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A Cost Estimate for Uranium Recovery from Seawater Using a Chitin Nanomat Adsorbent

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A Cost Estimate for Uranium Recovery from Seawater Using a Chitin Nanomat Adsorbent

by

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Thesis

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Dedication

This thesis is dedicated to the practical application of scientific research to achieve sustainable life on earth. I would also like to thank the following people for their support, patience, and understanding: my mom, dad, brother, sister, grandma, and friends.

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Abstract

A Cost Estimate for Uranium Recovery from Seawater Using a Chitin Nanomat Adsorbent

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The University of Texas at Austin, 2014

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Even at 3.3 ppb, seawater contains a uranium supply large enough to power the world's nuclear fleet for 13,000 years. This large supply has prompted interest in technologies for recovering uranium from seawater. Since the 1960's, economic models of such technologies have failed to produce an economically competitive strategy when compared to conventional uranium recovery from terrestrial mining. Thus, uranium from seawater is researched as a potential price ceiling because of the large supply but high recovery cost. Such an upper bound is still valuable research because it allows for more certainty in uranium prices for planning, research, development and deployment of nuclear power systems. This thesis explores past cost estimates for uranium recovery from seawater and adds a new cost estimate to the pool of literature.

The past estimates showed a development from systems that actively moved seawater to systems that allowed adsorbent to sit passively in seawater. The adsorbent material changed from hydrous titanium oxide to the higher-capacity amidoxime ligand. Capacity was the strongest driver of cost. Early models with the amidoxime ligand used an acrylic substrate or backbone. This substrate was later replaced by polyethylene because of its increased durability and lower cost. However, each of those materials could contribute to the problem of plastics in the ocean.

The new technology assessed for cost in this paper attempts to address the plastics concern by replacing the plastic with a high molecular weight chitin nanomat as the substrate for the amidoxime ligand. The cost assessment showed the technology is presently cost prohibitive largely due to the adsorption capacity and chitin nanomat production costs. To increase capacity, the grafting efficiency onto the chitin substrate must be improved in order to achieve capacities comparable to those observed for the amidoxime-polyethylene adsorbent. To reduce chitin nanomat production costs, the ionic liquid (IL) consumption must be reduced and the recyclability of IL must be achieved.

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Introduction

Securing an independent energy supply is a priority for many countries. This is rightfully so: dependence on foreign countries for energy supply lends to an uneven balance of power. That power discrepancy could lead to abuses in supply or price which could have severe economic, social, and safety implications for the native country. For nuclear energy, traditional uranium sources come from terrestrial mines that are concentrated in a few countries including Kazakhstan, Australia, Niger, and Canada. That leaves many countries without their own source for uranium and requires them to purchase it at an international market. To overcome this, it would be desirable to develop an unconventional source of uranium to which virtually any country might have access. One such source is seawater, which boasts 3.3 parts per billion concentration of uranium. The source for uranium in seawater is the seawater floor dissolving into the oceans over the millions of years of earth's history. The total volume of seawater contains about 4.5 billion tonnes of uranium. That supply is around 1,000 times greater than the known terrestrial source of conventional uranium. Uranium from seawater could power the world nuclear power fleet at current rates of uranium consumption for about 13,000 years – an effectively infinite supply. Conversely, the supply of uranium from terrestrial, conventional sources is known to be sufficient for around 80 years of current rates of uranium consumption even when accounting for increased demand due to nuclear power growth worldwide - growth largely led by China. In addition, discovery of uranium resources has outpaced consumption of uranium and growth of the nuclear power industry.

Why is no country mining seawater for uranium? The cost of doing so is currently and historically at least 2 to 6 times greater than the price of uranium from conventional sources. The study of uranium recovery from seawater dates to the 1960's with many countries taking part in the research. Yet, the technology is still immature with current funding from the U.S. Department of Energy for uranium recovery from seawater listed under the "Blue Sky" funds for research that might be viable far into the future.

Uranium recovery from seawater has many challenges. The first is the low concentration of uranium in seawater. Given the low concentration, the extraction strategy must physically place a ligand or adsorbent material into contact with large volumes of water, or move large volumes of seawater into contact with an adsorber. The second challenge is that uranium exists as uranyl ions in seawater in carbonate complexes, $UO_2(CO_3)_3^{-4}$, which are relatively stronger than many ligands. Other chemical design challenges are that the ligand must be efficient at extracting uranium at the pH of seawater and the ligand (and whole adsorbent) must be insoluble. Another challenge is uranium concentration in seawater is comparatively low compared to other ions in seawater. A ligand that adsorbs uranium is likely adsorbing many other ions that are far less valuable. Conversely, the ligand may adsorb some valuable co-products. Although, research has been unable to adsorb the other valuable ions in concentrations enough to be included in cost analyses.

Because of the high cost and practically infinite supply, uranium from seawater would be *the* highest price of uranium. The highest price is called the price ceiling. Certainty of prices provides stability to markets. The price ceiling for uranium allows industry to model long term costs with more certainty. That certainty can be translated to lower interest rates for borrowing capital and thus lower costs. With large capital costs for multi-year construction projects for nuclear power facilities being the greatest barrier to new nuclear growth in the United States of America, reducing the price of debt is paramount to promoting nuclear energy. Recognition of this challenge is seen in the U.S. Department of Energy's Loan Guarantee program which is designed to reduce the interest rate on debt for nuclear power facility capital costs by backing loans for nuclear power.

