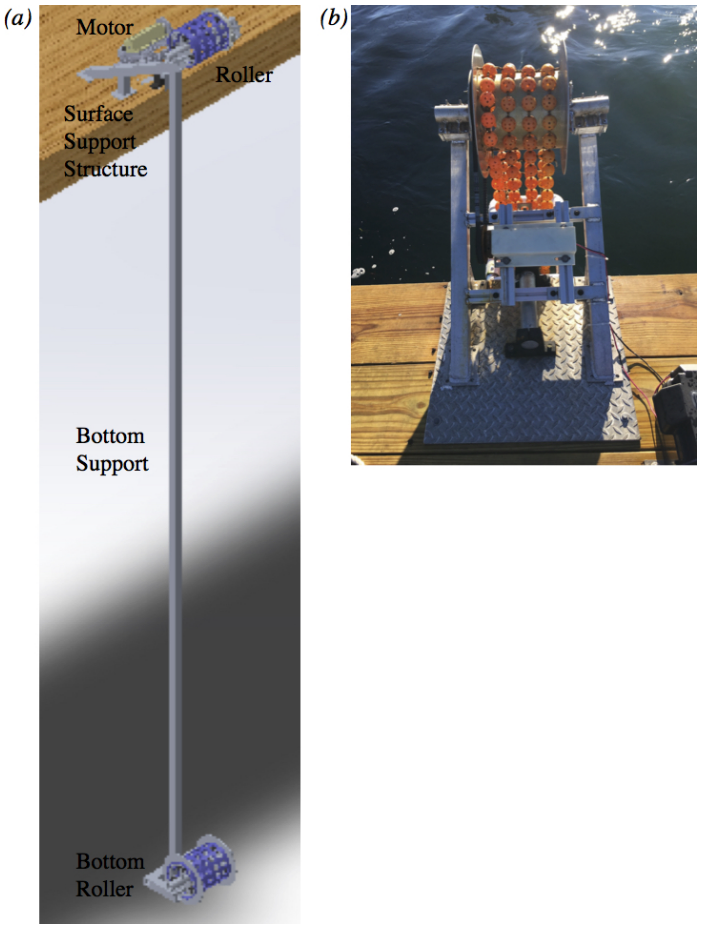

Fig. 8 Continuous system design shown as (*a*) solid model and (*b*) fabricated surface structure.

a common AI8 adsorbent braid prepared by Oak Ridge National Laboratory. Each mini braid was weighed before deployment, after retrieval, and also after sample digestion. The weight after retrieval would include any amount of biofouling (the growth of organisms on the fiber), however it would not account for any loss of fiber occurring during the deployment. The weight after sample digestion would allow for the determination of adsorption capacity as a function of the adsorbent mass.

The stationary system included two mini braids per shell while the continuous system had about one-two mini braids per shell. Additionally, mini braids were included in two nylon mesh bags at the bottom of the stationary net to act as controls (i.e. to determine if the shells signifi-

Fig. 9 Pre-weighed adsorbent mini braid. One to two of these mini braids were placed in each shell design on each of the two prototypes.

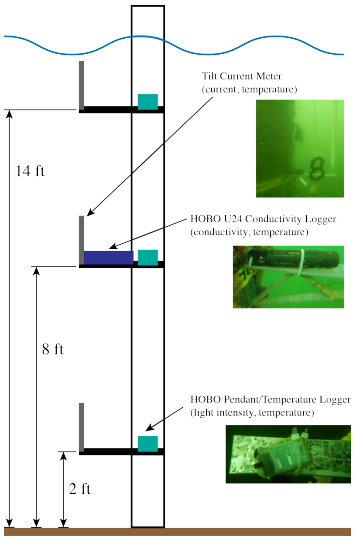

Fig. 10 Layout of instruments attached to piling at the end of the dock.

cantly inhibited the uptake of uranium due to shell's obstruction of seawater flow). The first adsorbent sample was collected 24 hours after deployment. The eight subsequent samples were collected every seven days after deployment. This sampling resulted in a determination of uranium adsorption as a function of time for each system, each shell design, as well as the control bags. Water samples were also collected on each of the nine sample dates for trace metal analysis.

