Decoupling the Functional Requirements of an Adsorbent for Harvesting Uranium from Seawater through the use of Shell Enclosures

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INTRODUCTION

Uranium is present in the world's oceans as dissolved ions at a uniform concentration of approximately 3.2 ppb [1], which, over the total volume of the oceans, amounts to approximately 4.5 billion metric tons, about 1000 times more than exists in conventional terrestrial uranium reserves [2]. Extraction of uranium from seawater has been researched since the 1960s when, after World War II, Britain desired a secure uranium supply at a time when the production of uranium was uncertain [3]. Of all present uranium recovery technologies, uranium adsorption by chelating polymers has been found to be the most promising in terms of cost, adsorption capacity, and environmental footprint [4, 5, 6, 7].

Chelating polymers are first deployed in seawater and remain submerged until the amount of captured uranium approaches the adsorption capacity. Afterward, the adsorbent polymer is immersed in an elution bath to strip off the uranium and other elements that have bonded to the polymer. The polymer may undergo a number of elution cycles before being regenerated by an alkali wash so that its functional groups are freed and the adsorbent can be reused. The output from the elution process undergoes purification and precipitation typical for mined uranium to produce yellowcake.

Since the early 2000s, offshore systems have been developed in which 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 deployed utilized non-woven adsorbents with uranium adsorption capacities of about 1.5 g-U/kg-adsorbent after 30 days immersion in seawater [6]. However, due to their low mechanical strength, these non-woven adsorbent fibers had to be incorporated into large "sandwich stacks" composed of spacer nets and stack holders placed on large, heavy, floating frames. This eventually proved too costly for implementation and furthermore, the sandwich stacks containing the non-woven adsorbent prevented good accessibility to the seawater, resulting in low adsorption capacities.

To decrease the weight and cost of the system, buoyant braided adsorbents have also been studied. These are composed of continuous polyethylene fibers that are braided around a porous polypropylene float that can be made into long lengths [8]. While these braided adsorbents have high mechanical strength, durability, chemical resistance, and low cost, their uranium adsorption capacity is low, at 1.5 g-U/kg-adsorbent after 30 days of immersion in seawater. This adsorbent capacity is too low to be cost effective for implementation. In general, uranium-adsorbing materials with the optimal chemical properties for high adsorbent capacity have inherently low tensile strength and durability [9].

THEORY

This paper details a method for overcoming the limitation of mechanical strength and adsorbent capacity for the harvesting of uranium from seawater. A hard permeable outer structural shell housing the inner adsorbent material allows for the decoupling of the mechanical and chemical requirements of an offshore uranium harvesting system. The chemistry of the inner material can thus be optimized for higher adsorbent capacities, while the mechanical properties required of the system are achieved by the hard permeable outer structural shell, resulting in a system that is more cost effective for implementation.

A two-part system is developed to decouple the mechanical and chemical needs of an adsorbent for seawater harvesting of uranium. In the system, a hard permeable outer shell with sufficient mechanical strength and durability for use in an offshore environment and chemical resilience against elution treatments serves as the protective element for uranium adsorbent material with high adsorbent capacity in its interior. Figure 1 depicts one shell design in which a spherical hard permeable outer shell encloses uranium adsorbing material inside. The uranium adsorbing material is wound into a ball with filaments extending radially outward from the center core (referred to as the filament ball for the remainder of this paper). The holes in the outer shell are sized so that seawater may continually pass relatively easily to the interior of the shell where the uranium adsorbing material is housed, while maintaining sufficient mechanical strength to withstand the forces of the offshore system that must move the units through the water and collect and disperse them. The outer shell is preferably made of plastic, such as polyethylene, so that it can have high chemical resilience and therefore can withstand multiple elution cycles as required by the offshore seawater uranium

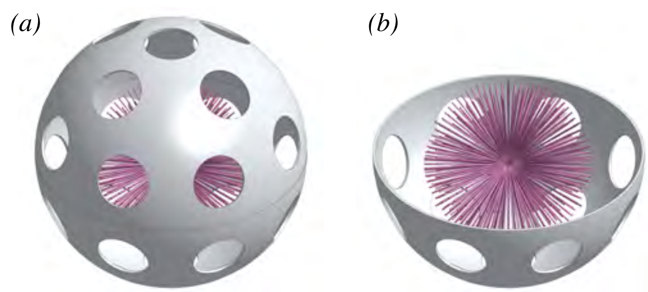

Fig. 1. Initial adsorbent concept with decoupling of mechanical and chemical requirements. Soft, inner adsorbent sphere is encased in tough, outer protective sphere. Outer sphere features holes to allow adequate seawater to adsorbent interior.

harvesting system. By making the outer shell out of two distinct upper and lower hemispheres, it can be disassembled and reassembled for the easily placement and replacement of the inner uranium adsorbing material and can be reused many times for multiple changes of adsorbents.