HOW ION RECOVERY FROM SEAWATER WORKS

Uranium exists as uranyl ions in seawater. The uranyl ion is bonded to carbonate to form the complex uranyl carbonate,$UO_2(CO_3)_3^{-4}$. The complex moves around freely in seawater. When it comes into contact with the adsorbent's ligand, the ion can leave the carbonate for a better chemical fit of the ligand, if the ligand is properly designed. Finding a ligand that can adsorb the most uranium per mass, also known as adsorption capacity (g U / kg adsorbent), is the key variable for the practical and economic viability of uranium recovery from seawater.

The general methodology for recovering uranium or other valuable ions from seawater is to produce an adsorbent or ion adsorbing sponge, make seawater to come in contact with the adsorbent (often through mooring or pumping), wait for the adsorbent to recover uranium, elute the adsorbent to recover the product, and prepare the adsorbent for another use of recovering ions.

CURRENT METHODOLOGY FOR URANIUM RECOVERY FROM SEAWATER - ORNL

The current methodology for uranium recovery from seawater comes from research out of Oak Ridge National Laboratory based on research conducted by the Japanese Atomic Energy Agency (Tsouris, et al. 2012) (M. Tamada, et al. 2006). The adsorbent is an amidoxime ligand bonded to high density polyethylene using radiation graft polymerization. The adsorbent is moored in the ocean in a kelp field like fashion where weights and chains hold one end of the adsorbent down and the rest floats up towards the surface. Figure 1 below shows this scheme. Small boats winch and move the adsorbents to a large ship that conducts the elution. A supply ship takes product and spent chemicals from the elution ship and supplies it with fresh chemicals.

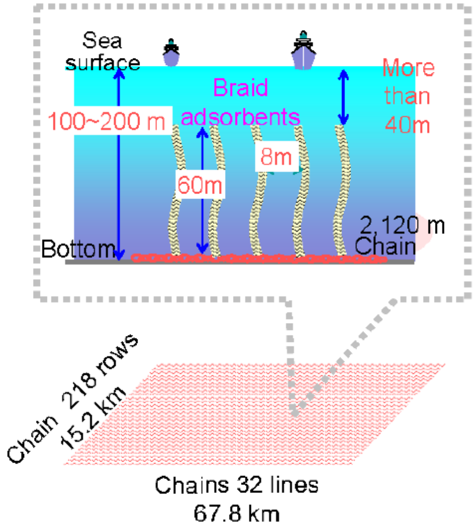


Figure 1. Mooring scheme for uranium recovery from seawater (M. Tamada, et al. 2006)

One critique of this system is that it is placing large amounts of plastic (polyethylene) into the ocean when the ocean already has a pollution problem largely stemming from plastic waste. That is a valid argument as the field size for uranium recovery from seawater capturing 1,200 tonnes per year, a standard reference value from the recent cost estimations, is greater than the city area of Dallas, Texas, and the ocean has a documented pollution problem from plastics. To address this concern, scientists at University of Alabama combined a recent innovation of high molecular weight chitin nanomats from shrimp and crab shells with the uranium recovery from seawater technology to create a potentially more environmentally friendly option (Barber, Griggs, et al. 2013) (Barber 2013). The chitin nanomats replaced the polyethylene as the backbone or substrate for the adsorbent.

CHITIN NANOMATS ADSORBENTS

The process for producing high molecular weight chitin nanomats is outlined in (Barber, Griggs, et al. 2013). The process involves turning wet shell waste into dry shell powder through pressing, drying, and grinding then dissolving the dry powder in an ionic liquid and electrospinning the solution to produce the high molecular weight chitin nanomat (the University of Alabama innovation.) After the chitin nanomat is made, the amidoxime ligand is chemically grafted to the chitin nanomat. The rest of the uranium recovery process follows as previously described.

The ionic liquid, 1-ethyl-3-methylimidazolium acetate, is a relatively new and unstudied chemical. That was exemplified by obtaining multiple material safety data sheets (MSDS) for it, which stated the chemical was understudied and many of the safety details were unknown. Future research will improve the economics and chemical usage of the high molecular weight chitin nanomat production process.

The next section reviews historical cost estimates for uranium recovery from seawater. This meta-analysis was partially conducted in (Tamada 2009), but not completed in a comprehensive fashion since (M. Kanno 1984). The goal of this meta-analysis is to gather all of the past cost estimates for uranium recovery from seawater into one paper and present them in comparison, highlighting key variables. The methodology is the standard literature review protocol: searching databases, searching past literature, and obtaining original sources. This meta-analysis is important as it will allow for an easier view of the progress of the technology and comprehensively documents recent work from various laboratories. The work is novel because it updates meta-analysis research completed in the past 30 years.