Ocean test measurements

In addition to the mechanical testing of the physical prototype, sensors were placed throughout the water column to measure physical properties of the ocean during the deployment that directly affected the uranium adsorption rates of the fibers. Most of the sensors were mounted at various depths along a piling at the end of the dock at MMA, within 3 ft of the wooden float with the prototypes. Fig. 10 shows the distribution of sensors along the piling. All sensors placed on the piling were deployed on August 10, 2016 and retrieved on December 18, 2016. In addition to the sensors on the piling, a Xylem EXO-2 Sonde measured salinity as part a water quality assessment of Buzzards Bay from October 4, 2016 to December 13, 2016.

Temperature has been shown to have strong implications of the adsorbent's uranium uptake (Sekiguchi et al. 1994). For instance, a 10°C increase in temperature results in a 3-fold higher adsorption rate for amidoxime-based polymeric adsorbents (Sekiguchi et al. 1994). In the case of the AI8 fiber, the relationship between temperature has been seen to affect the parameters β_{max} and K_D (Byers, personal communication), specifically modifying equation (1) to be

$$y = \frac{(377.5T - 2077)t}{(0.4083T + 14.13) + t}. \tag{3}$$

For these reasons, temperature was measured throughout the water column as well as on the two prototypes using ONSET Tidbit Water Temperature Loggers. One Tidbit was mounted on the continuously moving net below the adsorbent shells sampling in 30 second intervals, another was mounted in a similar location on the stationary system sampling at 5 minute intervals, and a third was placed in one of the nylon mesh bags at the bottom of the stationary system sampling at 5 minute intervals.

Salinity, also shown to have a large impact on the adsorbent's uranium uptake as it directly indicates the amount of uranium present in the water (Owens et al., 2011), was measured at approximately mid-depth using a HOBO U24 Conductivity Logger (which also measured temperature), sampling at 15 minute intervals. It was also measured by the XYlem EXO-2 Sonde, mounted 3 ft above the seafloor, also sampling at 15 minute intervals.

In order to gather quantifiable data related to biofouling, light was measured at three depths using HOBO Pendant Light/Temperature Loggers (which also measure temperature), sampling at 10 minute intervals. The amount of light has been shown to have strong affects on the biofouling of the adsorbent and the related uranium uptake (Park et al., 2016).

Previous work has shown that the uranium adsorbed by the AI8 fibers is also highly dependent on the flow rate of the water (Gill et al., 2015). In order to gather information regarding the water flow seen by the two prototypes, current was measured using Tilt Current Meters from Lowell Instruments, placed at three depths. They also measured temperature and were set to sample every second.

RESULTS

The prototypes were deployed for a total of 56-days, starting on October 18, 2016. The first adsorbent sample was taken 24 hours after deployment on October 20, 2016 and the ninth and final sample was completed on December 13, 2016, 56-days after deployment. The results described below include insights gained from the mechanical testing of the system, comparison between the stationary and moving systems, as well as the physical properties and changes over time of the ocean site itself.

Continuous system modifications

Originally, the continuous net system required the use of a roller above the ocean surface and one attached to the bottom support structure, such that the adsorbent net was placed in tension between the two rollers, thereby acting to transmit the movement from the upper roller to the submerged roller. Ensuring there was enough tension in the system in order to accomplish this proved to be difficult as the currents could be extremely strong and resulted in either causing the adsorbent net to slip off the bottom roller (Fig. 11(*a*)), or, after additional guides were welded on, to move out of alignment on the roller (Fig. 11(*b*)).