RESULTS

Adsorbent Interior

The feasibility of the uranium adsorbent material to be wound into filament ball is detailed in Figure 2. Lines 1-12 determine the amount of adsorbent required by the system, lines 13-17 calculate the adsorbent required per ball, lines 18-26 compute the limit of how much adsorbent can be incorporated in each ball, and line 27 indicates the feasibility of the overall design. Red boxes indicate design requirements of the offshore harvesting system, yellow boxes indicate adsorbent specific values, and green boxes indicate tunable parameters of the mechanical system. The offshore uranium harvesting system is designed with the requirement of harvesting enough uranium to power a 5-MW nuclear reactor annually, approximately 1.2 metric tons.

For this study, the reference adsorbent was taken to be the AF1 braid adsorbent manufactured by Oak Ridge National Laboratory [10]. Using a one-site ligand-saturation model, the uranium uptake, y, after a certain exposure time in days, t, is given by

Line #	Offshore uranium harvesting system adsorbent requirement	
1	uranium per year for 5 MW reactor (metric tons)	1.2
2	exposure time (days)	60
3	half-saturation time, Kd (days)	21.00
4	saturation capacity, adsorbent Beta_max (kg-U/t-fresh ads)	5.30
5	capacity of adsorbent with 250% grafting (kg U/t-ads)	3.93
6	capacity of adsorbent after initial alkaline conditioning (kg U/t-ads)	3.53
7	degradation per elution cycle (%)	5
8	number of elution cycles before replacement	15
9	overall uranium adsorbed (g-U/kg-ads)	37.93
10	amount of adsorbent required (kg)	31639
11	length of system (m)	4000
12	adsorbent kg/m	7.91
	Adsorbent required per ball	
13	density (kg/m^3)	1000
14	adsorbent fiber diameter (mm)	1
15	diameter of a outer shell (mm)	500
16	absorbent per ball (kg)	3.95
17	required length of fiber in ball (m)	5036
	Adsorbent limit per ball	
18	filament ball core diameter to outer shell diameter (%)	50
19	surface area of filament ball core (mm^2)	196350
20	distance between filament ball core and outer shell (mm)	250
21	distance between filament ball outer diameter and outer shell (mm)	25
22	cross sectional area of adsorbent fiber (mm^2)	0.79
23	packing density (%)	70
24	effective area required per fiber base for attachment (mm^2)	1.12
25	number of adsorbent fibers	175000
26	total length of adsorbent fibers (m)	39375
27	**feasible design?**	**YES**

Fig. 2. Feasibility calculations for adsorbent filament ball.

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

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 [11]. Line 2 is the exposure time, the number of days the adsorbent is submerged in seawater before being stripped of its uranium by an elution bath. After each elution bath, the adsorbent will be degraded by some percentage, shown here in line 7. Line 8 is the number of elution cycles the adsorbent undergoes before replacement. Lines 2 and 8 are mechanical design parameters of the system. From the combination of these chemical and mechanical parameters, line 9 calculates the overall uranium adsorbed by the system per kg adsorbent. In conjunction with line 1, the value from line 9 can be used to calculate the amount of adsorbent required per year in kg, detailed in Line 10. Line 11 is the total length of the system in m, another mechanical design parameter. Lines 10 and 11 can then be used to determine the amount of adsorbent required per m of the system.