The following sections develop and analyze a new cost estimate for uranium recovery from seawater using a chitin nanomat based adsorbent with the amidoxime ligand. This is the first time chitin is used as a substrate for the most effective ligand, amidoxime. The reason for this analysis is the potential for a viable replacement to the plastic, polyethylene, based adsorbent. Thus, this might allow for fewer plastics to be placed in the ocean. The goal of this estimate is to explore if the early research into chitin nanomats combined with the amidoxime ligand can be economically competitive with recent polyethylene-amidoxime adsorbents for uranium recovery from seawater. The methodology used to assess this is the same as recent past estimates, a life cycle discounted cash flow approach using the code of accounts developed by the Economic Modeling Working Group (Economic Modeling Working Group of the Generation IV International Forum 2007). The past estimates on which this estimate was based are Sugo 2001, Tamada 2006, and Schneider 2011, 2012, 2014. This work is important as it is the first time the substrate has been changed since the 1990's from acrylic to polyethylene. The work is novel as it is the first time the substrate is made from naturally occurring waste products (the chitin comes from the shrimping and crab industry waste.) After the analysis is presented, a sensitivity analysis, discussion, and a conclusion follow.

Literature Review: Costs and Methods for Uranium Recovery from Seawater

This section reviews cost estimates for past and contemporary technologies for extracting uranium from seawater. This meta-analysis fills an important gap because similar reviews of seawater uranium technology costs are over 20 years old or incomplete. (Davies 1964) (M. Kanno 1984) (Tamada 2009) An up-to-date, complete survey of technology cost analyses will provide context for the analysis presented in this work.

Most technologies and processes for recovering uranium from seawater share a few distinct characteristics. First, the chemical ligand/method used capture the uranyl ions (the ion that uranium forms in seawater) is a key driver of performance and ultimately cost. A ligand must successfully compete with the carbonate in the complex, $UO_2(CO_3)_3^{-4}$, that forms in seawater. The ligand plays a large part in determining the adsorption capacity, which is a major determinant of the cost of recovering uranium from seawater. The ligand can be complicated to produce and/or made from specialty chemicals. Therefore, if the chemicals used in preparing and grafting the ligand are too costly, the system will not be economical even if adsorption capacity is high.

The ligand attaches to or is precipitated on a substrate. The substrates vary widely in composition and cost. The substrates are usually long chains of a particular molecule ranging from high density polyethylene to chitin. Other substrates include glass wool and loosely woven cotton fabric. The ligand – substrate combination is referred to as adsorbent.

Closely related to ligand chemistry, albeit less fully documented or understood, is the degree of grafting (DOG). This measure is typically defined as a ratio of the mass or molarity of chemical ligand to substrate. If the degree of grafting is too low, there is little ligand attached to the substrate and capacity will be poor. If the DOG is excessively high, on the other hand, binding sites may be masked by other ligand and capacity ceases to increase with DOG. The economics suffer given that expensive grafting chemicals are not used optimally.

After the adsorbent is produced, a mooring strategy must be devised to efficiently contact the adsorbent with seawater. Mooring strategies range from placing structures in the ocean (floating or on the sea floor) to utilizing tides, building lagoons to run water through adsorbent beds in a controlled fashion, attaching adsorbent to ship hulls or off-shore platforms or wind turbines, to anchoring buoyant adsorbent on the sea floor. These systems can be broadly classified into those that involve pumping or otherwise inducing flow through the adsorbent and others that are passive and rely on currents, tides and local advection. The less energy intensive passive systems have proven to be more economical.

The length of campaign is the amount of time the adsorbent has been in contact with seawater. A longer campaign can increase the amount of uranium adsorbed, but the rate of adsorption decreases over time, as the saturation capacity is approached. The optimal length of campaign is dependent on mooring and deployment costs. It may also be related to the flow rate of seawater over the adsorbent. Some schemes have found a significant impact from this (M. Kanno 1984) while others have not (Tsouris, et al. 2012). Likewise, the adsorption kinetics are affected by water temperature, with higher temperatures generally promoting more rapid adsorption. The temperature effect is not well understood and past modeling and experimental work has been limited (Tsouris, et al. 2012).

After the adsorbent is eluted for the uranium product, it can be chemically prepared for re-entry into seawater for another mooring stage of uranium recovery.

Reusing the adsorbent a number of times can greatly reduce the uranium production cost as the expensive adsorbent produces more uranium over its life cycle. On the other hand, there is generally a loss of uranium adsorption capacity each time the material is reused. The loss of capacity may be due to damage to the ligand during elution or from occupation of sites by ions that are adsorbed in addition to uranium. These ions may not be removed from the ligand during the elution step. If they have negligible economic value, they are termed fouling co-products. Fouling co-products for the amidoxime adsorbent include vanadium, lead, iron, and magnesium (Sugo, et al. 2001).

Potentially valuable co-products also exist and include many precious metals: molybdenum, gold, silver, platinum, and palladium. Most of these ions exist in seawater at much lower concentrations than uranium (Turekian 1968). Thus in any small scale adsorbent test, any small amount of positive co-product collected is so small that it may be difficult to measure with mass spectrometry techniques (Mayes 2012). Hence very limited data has been reported concerning uptake of potentially valuable co-products.