Because providing enough tension was difficult, the moving bottom roller was replaced with a stationary 4 in diameter PVC pipe. This allowed for the adsorbent net to easily slide over the pipe and be completely driven by the upper roller. Additionally, to prevent movement and tangling between the two sides of the net due to the strong currents, guides were added at four points along the length of the bottom support that separated the two sides of the net and ensured good alignment with the net as it exited the water and reached the upper roller.

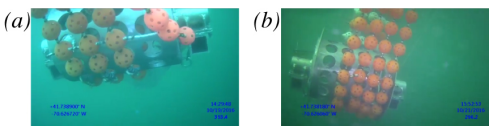

Fig. 11 Issues with the bottom roller that arose due to the inability to provide enough tension for prolonged periods of time. The adsorbent net was found to (*a*) slip off or (*b*) fall out of alignment with the roller.

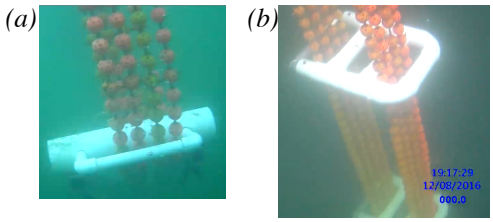

Fig. 12 Major modifications made to the continuous system consisted of a (*a*) stationary 4 in diameter PVC pipe to replace the moving bottom roller and (*b*) a series of PVC guides along the length of the bottom support to keep the net separated and prevent tangling and misalignment due to strong currents.

These complications and design modifications resulted in intermittent operation of the continuous system. In total, the continuous system was moving for approximately 37% of the total deployment with the longest three operations being 5.9 days, 5 days, and 4.7 days. Failures toward the end of the deployment were due to ice build up caused by the dropping temperatures off the coast of Massachusetts with the onset of winter.

Biofouling

As mentioned previously, biofouling of the adsorbent fibers can have a detrimental affect on their ability to uptake uranium (Part et al., 2016). One striking result between the two systems was the difference in biofouling. At the end of the 56-day ocean test, the stationary system had a significantly higher amount of biofouling on its shells than the continuously moving system (Fig. 13). Biofouling begins with a thin biofilm and microorganisms followed by the attachment of larger organisms. There may have been a few factors which limited the amount of initial biofilm the formed on the shells of the continuously moving system and hence inhibited larger growth.

The first factor is thought to be that the shells in the continuously moving system were periodically exposed to air. Every 85 seconds, for a period of 20 seconds, the net reached the upper roller, and was exposed to air. In comparison, the stationary net system was only exposed to air when adsorbent samples were taken, hence a total of nine times during the 56-day deployment for no more than 10 minutes at a time. This air exposure of the continuous system could have been enough to deter large amounts of growth from microorganisms and hence limited the amount of macrofouling that could have occurred.

Another cause for the marked reduction in biofouling of the continuous system could have been due to the rubbing of the shells against the PVC pipe on the bottom support or at various points of the separation guides. Given that the net was inherently buoyant, once it reached the stationary PVC pipe at the bottom of the system, the shells would rub up against the bottom of the pipe as they moved past. Additional rubbing was noted to occur on various points of the separation guides along the length

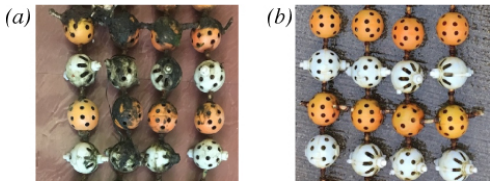

Fig. 13 Biofouling on the (*a*) stationary net and (*b*) continuously moving net at the end of the ocean test.

