

Design of a Symbiotic Device to Harvest Uranium from Seawater through the use of Shell Enclosures

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INTRODUCTION

At the current consumption rate, the global conventional reserves of uranium, 7.6 million tonnes, could be depleted in a little over a century [1]. As reserves decrease, future uranium is expected to come from lower quality sites, resulting in higher extraction costs and even greater environmental impact. Fortunately, uranium is present in the ocean as uranyl ions at low concentrations of 3 ppb [2], which, over the total volume of the oceans, amounts to approximately 4.5 billion tonnes of uranium, nearly a thousand times that of conventional reserves [3].

Methods to extract uranium from seawater have been studied since the early 1960s, when, at a time when uranium production was uncertain, post-World War II Britain desired a secure uranium supply [4]. A recent review of uranium recovery technologies by [5] found that uranium adsorbent by chelating polymers was the most promising in terms of adsorbent capacity, environmental footprint, and cost [6, 7, 8].

In this technology, chelating polymers are deployed in seawater and remain submerged until the amount of captured uranium approaches the adsorption capacity. Then, an elution bath is used to strip metal ions, such as uranium, off the adsorbent polymer. A polymer may be immersed in a number of elution baths before it is regenerated by an alkali wash to free its functional groups, allowing for the reuse of the polymer. The output from the elution process undergoes purification and precipitation typical for mined uranium to produce yellowcake.

Offshore systems for the extraction of uranium from seawater have been developed since the early 2000s. In these systems, the adsorbent is deployed and moored for extended periods of time, brought back to shore for the elution process, and redeployed afterward. The first system, developed by [7], used non-woven adsorbents that were immersed for 30 days in seawater. Due to the low mechanical strength of these fibers, they had to be incorporated into stacks composed of spacer nets and holders placed on large, heavy, floating frames, which resulted in a design that was too costly for implementation.

More recently, buoyant braided adsorbents have been studied as a way to decrease the weight and cost of the system. In these systems, continuous polyethylene fibers are braided around a porous polypropylene float that can be made into long lengths [9]. However, because this deployment scheme requires the adsorbent be brought back to shore for the elution process and redeployed afterward, this stand-alone, intermittent operation system has significant practical and economic deployment challenges [7] and to date none of these systems have become economically viable.

Detailed economic analysis by [10] found that a major cost driver of seawater uranium extraction is the mooring and recovery of the adsorbent. Based on these results, [11] first

developed the development of a system that is attached to an offshore wind turbine and continuously takes the adsorbent from the ocean through an elution process and then returns it to the ocean. More recent designs by [12] further build upon this idea. The integration of the design of a uranium harvesting system into an offshore wind turbine tower is pursued because the development of offshore wind or uranium harvesting by themselves bears a high capital cost for the structures, but if the mooring function can be shared, the overall cost for each will be lower. Furthermore, initial design analysis and prototyping of these symbiotic systems has proven they are technical feasible [11] and [12].

FUNCTIONAL REQUIREMENTS

The functional requirements of a symbiotic device to harvest uranium from seawater are:

1. Use the amidoxime polyethylene braid adsorbent developed by Oak Ridge National Laboratory known as AF1 [13].
2. Recover 1.2 tonnes of uranium from seawater annually, enough to power a 5-MW nuclear power plant for one year.
3. Bring the cost of uranium extraction from seawater as close as possible to terrestrial uranium mining.

The uranium uptake for this system 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

$$y = \frac{\beta_{max}t}{K_D + t} \quad (1)$$

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 [14]. Further analysis on the adsorbent behavior, recovery rate, and degradation as described by [12], reveals that to achieve functional requirement (2), the sorption process can be optimized on the device using approximately 45 tonnes of adsorbent that is submerged in seawater for 23 days and cycled 15 times.

ELUTION AND REGENERATION

Unlike previous designs developed by [11] and [12], which utilize on-site continuous acidic elution and bicarbonate regeneration processes, this design employs a single, 24-hour bicarbonate elution as described by [15]. Recent work has shown that the acidic elution process leads to degradation of the adsorbent with subsequent reuse, which may be mitigated

or removed altogether by the replacement of a potassium bicarbonate solution [15]. Additionally, the adsorbent no longer needs to be regenerated with alkaline solution since a basic solution has replaced the previously used acids. The elimination of this step provides a significant cost savings through the reduction of chemical consumptions [16].