This section organizes methodologies and cost estimates chronologically. A summary table is provided at the end of the section. For each reviewed methodology, the table includes a recovery description, capacity, substrate, ligands, substrate structure, mooring strategies, adsorbent uses, degradation, and cost. All costs given in the reviewed documents are adjusted to year 2010 dollars using the Consumer Price Index (CPI). (U.S. Bureau of Labor Statistics 2014)

URANIUM RECOVERY FROM SEAWATER IN 1960'S AND EARLIER

British and Russian scientists independently confirmed that the predominant molecular ion that uranium forms in seawater is $UO_2(CO_3)_3^{-4}$. (Davies 1964) Hence this carbonate was identified as the chemical competition for any ligand. Scientists also recognized the challenge of grafting the ligand to a solid insoluble substrate. In (Davies 1964), this substrate was assumed to be an organic resin matrix.

(Davies 1964) was inspired by uranium adsorption on rust (hydrated ferric oxide) to pursue inorganic adsorbents. He precipitated inorganic salts on glass wool and placed these into a glass column for testing. He also considered muslin, a durable woven cotton fabric. (Davies 1964) published an estimate of the cost of uranium recovery from seawater in 1964. He tested many ligands and substrates (resins in his paper.) The ligands included phosphonic acids, kojic acid, salicylic acid, amion-carboxylic acid, amino-phosphoric acid, and hydrous titanium oxide. A promising result came from resorcinol arsenic acid (1.010 g / kg in 112 days from the dry H+ form.) However, that material lost capacity with continued use as a hydrolytic attack degraded the carbon and arsenic bond (Gupta and Singh 2003). He noted lead naphthalene tetracarboxylate gave 1.074 mg/g in 35 days, but it was unstable in seawater as well as the sodium carbonate eluent. Davies thus based his cost estimate on hydrous titanium oxide precipitated on glass wool or muslin. He saw 0.26 g U / kg adsorbent for muslin in 7 days and 0.26 g / kg for glass wool in 20 days. Hydrous titanium oxide would continue to be the main focus of research for the next two decades.

(Davies 1964) assumed the tidal drift of seawater would be sufficient for supply of fresh uranium-bearing seawater given the rate of extraction was not too high. His system involved upper and lower lagoons that were opened and closed by a series of gates and dams. The seawater would flow into the upper lagoon then into the lower in a controlled fashion. The lower would have packed adsorbent beds. An associated chemical plant would sit on-site near the lower lagoon. For a site producing 1,000 tonnes of uranium per year (1,300 short tons of U_3O_8), he estimated the cost would be \$204 to \$408 per kg U in 2010 dollars or \$11-\$20 per lb of U_3O_8 as published. It was unclear how Davis achieved the low cost, but it was likely a combination of a low cost of mooring and a low cost of materials as his adsorption capacity was in-line with other hydrous titanium oxide based adsorbents. He noted that his mooring system was analogous to the planned Passamaquody Tidal Power Project from the U.S. Army Corps of Engineers.

1970'S AND 1980'S

(M. Kanno 1984) published a review of cost estimations for uranium recovery from seawater, many of the adsorbents were theorized and their experiments were conducted in the 1970s. In his assessment, he assumed the existing materials and capacities such as hydrous titanium oxide and its capacity. He explored various mooring schemes in which seawater would need to actively be pumped. Kanno approached the recovery by calculating the amount of seawater required to produce 990 tonnes of uranium per year. He calculated the amount of seawater needed given its concentration of 3.3 mg U/ liter of seawater (3.3 ppb) and assuming 100% uranium extraction, to be 3 x 10^{11} m^3/yr. It appears Kanno measured adsorption capacity as a recovery percentage, scaling water pumping requirements up from the amount of water needed given full recovery.

The early designs Kano assessed assumed pumping seawater through a fixed packed bed of hydrous titanium oxide adsorbent. The ligand exists as a precipitate and was prepared by sifting onto a mesh as discussed in (Yamashita, et al. 1980), yielding adsorption performance measured at 0.196 g U / kg adsorbent in 10 days. In his cost analysis, Kanno used the adsorbent 25 times with 0.1% capacity loss per use. The adsorbent was packed into beds, which are held in place at a seaside facility. The facility stretched 5.5 miles sitting on shore, parallel to the shoreline. Its 467 pumps pumped 80

m^3 water / s through the 5.19 x 10^4 tonnes of adsorbent. The power requirement for the pumps was 67 x 104 kW. The system cost was reported as $868 / kg U in 1976 dollars or $3,300 in 2010 dollars (M. Kanno 1981). (M. Kanno 1984) A second design employed larger pumps with a capacity of 500 m^3/s, around a 600% increase. The facility was redesigned to extend from the shore in the fashion of a breakwater. Figure 2 shows this facility. With the increased pumping capacity, the facility was shorted to 2.7 miles (4.3 km) including the regeneration facility (used to prepare an eluted adsorbent for re-entry in seawater) and the number of pumps reduced to 60. Using this system, the uranium production cost was estimated to be $580 / kg U in 1976 dollars or $2,200 in 2010 dollars. (M. Kanno 1981) (M. Kanno 1984)