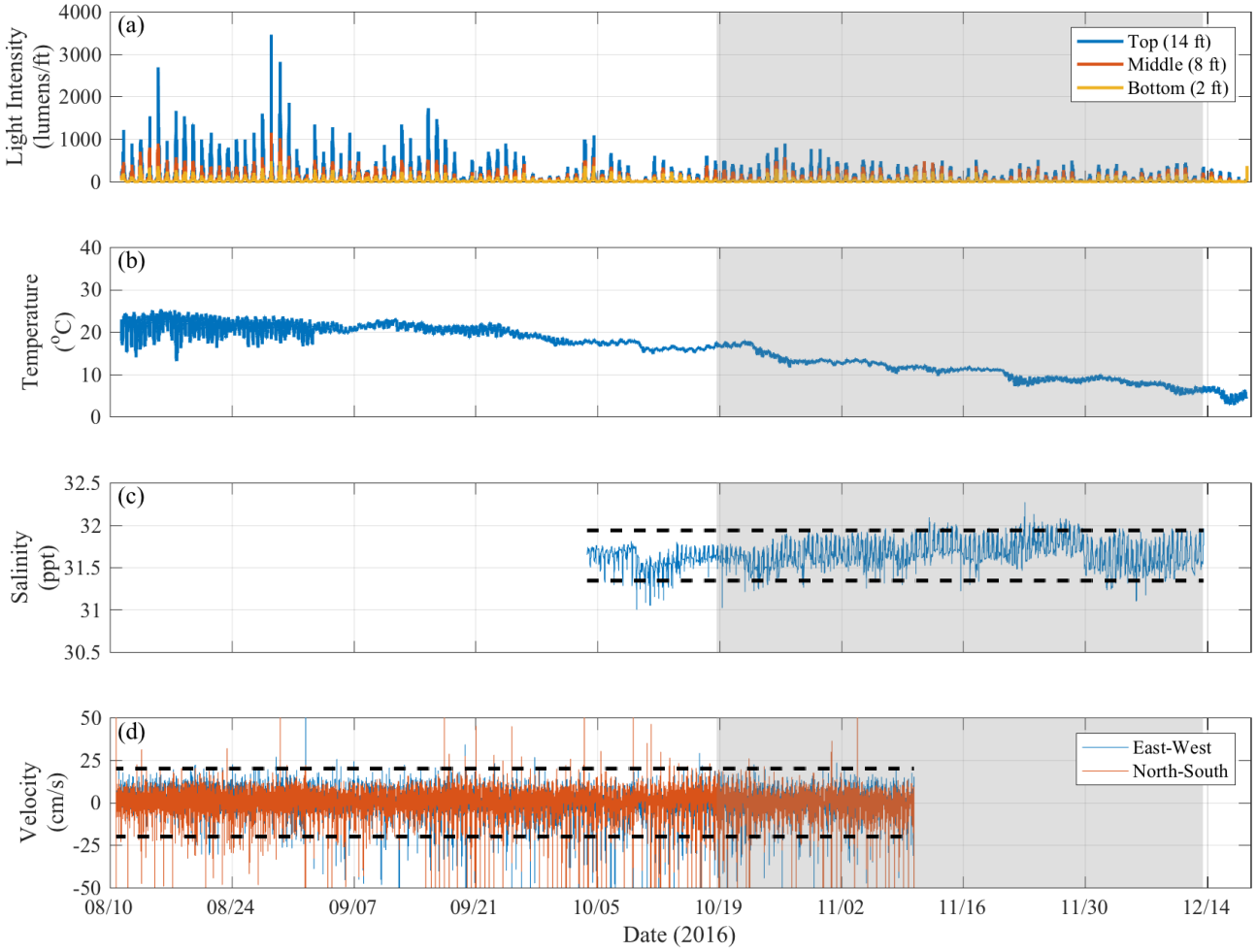

Fig. 14 (*a*) Light intensity as measured by the top, middle, and bottom light sensors. (*b*) Temperature as measured from the U24 conductivity logger. (*c*) Salinity as measured from the Xylem EXO-2 Sonde salinity meter where the dashed lines indicate $\pm 2\hat{\sigma}$ where $\hat{\sigma}$ is the robust standard deviation. (*d*) Current as measured from the bottom current meter with the dashed lines indicating ± 20 cm/s. The gray rectangle indicates the period of the ocean test.

of the bottom support. This rubbing could have inhibited biofouling and even removed any growth that had already accumulated on the shells.