MOORING AND RECOVERY

Uranium-adsorbing materials with the optimal chemical properties for high adsorbent capacity, in general, have inherently low tensile strength and durability [17]. Hence, the designs previously studied by [11], which require the adsorbent into a belt held in tension, are likely not feasible with the AF1 adsorbent as it will probably not possess the durability and tensile strength required. The design presented here follows those described by [12] which utilize a two-part system to decouple the mechanical and chemical needs of an adsorbent for seawater harvesting of uranium. In these designs and the system presented here, the uranium adsorbent material with high adsorbent capacity is enclosed in a hard permeable outer shell with sufficient mechanical strength and durability for use in an offshore environment and chemical resilience against elution treatments [18]. Fig. 1 depicts one shell design in which a spherical hard permeable outer shell encloses uranium adsorbent material inside.

SYMBIOTIC MACHINE FOR OCEAN URANIUM EXTRACTION

The design presented in this paper utilizes adsorbent shells that are incrementally spaced along high strength mooring rope, resembling conventional ball-chain belts, similar to those in the designs by [12].

Design analysis and prototype testing by [12] found that devices which used multiple subsystems for uranium harvester, allowed for a higher device uptime because should any complications arise at sea, it is highly unlikely that all subsystems would be affected. However, because the cost of such a device is closely related to the material required, the considerable number of large gears to move the ball-chain enclosures suggested that the designs investigated by [12] were likely to be extremely costly to fabricate, deploy, and maintain.

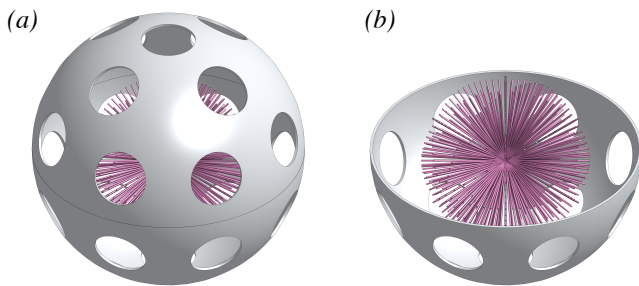


Fig. 1. Initial adsorbent concept with decoupling of mechanical and chemical requirements. Soft, inner adsorbent sphere is encased in tough, outer protective sphere. Outer sphere features holes to allow adequate seawater to adsorbent interior.

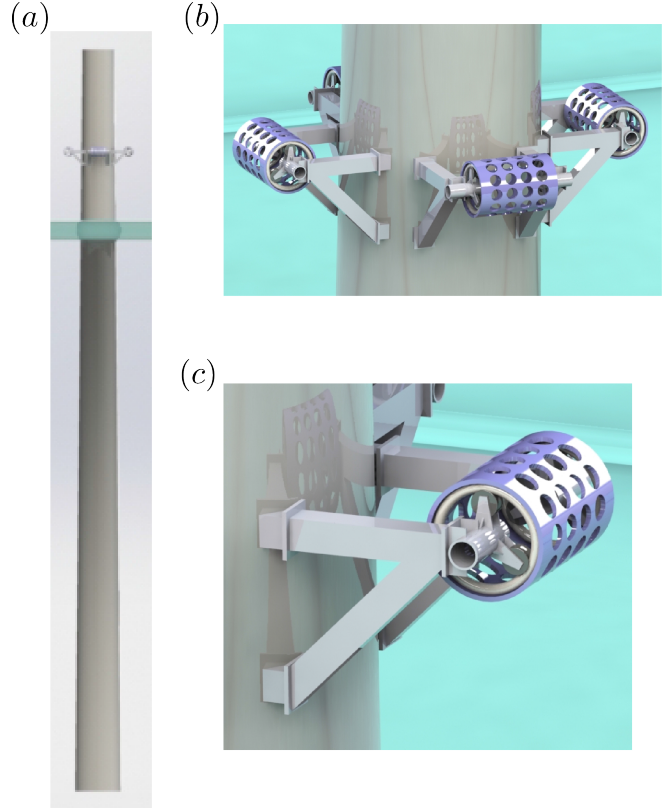


Fig. 2. Three-dimensional 1/10th physical scale model of SMORE. The full model on a 1/10th scale turbine spar is shown in (a), whereas (b) shows a close-up of the upper platform, and (c) is a close up of one of the roller (shown in purple) subsystems. In the 1/10th physical scale model, the roller only engages four shells along its width, while in the full scale model it was sized to engage ten.