Next in Figure 2, line 13 details the adsorbent density in kg/m^3, a property of the adsorbent material. Lines 14 and 15 set the adsorbent fiber diameter in mm and the full diameter of the hard permeable outer shell in mm respectively. These values can be used to determine the adsorbent per ball in kg line 16, and the required length of adsorbent fiber in m that must be inside each hard permeable shell, line 17. Line 18 details the ratio of the filament ball core diameter to which the adsorbent fibers are attached, to the hard permeable outer shell in percent and from this line 19 computes the total surface area of the filament ball core in mm^2 while line 20 computes the distance between the filament ball core surface and the outer shell in mm. Line 21 indicates how much distance there is between the edge of a single adsorbent fiber attached to the filament ball core and the outer shell in mm. Line 22 uses the adsorbent fiber diameter indicated in line 14 to compute the cross sectional area of an adsorbent fiber in mm^2. Line 23 indicates the packing density in percent of the adsorbent fibers onto the filament ball core. From this and line 22, the effective area required per fiber base on the filament ball core for attachment in mm^2, line 24. Line 24 in conjunction with Line 19 is then used to determine the number of adsorbent fibers required per filament ball. This then combined with lines 20 and 21 is used to determine the total length of adsorbent fibers per filament ball in m presented line 26. So long as the total length of adsorbent fibers required per filament ball (line 26) is greater than the required length of fiber in each ball (line 17), the design is considered feasible. The results with extremely conservative estimates of various mechanical parameters as shown in Figure 2 prove the concept of an adsorbent filament ball to be mechanically feasible.

Shell Enclosure

Given the feasibility of an adsorbent filament ball, various shell enclosures were investigated for their structural strength and feasibility for use with the inner adsorbent filament ball. A strength comparison was performed of an dodecahedron, octahedron, and cube shell with circular holes in the center of

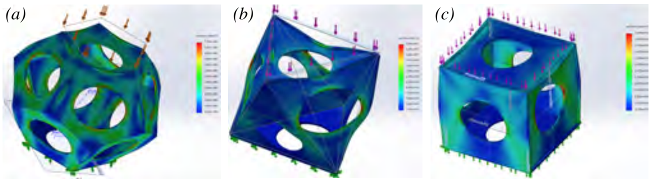

Fig. 3. von Mises stress results for vertical loading of a (*a*) dodecahedron, (*b*) octahedron, and (*c*) cube shell enclosure.

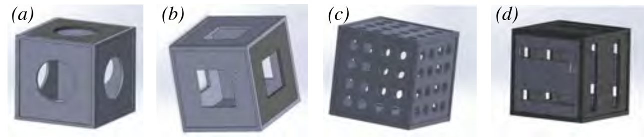

Fig. 5. Solid models depicting cube shell enclosure with (*a*) large circular, (*b*) large square, (*c*) small circular, (*d*) rectangular slit hole geometries.

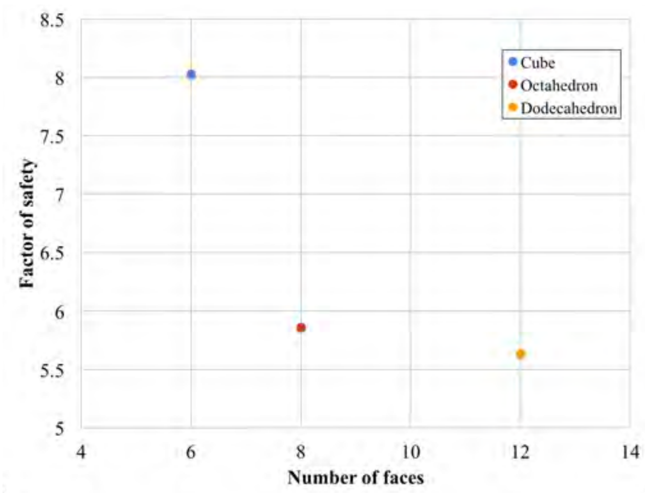

Fig. 4. Factor of safety as a function of number of faces for the dodecahedron, octahedron, and cube shell enclosures.

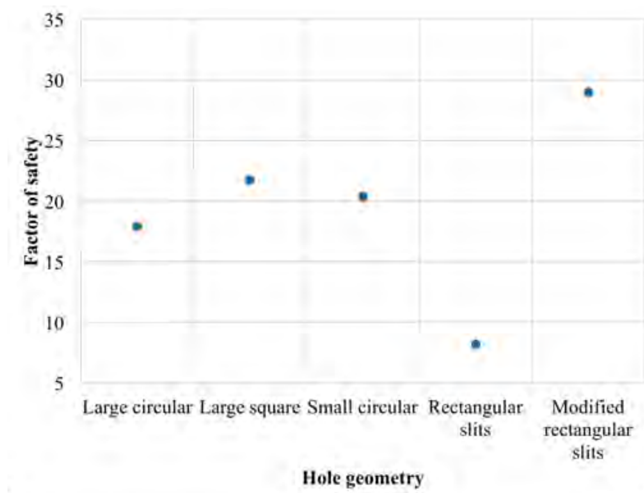

Fig. 6. Factor of safety as a function of hole geometry for the cube shell enclosure.