If either of these factors caused a drastic reduction in biofouling, it lends credence to a few design ideas for mitigating biofouling in such a uranium harvester. Specifically, air exposure could be optimized to reduce the likelihood of microorganism grown, while maximizing the amount of water flow seen by the adsorbent. Secondly, a bristle brush could be added at various parts of the structure to gently brush the shells as they pass, further reducing chances of growth. Additionally, UV light has been shown to have strong antibacterial properties (Lakretz et al., 2010). Adding UV LEDs to a point in the adsorbent net's path could also prevent the formation of biofilm and hence reduce biofouling. Further analysis on the adsorbent fibers collected from the stationary and continuous system is required to determine if the reduction in biofouling on the shell exterior translated to a reduction in biofouling of the enclosed fibers.

Sensor data

The 56-day deployment of the prototype lasted from October 18, 2016 to December 13, 2016. With the exception of the failure of the Tidbit temperature sensor located with the shells of the stationary net, the premature battery failure of the current meters which stopped logging at approximately day 25 of the 56-day deployment, and an issue with the U24 meter's conductivity readings, data was collected from all sensors through the entirety of the experiment.

As expected, the light intensity dropped off exponentially with depth (Fig. 14(*a*)). Additionally, the exponential drop off is most pronounced in the beginning of September (with the largest variation in the light intensity between the upper and lower light sensors, a maximum difference of about 88%) and is least pronounced in December (with the smallest variation between the upper and lower light sensors, a difference of about 59%). This reduction in light attenuation was likely due to less plankton and biota in the water in the fall and winter than the summer.

Similarly, seasonal variations could also be seen in the temperature data as shown in Fig. 14(*b*) (note that the temperature measured by all instruments, those on the piling as well as those on the nets, were in excellent agreement, so only the data from the conductivity logger is shown). The short term temperature differences were linked to the tidal variations at the site, with these variations becoming less pronounced over time. However, from equation (3), it is clear that temperature has a major affect on the uranium uptake. For instance, at a temperature of

18°C, as seen close to the start of the 56-day deployment, by (3), the adsorbent capacity is estimated to be approximately 3.47 kg-U/t-ads after 56 days. On the other hand, at a temperature of 5°C, as seen close to the end of the 56-day deployment, the capacity is predicted to be decreased by 83% to approximately 0.60 kg-U/t-ads. The results of the adsorbent analysis will help determine how much of a role temperature affected the uranium uptake. Given that the incremental adsorption of uranium decreases overtime, it is hypothesized that the colder temperatures could have a minimal affect on the uptake since they occurred toward the end of the deployment.

In terms of salinity, as shown in Fig. 14(*c*), the salinity of the region also varied with tides. Overall, the salinity remained between 31 ppt and 33 ppt. There was no clear seasonal pattern in salinity variations. Measurement of the salinity will help determine the expected uranium concentration in the water at any given time as there is a well-defined relationship between ^{238}U concentration in seawater and salinity where the concentration of ^{238}U in $\left(\text{ng g}^{-1}\right)$ is explained by the equation

$$^{238}\text{U}(\pm 0.061) = 0.100 \times \text{S} - 0.326 \quad (4)$$

where S is the salinity. (Owens et al., 2011).