This design presented in this paper builds upon the work by [12] which is modularized yet uses few components. In this design, known as the Symbiotic Machine for Ocean uRanium Extraction (SMORE), large rollers are used to move multiple ball-chain lengths at once. Each roller is sized to fit 12 shell enclosures around its circumference and the number of rollers per device is determined by the overall adsorbent required. By functional requirement (2), the device must be sized for approximately 45 tonnes of adsorbent. It is found that this can feasibly be done with a shell diameter, d_s of 0.25m, and a total number of shells, $N_{st} = 15,715$ using the analysis detailed in [18]. Furthermore, the spacing between shells, L_s is taken to be 0.05m. Fig. 2 shows a three-dimensional sketch of a 1/10th physical scale model of this design.

The full-scale system design was formulated for use with the 5-MW OC3-Hywind offshore wind turbine which has a total draft of $D_{system} = 120\text{m}$, an upper spar diameter of $d_{upper} = 6.4\text{m}$ and a lower spar diameter of $d_{lower} = 9.4\text{m}$ [19]. Designing the device so that there are four roller subsystems requires that each roller be designed to hold ten ball-chain lengths. With a spacing between each ball-chain of 0.05m, this requires a roller length of at least $L_{roller} = 3\text{m}$. The roller

diameter is determined by

$$d_{roller} = \frac{\sqrt{d_s^2 + L_s^2 - 2d_s L_s \cos(\alpha)}}{2 \sin\left(\frac{\pi}{2N_{roller}}\right)}, \quad (2)$$

where d_s is the shell diameter, L_s is the spacing between shells on the same ball-chain length, α is the angle of the equivalent regular polygon inscribed by the irregular polygon created by forming the midpoints of the shells and spaces that make up the circumference of the roller, and N_{roller} is the number of shells engaged by half of the roller, taken to be six in this design (so that the roller has places for 12 shells total around its circumference). By geometry, the angle α is given by

$$\alpha = \pi \left(1 - \frac{1}{2N_{roller}}\right). \quad (3)$$

Equations (2) and (3) result in a roller outer diameter of approximately $d_{roller} = 1.2\text{m}$ and length of at least $L_{roller} = 8.2\text{m}$. These rollers can be manufactured out of steel pipe, sized to be at least 0.05m thick.

To determine the platform length, a spacing of $L_{sp,roller} = 2\text{m}$ between rollers is assumed. With this in mind, the total platform length required in order to fit all the rollers around the turbine (such that when viewed from above the turbine is circumscribed by a polygon made up of the rollers and spaces between them) is given by

$$L_{pt} = \frac{N_{roller}(L_{roller} + L_{sp,roller})}{2\pi} - r_{upper} \quad (4)$$

where N_{roller} is the number of rollers (four for this design), L_{roller} is the length of the roller, $L_{sp,roller}$ is the spacing between rollers, and r_{upper} is the radius of the turbine at the top ($r_{upper} = \frac{d_{upper}}{2}$). Equation (4) yields a platform that must be at least $L_{platform} = 0.2\text{m}$ long, from the edge of the turbine. Furthermore, to ensure that the rollers are out of water and not impacted by slamming loads due to waves, the platform would be raised approximately $H_{platform} = 10\text{m}$ above the sea surface. Further analysis for a real ocean implementation would require that this height be adjusted according to the wave climate of the region of deployment.