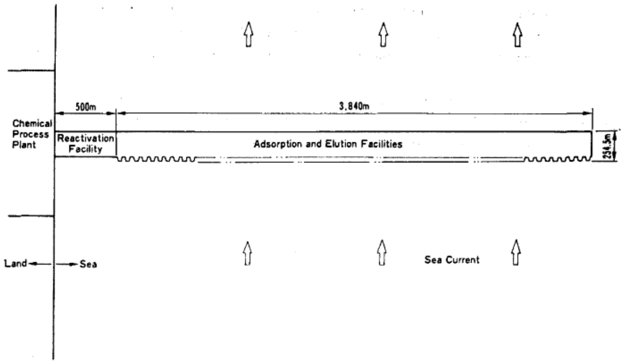


Figure 2. Early design of seawater processing facility (M. Kanno 1984)

Kanno presented a sensitivity analysis based on experimental data where he increased the adsorption recovery efficiency from 60% to 80% of uranium in the seawater and increased the uranium concentration in the eluate from 10 ppm to 20 ppm (eluate is the solution obtained from elution.) This allowed the facility size to be reduced by 1 km from 4.3 km and the number of pumps to be reduced by 20 from 60. Kanno estimated the cost to be $420 / kg U in 1976 dollars or $1,600 in 2010 dollars. (M. Kanno 1984)

Kanno also explored a concept that directly utilized sea currents by placing adsorbent 'units' on the sea floor (M. Kanno 1981). A unit consisted of 5 m x 5 m x 5 m adsorbent cubes stacked three high in series, and parallel (Figure 3). The cubes were structures that held loosely packed beds of adsorbent that seawater would flow through. Kanno continued to use the hydrous titanium oxide adsorbent. The unit was placed in on the sea floor in flat, shallow waters. The reasoning appeared to be ease of mooring scheme where materials could easily be exchanged between the facility and shore. The unit dimensions were calculated to be 17.3 m in width, 45 m in height and 1.7 km in length (1 mile). 30 units were deemed necessary to adsorb 1,000 tonnes of U per year. Kanno estimated the cost of recovering uranium with this system to be $650 / kg U in 1976 dollars or $2,500 in 2010 dollars. Kanno provided a sensitivity analysis where the 'units' were reconfigured into thin packed beds of adsorbent placed between two porous supporting plates. He estimated the cost to be $470 / kg U in 1976 dollars or $1,750 in 2010 dollars. (M. Kanno 1984)

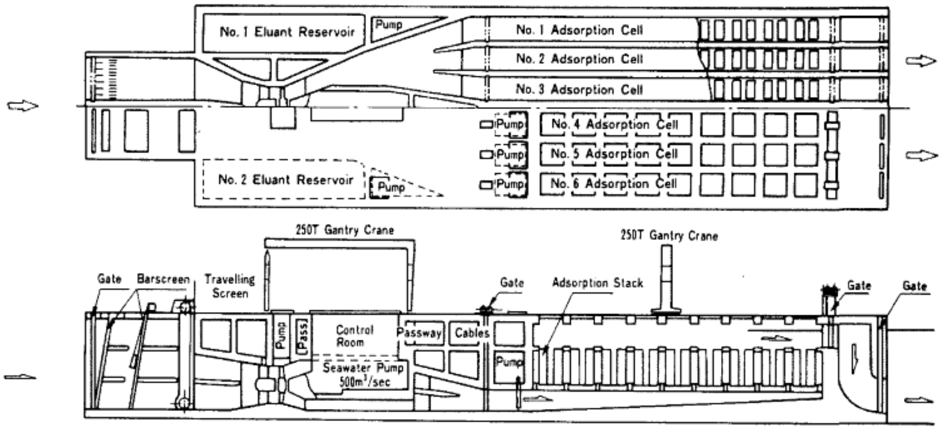


Figure 3. Design of a sea current utilizing 'unit'. (M. Kanno 1984)

In summary, Kanno's work explored many mooring strategies utilizing the hydrous titanium oxide adsorbent. His cost analyses were affected by several assumptions regarding the capacity and durability of the material. For example, it was evident from subsequent work that the degradation per use (0.1%) and the number of times the adsorbent can be used, 25, were overly optimistic. Another key assumption underlying his analyses was that the adsorbent would capture 60 or 80% of the uranium in a given mass of seawater. A simple mass balance based on measured uptake rates of less than 1 g U/kg ads over 10 to 20 days would show that the uranium recovery fraction was in fact orders of magnitude lower. Thus the pumping requirements in Kano's schemes are too small and the cost estimates unrealistically favorable.

An experimental plant using hydrous titanium oxide operated from 1981 to 1988 by Agency for Natural Resource and Energy, the Ministry of International Trade and Industry and Metal Mining Agency of Japan (Tamada 2009) The adsorption ability of the hydrous titanium oxide was reported at 0.1g U / kg adsorbent, which was deemed not economically feasible. The Japanese team estimated that to be economically feasible, the adsorption capacity would need to increase by a factor of 10 (Tamada 2009. Hence the 1980's saw a move away from hydrous titanium oxide to polyacrylamidoxime adsorbents.

The Massachusetts Institute of Technology (MIT) team of Driscoll, Borzekowskim, Best, and others switched to an amidoxime ligand on acrylic based adsorbent because of its increased adsorption (Driscoll 1983). MIT also adopted a small diameter fiber or wool-like adsorbent or as opposed to particle beds because the beds were shown to reduce capacity (Varela 1983). This was likely due to water being unable to penetrate them as well. Driscoll observed that adsorption is the key factor in determining economic viability, and the packed bed concept reduced overall adsorption.