Unfortunately, due to premature battery failure of the current meters from an error in programming upon deployment, the current data does not span the entirety of the deployment. As can be seen from Fig. 14(*d*), depicting the currents measured from the instrument near the bottom of the piling (approximately 2 ft from the seafloor), while there were large short term variations in the currents (likely due to tides), overall there were little seasonal changes in the currents. In general, the currents were approximately 10-15 cm/s, with stronger periods of over 80 cm/s at times. Note that the current meters saturate at approximately +/- 80 cm/s and therefore readings beyond this are not reliable. At present, the adsorbents have only been tested in lab settings with flow rates up to 5.52 cm/s (Gill et al., 2015, Haji et al., 2017). The currents seen at this ocean site are much larger than those tested in a lab setting and it is unclear how the uranium uptake of an unprotected adsorbent might be affected in these conditions or in those of the truly open ocean. If the uranium adsorption appears to be hindered by the intense currents, the shell enclosures could further act to reduce the flow rate seen by the fibers within the shells. Previous research on wiffle balls has shown that there is up to 75% reduction in the fluid flow within the balls as compared to the free-stream flow (Rossmann and Rau, 2007).

CONCLUSIONS AND CONTINUED WORK

This paper discussed the design, fabrication, and deployment of two prototypes for the harvesting of uranium from seawater using fiber adsorbents. These prototypes were successfully tested in the ocean off the coast of Massachusetts in collaboration with Massachusetts Maritime Academy for a total of 56-days. Throughout the deployment, adsorbent fibers were sampled from the two different prototypes, and from two different shell designs on each prototype, as well as a nylon mesh bag as a control. Analysis of the fibers is still being conducted in collaboration with Pacific Northwest National Laboratory and these results will help answer the following questions:

1. By comparing the uranium uptake of the adsorbents in the nylon mesh bags and the shell enclosures, is the uranium uptake of the adsorbent greatly inhibited by the shells?
2. If so, which of the two shell designs inhibits the uranium uptake the least?
3. Does the movement of the adsorbent net in the continuous system create a significant difference in the amount of uranium adsorbed as compared to the stationary net?
4. Does the decreased biofouling of the shell enclosures on the continuous system translate to decreased biofouling of the fibers within them, as compared to the shells of the stationary system?

To help answer question (3), a novel method using the collection and measurement of radium extracted onto manganese oxide coated fibers is being developed to quantify the volume of water passing through the fibers. This method can be utilized to quantify the water flow through each of the different types of enclosures (i.e. the nylon mesh bag, the two shell designs on each of the two systems).

Finally, a detailed cost-analysis is being conducted to determine the total cost of uranium from a full-scale system using either the stationary or the continuous system. In the event that the shells in the continuously moving system see a significantly higher volume of water, a lower amount of biofouling, and an increased amount of uranium adsorbed, this cost-analysis will help determine if the additional cost of complexity due to the moving system is offset by the value earned from the additional uranium extracted. All of these results will inform the final design of a full-scale system.

ACKNOWLEDGMENTS

This work was supported by the U.S. Department of Energy Office of Nuclear Energy under Contracts No. DE-NE0008268 and DE-NE000731, and the National Academies Keck Futures Initiative. The salinity data from the Xylem EXO-2 Sonde was provided courtesy of the Buzzards Bay Coalition monitoring that is funded by a grant from the EPA.

This material is based upon work supported by the National Science Foundation Graduate Research Fellowship under Grant No. 1122374. Any opinion, findings, and conclusions or recommendations expressed in this material are those of the authors and do not necessarily reflect the views of the National Science Foundation.

Thanks to Oak Ridge National Laboratory for the preparation of the adsorbent fibers for use in this study and to G. Gill and other researchers at the Pacific Northwest National Laboratory for the analysis of the fibers post-deployment.

The authors would also like to thank the staff and students of Massachusetts Maritime Academy for all their help and assistance during this prolonged test. Specifically, Tom Pham, Prof. Bill Hubbard, Bill Klimm, Thomas McEntee, Thanh Nguyen, Judson Poole, James Wall, Matthew Simms, and Jimmy Benedetto, John Edwards and Walter Yohai played an integral role in ensuring the success of this study.

REFERENCES

Anirudhan, T S, Tharun, A R, Rijith, S and Suchithra, P S (2011). "Synthesis and characterization of a novel graft copolymer containing carboxyl groups and its application to extract uranium (VI) from aqueous media,"*J. Appl. Polymer Sci.*, 122(2), 874-884.