Given that the bicarbonate elution process requires 24 hours of polymer immersion time, the rollers on SMORE would act mostly as anchors for the ball-chain lengths hanging off the system. The rollers would be motorized so that after a campaign length (taken to be 23 days for this design), the ball-chain lengths could be pulled up and deposited into a chemical tank beneath the rollers. This tank would then be filled with the solution required for elution of the adsorbent polymer. After 24 hours, the rollers would be powered in the opposite direction to redeploy the uranium adsorbent. Because there are multiple subsystems, there could be one chemical tank per subsystem or there could be one chemical tank that travels on a track around the circumference of the turbine to each of the subsystems. Further design analysis is required to determine the details of each of these tank systems.

As described previously, each roller would be motorized in order to wind and unwind the ball-chain lengths. This is accomplished using grooved wheels on a circular track welded

to the interior of the roller on either end. The number of grooved wheels required is determined by using the maximum pressure of the contact for an ellipsoid Hertz contact between the wheels and the groove, given by

$$P_{max} = \frac{3F_c}{2\pi cd}, \quad (5)$$

where F_c is the contact force between each wheel and the rail (taken to be half the force on the roller divided by the number of wheels) and c and d are the major and minor contact area elliptical semi-axes, respectively. The semi-axes are a function of the geometry and material of the wheel and rail, and the angle between the planes of principal curvature of the two bodies. Their definitions can be found in [20].

In order for the design to be feasible, two criteria must be met with respect to the wheels:

$$p_{max} \leq 1.5\sigma_{ult} \quad (6)$$

and

$$\gamma > 20^\circ \quad (7)$$

where σ_{ult} is the ultimate tensile strength of the grooved wheel and γ is the contact angle in degrees between the groove and the rail, found by

$$\gamma = \tan\left(\frac{r_{groove}}{b}\right)^{-1}. \quad (8)$$

where r_{groove} is the radius of the groove on the wheel. Analysis using equations (5)-(8) suggests that three polyurethane wheels of approximately 0.25m diameter with a groove diameter of approximately 0.2m on a 0.15m diameter steel track would bent into a circle of 1.15m in diameter would suffice. Furthermore, a 0.15m diameter pipe may be bent into a minimum of a four times its diameter, or a 0.6m diameter circle [21], therefore bending it to fit inside the 1.15m inner diameter of the roller is feasible. To support the weight of the roller and the ball-chain lengths, each subsystem would be supported by circular steel tubing of appropriate diameter and thickness with a 45° angle cross-brace.

In order to move the rollers, one of the polyurethane wheels would be oriented completely vertically, such as to take the total load of half of the roller, and actuated using a motor. The torque provided by the friction between the wheel and the rail is found by

$$\tau_{fr} = \mu F_N \left(\frac{d_{roller}}{2} - d_{rail}\right) \quad (9)$$

where μ is the coefficient of friction between the polyurethane groove and the steel rail (taken to be $\mu = 0.2$) and F_N is half the total force on the roller due to the shells and its mass. Analysis of this friction force indicates that the friction is sufficient enough to provide the total torque needed to move the rollers.

CONCLUSIONS

This paper detailed the design and analysis of a symbiotic system to harvest uranium from seawater. Building upon lessons learned regarding the adsorbent strength [18] as well

as the results of previous designs and testing of 1/50th scale systems [12], the Symbiotic Machine for Ocean Uranium Extraction (SMORE) utilizes a modularized design with minimal material. It is hypothesized that the limited material used will translate into low manufacturing, deployment, and operational costs. Detailed cost-analysis of SMORE is underway and will be the topic of a future publication.

At present, this design is being developed into a 1/10th scale prototype for testing in an ocean environment. The results of this fabrication will inform the feasibility of manufacturing such a system on a large scale, while the ocean testing will provide valuable experience which will inform further improvements to the design to make it less susceptible to failure in a marine environment. In tandem, failure mode effect analysis and wave loading analysis are being conducted on the structure. Finally, the stationary and motorized chemical tank systems are currently being designed and built for bench testing, the results of which will be the topic of a future publication.