each face. The geometry of the three shell types was adjusted so that they all had a maximum width of 0.5 m. All were submitted to a vertical distributed load of 3 kN as applied to the rim of the top face, with the bottom face full constrained. Each shell was assumed to be made of high density polyethylene (HDPE) which has yield stress of approximately 26 MPa. For each shell, the hole diameters were adjusted for each face so that the ratio of hole to solid area for each model was the same. Finally, the thickness of each structure was adjusted such that the mass of all three shells was the same. Figure 3 depicts the von Mises stress distribution for each of the three shells.

In addition to the von Mises stress, the factor of safety for each shell enclosure geometry was analyzed. The shell enclosure will start to fail if a new load is applied equal to the initial 3 kN load multiplied by the resulting factor of safety. The results of this analysis are shown in Figure 4. As can be seen from the figure, the cube, with the smallest number of faces, has the highest factor of safety, whereas the more spherical-like shells such as the dodecahedron, have a much lower factor of safety. Additionally, the factor of safety decreases nonlinearly as the number of faces increases.

In addition to the structural shell, the geometry of the holes in the shell may also be varied. The holes must be large enough so as to allow adequate seawater flow to the enclosed adsorbent, without greatly affecting the structural strength of the shell. The effect of varying hole geometries on the overall strength of the shell was investigated for the cube shell enclosure, given that it had the highest factor of safety. A varied set of four hole geometries was implemented, depicted in Figure 5. As in the case of varying shell structures, the factor of safety was determined for each of the four types of hole geometries on the cube shell enclosure. The total hole area was kept constant for each model. The results are shown in Figure 6. As can be seen from the figure, the factor of safety for the standard rectangular slits (shown in Figure 5(*d*)) was significantly lower than for the other hole geometries. In this model, both horizontal and vertical slits were used and failure was found to occur at the edge of the horizontal slits when under a vertical load. Replacing these horizontal slits by vertical slits resulted in a "Modified rectangular slits" hole geometry, which yielded the highest factor of safety of 29.01.

CONCLUSIONS

In the case of ocean deployment of an offshore system for harvesting uranium from seawater, adsorbent materials will need to withstand the harsh environment of the ocean as well as the likelihood of rough handling during transport and deployment. Currently, adsorbent polymers with high tensile strength tend to have poor uranium adsorption capacity. However, the mechanical requirements of an offshore uranium harvesting system can be decoupled from the chemical requirements through the use of an exterior shell enclosure surrounding an adsorbent polymer. Furthermore, the adsorbent polymer may be wound into a ball with filaments extending radially outward from the center core. This study proved the mechanical feasibility of winding an adsorbent polymer into a filament ball to meet the annual uranium needs of a 5-MW nuclear reactor.

With the structural strength of the system now provided by a shell enclosure instead of the adsorbent itself, the strength of various shell designs under vertical distributed loading was investigated. It was found that the factor of safety increased as the number of faces of the shell enclosure decreases. The cube shell likely appears to be the strongest, with a factor of safety of 8.03, because its vertical walls were the most effective at resisting vertical loads. Further investigation should be done into the performance of the shell geometries under point loads. Additionally, the performance of a spherical shell under similar loading conditions should be studied for comparison.

Given that adequate seawater flow to the adsorbent interior is crucial to the total uranium adsorption of the device, the impact of four different hole geometries on the strength of the cube shell was also studied. It was determined that the vertical rectangular slits resulted in the highest factor of safety of 29.01, which follows on in the view that vertical geometries should resist vertical loads better. However, given that the loads on the shells will be random, it is likely that the large square holes, with the second highest factor of safety of 21.76, will prove to be the strongest in practice. Additional analysis needs to be conducted to determine which hole geometry is best for adequate seawater flow to the adsorbent interior. Future work should also focus on determining the distance between the filament ball and the shell enclosure for the optimal fluid flow and resulting uranium adsorption.

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