Byers, M F, and Schneider, E (2015). "Optimization of the Passive Recovery of Uranium from Seawater, "Master's thesis.

Byers, M, Haji, M N, Schneider, E A, and Slocum, A H (2016). "A Higher Fidelity Cost Analysis of Wind and Uranium from Seawater

Acquisition SymBiotic Infrastructure,"*In Proc. of the 2016 ANS Winter Meeting and Nucl. Tech. Expo*, Las Vegas, NV.

Davies, R V, Kennedy, J, McIroy, R W, Spence, R, and Hill, K M (1964). "Extraction of Uranium From Sea Water,"*Nature*, 203(495), 1110-1115.

Emsley, J (2001). *Natures Building Blocks: An A to Z Guide to the Elements*, Oxford Univ. Press.

Gill, G A, Kuo, L, Strivens, J, Wood, J, Schlafer, N J, Northwest, P, Tsouris, C, Ladshaw, A, and Yiacoumi, S (2015). "Investigations into the Effect of Current Velocity on Amidoxime-Based Polymeric Uranium Adsorbent Performance,"*Milestone Report*.

Gill, G A, Kuo, L-J, Janke, C J, Park, J, Jeters, et al. (2016). "The Uranium from Seawater Program at the Pacific Northwest National Laboratory: Overview of Marine Testing, Adsorbent Characterization, Adsorbent Durability, Adsorbent Toxicity, and Deployment Studies,"*Ind. & Eng. Chem. Res.*.

Haji, M N, Vitry, C, and Slocum, A H (2015). "Decoupling the functional requirements of an adsorbent for harvesting uranium from seawater through the use of shell enclosure,"*In Proc. of the 2015 ANS Winter Meeting and Nucl. Tech. Expo*, Washington, DC.

Haji, M N and Slocum, A H (2016) "Design of a Symbiotic Device to Harvest Uranium from Seawater through the use of Shell Enclosures,"*In Proc. of the 2016 ANS Winter Meeting and Nucl. Tech. Expo*, Las Vegas, NV.

Haji, M N, Delmy, C, Gonzalez, J, and Slocum, A H (2016) "Uranium extraction from seawater using adsorbent shell enclosures via a symbiotic offshore wind turbine device, "*In Proc. of the Twenty-sixth (2016) Int. Ocean and Polar Eng. Conf.*,Rhodes, Greece.

Haji, M N, Gonzalez, J, Drysdale, J, Buesseler, K, and Slocum, A H (2017) "The effects of protective shell enclosures on uranium adsorbing polymers, "*in prep.*

Jonkman, J (2010). "Definition of the Floating System for Phase IV of OC3,"*Tech. Rep.*, NREL/TP-500-47535.

Kanno, M (1984). "Present status of study on extraction of uranium from sea water,"*J. Nucl. Sci. Technol.*, 21(1), 1-9.

Kim, J, Tsouris, C, Mayes, R T, Oyola, Y, Saito, T, Janke, C J, Dai, S, Schneider, E, and Sachde, D (2013). "Recovery of Uranium from Seawater: A Review of Current Status and Future Research Needs,"*Sep. Sci. Technol.*, 48(3), 367-387.

Kim, J, Tsouris, C, Oyola, Y, Janke, C J, Mayes, R T, Dai, S, Gill, G, Kuo, L-J, Wood, J, Choe, K-Y, Schneider, E, and Lindner, H (2014). "Uptake of Uranium from Seawater by Amidoxime-Based Polymeric Adsorbent: Field Experiments, Modeling, and Updated Economic Assessment,"*Ind. & Eng. Chem. Res.*, 53, 6076-6083.

Lakretz, A, Ron E Z, and Mamane H (2010). "Biofouling control in water by various UVC wavelengths and doses,"*Biofouling*, 26(3), 257–267.