(Borzekowski, Driscoll and Best 1982) used an amidoxime ligand on an acrylic and styrene based adsorbent to test adsorption in seawater with help from Woods Hole Oceanographic Institution. This appears to be one of the first amidoxime based tests. The longest campaign length they experimented with was 7 days. The highest adsorption capacity documented was 0.094 g U/ kg ads with the acrylic amidoxime adsorbent. They compared this to 2.0 – 2.4 g / kg for amidoxime adsorptions at 50 to 200 day campaign lengths reported from German and Japanese sources. They noted that in the 7 day trials, the adsorbent was far from its saturation capacity, which would be achieved with longer campaign lengths such as those used in the Japanese measurements. Vanadaium and molybdenum were observed as potential co-products. In addition to the amidoxime, two biosorbers, Rhizopus Arrizus and Penicillium Chryzogenum, were tested and showed near zero uranium uptake, although similar uptake to amidoxime- chitin nanomat based adsorbent explored later in this paper (0.00193 g U / kg biosober.) These biosorbers are fungi. The latter is the source for penicillin.

Driscoll published a cost estimate for the amidoxime-acrylic adsorbent that modeled a fixed-leg off-shore oil production platform with a submerged deck, shown in Figure 4 (Driscoll 1983). Each platform could produce 40 tonnes of uranium per year using pumps (low head, axial-flow). The adsorbent was a cylindrical roll of spinbonded acrylic amidoxime fiber sheet which was projected to have a loading rate of 700 ppm/d and a capacity of 5,000 ppm or 5 g U/ kg ads. Driscoll published the cost to be $360 / kg U in 1983 dollars or $800 in 2010 dollars. Taking credit for marketable co-products, molybdenum and vanadium, the cost became $290 / kg U in 1983 dollars or $630 in 2010 dollars. (Driscoll 1983) (M. Kanno 1984)

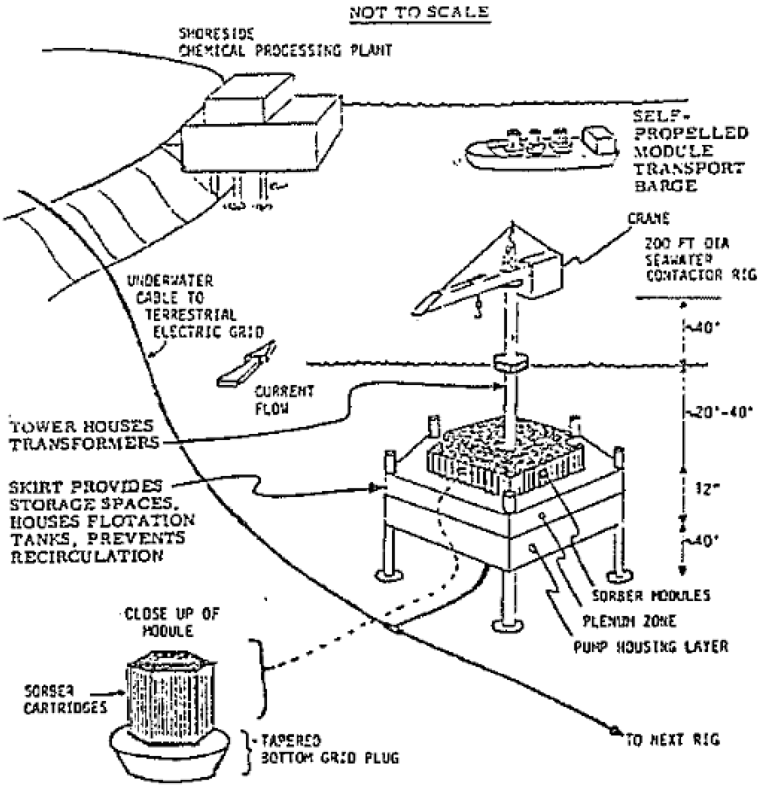


Figure 4. (Driscoll 1983) Mooring System with Platforms

Two large concerns arose with the previous systems: the high assumption for adsorption capacity and the active pumping system. The adsorption capacity used to model cost was not observed experimentally in this study nor was it observed in any study (including the most recent analysis.) A related flaw is how the capacity number was theorized- using a linear relationship between capacity and time. That relationship was also not seen experimentally or in any other study. The more accurate representation of the relationship between adsorption capacity and time is a logarithmic relationship where capacity rate is initially very large and then plateaus. The mooring system also actively pumped seawater. In retrospective analysis, the pumps may not have been necessary, but research using passive systems was not theorized until the 1990's as will be discussed in the following section.