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REFERENCES

1. OECD NUCLEAR ENERGY AGENCY, "Uranium 2014: Resources, Production and Demand," Tech. rep., OECD Nuclear Energy Agency and the International Atomic Energy Agency (2014).
2. K. OGUMA, T. SUZUKI, and K. SAITO, "Determination of uranium in seawater by flow-injection preconcentration on dodecylamidoxime-impregnated resin and spectrophotometric detection," *Talanta*, **84**, 5, 1209–1214 (2011).
3. M. TAMADA, "Current status of technology for collection of uranium from seawater," *Japan Atomic Energy Agency* (2009).
4. R. V. DAVIES, J. KENNEDY, R. W. MCIROY, R. SPENCE, and K. M. HILL, "Extraction of Uranium From Sea Water," *Nature*, **203**, 495, 1110–1115 (1964).
5. J. KIM, C. TSOURIS, R. T. MAYES, Y. OYOLA, T. SAITO, C. J. JANKE, S. DAI, E. SCHNEIDER, and D. SACHDE, "Recovery of Uranium from Seawater: A Review of Current Status and Future Research Needs," *Sep. Sci. Technol.*, **48**, 367–387 (2013).
6. A. ZHANG, T. ASAKURA, and G. UCHIYAMA, "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 (2003).
7. N. SEKO, A. KATAKAI, S. HASEGAWA, M. TAMADA, N. KASAI, H. TAKEDA, T. SUGO, and K. SAITO, "Aquaculture of uranium in seawater by a fabric-adsorbent submerged system," *Nucl. Technol.*, **144**, 2, 274–278 (2003).
8. T. S. ANIRUDHAN, A. R. THARUN, S. RIJITH, and P. S. SUCHITHRA, "Synthesis and characterization of a novel graft copolymer containing carboxyl groups and its application to extract uranium (VI) from aqueous media," *J. Appl. Polym. Sci.*, **122**, 2, 874–884 (2011).
9. M. TAMADA, N. SEKO, N. KASAI, and T. SHIMIZU, "Cost estimation of uranium recovery from seawater with system of braid type adsorbent," *Trans. At. Energy Soc. Jpn.*, **5**, 4, 358–363 (2006).
10. E. SCHNEIDER and D. SACHDE, "The Cost of Recovering Uranium from Seawater by a Braided Polymer Adsorbent System," *Sci. Glob. Sec.*, **21**, 2, 134–163 (2013).
11. 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 (2014).
12. M. N. 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 26th International Ocean and Polar Engineering Conference* (2016).
13. G. A. GILL, L.-J. KUO, C. J. JANKE, J. PARK, R. T. JETERS, G. T. BONHEYO, H.-B. PAN, C. WAI, T. KHANGAONKAR, L. BIANUCCI, J. R. WOOD, M. G. WARNER, S. PETERSON, D. G. ABRECHT, R. T. MAYES, C. C. TSOURIS, Y. OYOLA, J. E. STRIVENS, N. J. SCHLAFER, R. S. ADDLEMAN, W. CHOUYYOK, S. DAS, J. KIM, K. BUESSELER, C. BREIER, and E. D'ALESSANDRO, "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.*, **15** (2016).
14. E. SCHNEIDER and G. GILL, "Characterization and Deployment Studies and Cost Analysis of Seawater Uranium Recovered by a Polymeric Adsorbent System," in "Proceedings of International Symposium on Uranium Raw Material for the Nuclear Fuel Cycle," (2014).
15. L. W. W. C. M. O. Y. J. C. J. T. G. PAN, H-B and L. RAO, "SI: Carbonate-H₂CO₃ leaching for sequestering uranium from seawater." *Dalton transactions*, **43**, 28, 10713–8 (2014).
16. M. BYERS, *Optimization of the Passive Recovery of Uranium from Seawater*, Master's thesis, The University of Texas at Austin (2015).
17. R. MAYES, personal communication (2014).
18. M. N. HAJI, C. VITRY, and A. H. SLOCUM, "Decoupling the functional requirements of an adsorbent for harvesting uranium from seawater through the use of shell enclosure," *Proc. of the 2015 ANS Winter Meeting and Nucl. Tech. Expo* (2015).
19. J. JONKMAN, "Definition of the Floating System for Phase IV of OC3," Tech. rep., U.S. Department of Energy (May 2010).
20. A. H. SLOCUM, *FUNdaMENTALS of Design* (2008).
21. H AND H TOOLING, "Basic Tube Bending Guide," .