OECD Nuclear Energy Agency (2014). "Uranium 2014: Resources, Production and Demand,"*Technical report*, OECD Nuclear Energy Agency and the International Atomic Energy Agency.

Oguma, K, Suzuki, T, and Saito, K (2011). "Determination of uranium in seawater by flow-injection preconcentration on dodecylamidoxime-impregnated resin and spectrophotometric detection,"*Talanta*, 84(5), 1209-1214.

Owens, S A, Buesseler, K O, and Sims, K W W (2011). "Re-evaluating the ^{238}U-salinity relationship in seawater: Implications for the ^{238}U-Th- 234 disequilibrium method, "*Mar. Chem.*, 127 (14), 31-39.

Park, J, Gill, G A, Strivens, J E, Kuo, L-J, Jeters, R, Avila, A, Wood, J, Schlafer, N J, Janke, Chris J, Miller, E A, Thomas, M, Addleman, R S, and Bonheyo, G T (2016). "Effect of biofouling on the performance of amidoxime-based polymeric uranium adsorbents, "*Ind. & Eng. Chem. Res.*, 55(15), 55 (15), 4328-4338.

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

Rossmann, J, and Rau, A (2007). "An experimental study of Wiffle ball aerodynamics, "*American Journal of Physics*, 75(12), 1099.

Schneider, E, and Gill, G (2014). "Characterization and Deployment Studies and Cost Analysis of Seawater Uranium Recovered by a Polymeric Adsorbent System,"*Presented at the Intl Symposium on Uranium Material for the Nuclear Fuel Cycle: Exploration, Mining, Production, Supply and Demand, Economics and Environmental Issues*, Vienna.

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

Sekiguchi, K, Saito, K, Konishi, S, Furusaki, S, Sugo, T, and Nobukawa, H (1994). "Effect of seawater temperature on uranium recovery from seawater using amidoxime adsorbents,"*Ind. & Eng. Chem. Res.*, 33(3), 662666.

Seko, N, Katakai, A, Hasegawa, S, Tamada, M, Kasai, N, Takeda, H, Sugo, T, and Saito, K (2003). "Aquaculture of uranium in seawater by a fabric-adsorbent submerged system,"*Nucl. Technol.*, 144(2), 274-278.

Seko, N, Katakai, A, Tamada, M and Takanobu, S (2004). "Fine Fibrous Amidoxime Adsorbent Synthesized by Grafting and Uranium AdsorptionElution Cyclic Test with Seawater,"*Sep. Sci. Technol.*, 39(16), 3753-3767.

Sugo, T, Tamada, M, Seguchi, T, Shimizu, T, Uotani, M, and Kashima, R (2001). "Recovery System for Uranium from Seawater with Fibrous Adsorbent and Its Preliminary Cost Estimation,". *J. At. Energy Soc. Jpn.*, 43(10), 1010-1016.

Tamada, M (2009). "Current status of technology for collection of uranium from seawater,"*Japan Atomic Energy Agency*.

Tamada, M, Seko, N, Kasai, N, and Shimizu, T (2006). "Cost estimation of uranium recovery from seawater with system of braid type adsorbent,"*Trans. At. Energy Soc. Jpn.*, 5(4), 358-363.

Tularam, G A, and Ilahee, M (2007). "Environmental concerns of desalinating seawater using reverse osmosis,"*J. Env. Monitoring*, 9(8), 805-813.

Union of Concerned Scientists (2011). "Fact Sheet - Nuclear Power and Water: Quick Facts on Nuclear Power Generation and Water Use,"*Technical report*.

van Reis, R and Zydney, A (2007). "Bioprocess membrane technology,"*J. Membr. Sci.*, Vol 297, No 1-2, pp 16-50.

Zhang, A, Asakura, T, and Uchiyama, G (2003). "The adsorption mechanism of uranium (VI) from seawater on a macroporous fibrous polymeric adsorbent containing amidoxime chelating functional group,"*React. Funct. Polym.*, 57(1), 67–76.