Bitte of Uranerzbergbau Co. presented four different type concepts of floating structures using a polyacrylamidoxime resin adsorbent in fluidized beds. (Bitte, Keller and Ludwig 1983) Bitte assumed a linear adsorption of 20ppm per day (0.02g U / kg adsorbent) over 360 days, leading to a total uranium uptake of 7.2 g / kg U. The concepts are summarized in the following illustrations:

- Self-propelled, semisubmersible catamaran concept (Figure 5)

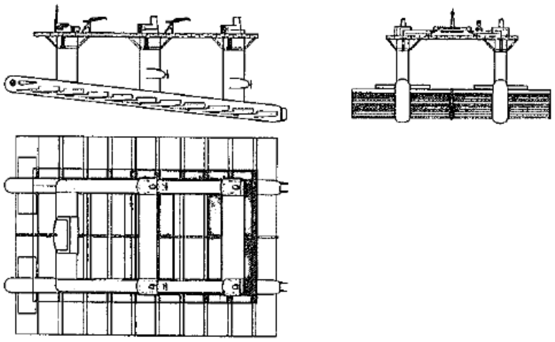


Figure 5. Self-propelled, semisubmersible catamaran concept (Bitte, Keller and Ludwig 1983)

- A moored semi-submersible catamaran concept (Figure 6)

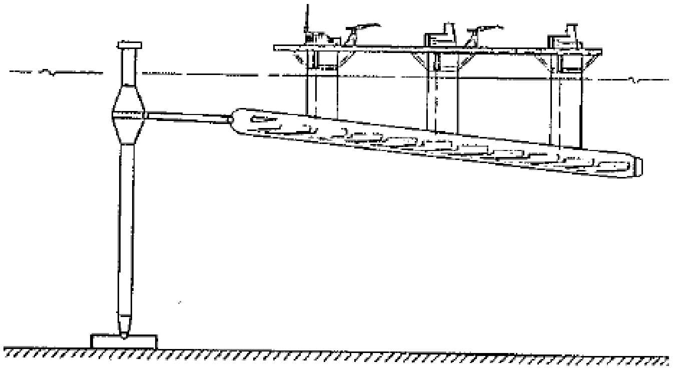
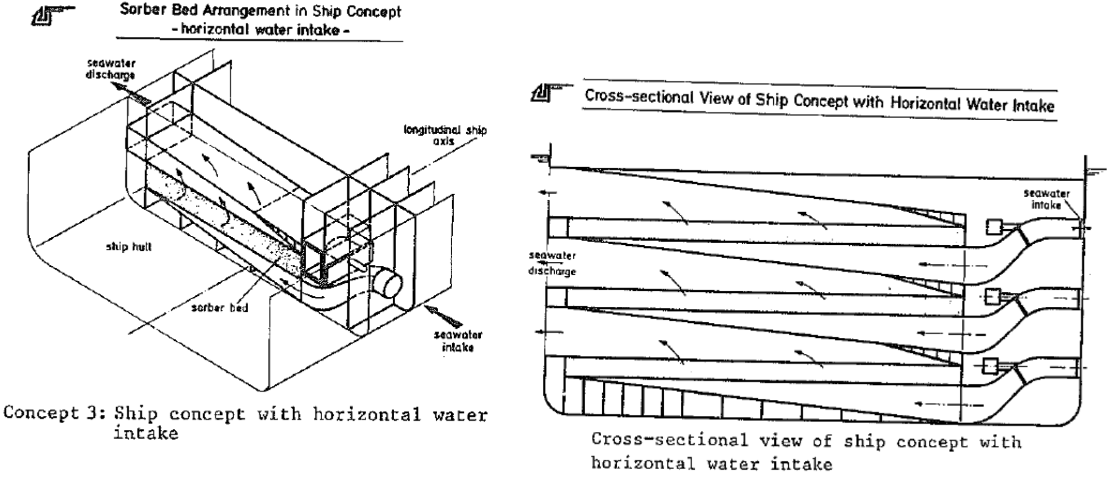


Figure 6. A moored semi-submersible catamaran concept (Bitte, Keller and Ludwig 1983)

- A ship concept with horizontal water intake (Figure 7)

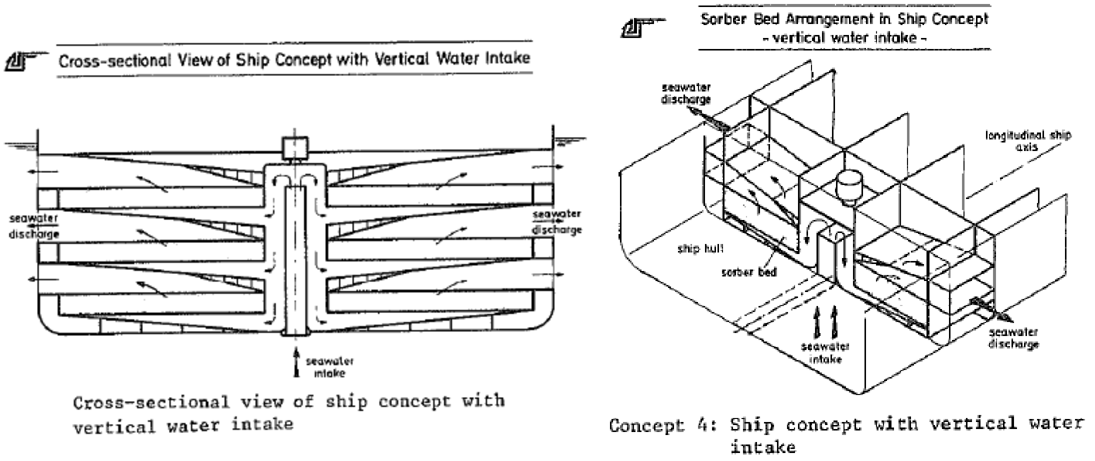


Concept 3: Ship concept with horizontal water intake

Cross-sectional view of ship concept with horizontal water intake

Figure 7. A ship concept with horizontal water intake (Bitte, Keller and Ludwig 1983)

- A ship concept with vertical water intake (Figure 8)



Cross-sectional view of ship concept with vertical water intake

Concept 4: Ship concept with vertical water intake

Figure 8. A ship concept with vertical water intake (Bitte, Keller and Ludwig 1983)

All of these schemes are forced convection, using pumps. The lowest cost estimate was for the first scheme: $650 / kg U in 1983 dollars or $1,400 in 2010 dollars. That was followed by the fourth, second, then third at a range of $1,900 / kg U to $2,650

/ kg with the cost of steel as a major driver of the economics. Sensitivity analysis on increasing the number of uses of adsorbent from 10 to 25 and increasing the bed velocity reduced the cost to $130 / kg U in 1983 dollars or $285 in 2010 dollars. The Bitte cost estimate assumed a time-invariant adsorption rate, which was not the behavior that was observed in marine tests. Neither this assumption nor the value used for the capacity, 7.2 g U/ kg ads, at 360 days of campaign length, were backed by experimentation

Koske of the University of Kiel cooperated with GKSS Research Center, (Gesellschaft zur Förderung der Kernenergie in Schiffbau und Schiffstechnik, German: Society for the Promotion of the Nuclear Energy in Shipbuilding and Naval Technology) Geesthachto, Germany to create a loop system, using gravity and suction to move water through a structure. Hence the system was free from the cost of pumping water. Koske was wished to move away from fixed and fluidized beds of adsorbent given the fouling and clogging issues that had arisen during experimentation. The adsorbent used in this scheme was granular and entrained in the flowing water. The In this closed loop scheme, Koske defined the adsorbent performance as the ratio of uranium recovered to total uranium passing through the structure. With a structure size of 200 m in length and 40 m in width and the gross tonnage of 58,384 GRT, a single unit could produce 20 tonnes of uranium a year. Figure 9 depicts this scheme. Varying the seawater flow rate from 42~12.5 cm/s, Koske estimated the cost to be $450 to $870 / kg U in 1983 dollars or $970 to $1,900 in 2010 dollars. (M. Kanno 1984)

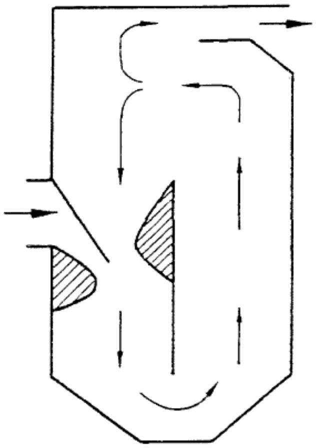


Figure 9. Suction unit scheme proposed by Koske (M. Kanno 1984)

Koske was unclear about how the velocity inside the structure was controlled, given that there were no pumps. In addition, the method for removing full adsorbent particles from the system was unclear. A best guess is the structure was removed from the seawater and the particles were recovered then.

Forberg of Royal Institute of Technology proposed a wave powered floating plant concept with fluidized beds of pellets and mat adsorbent (Forberg, Lagstrom and Valla 1983). He presented six schemes utilizing different polyacrylamidoxime adsorbents in pellet and mat form, along with several floating platform structures. In one such structure (Figure 10), a 600 tonnes of uranium per year facility was composed of floating units. Each unit's dimensions were 426 m x 65 m. The pellet structure adsorbent utilized 26 floating units and the mat structure adsorbent utilized 22 units. Forberg presented six cost estimates ranging from \$160 to \$880 / kg U in 1983 dollars or \$340 to \$1,900 in 2010 dollars, where the mat scheme was cheapest and the pellet scheme was the most expensive. (M. Kanno 1984) The reason the mat scheme was cheaper was an multi-fillament mat with greater exposed effective fiber was modeled. That corresponded to a

60% increase in uranium uptake per year. The reuses are not listed. The adsorption capacity degradation is noted as negligible.

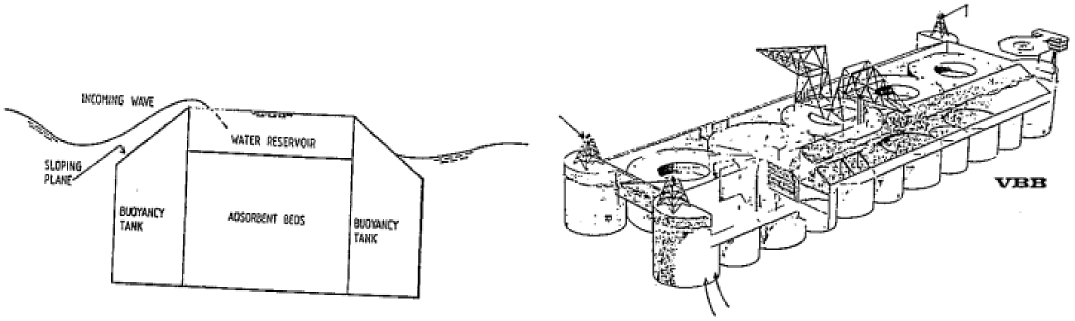
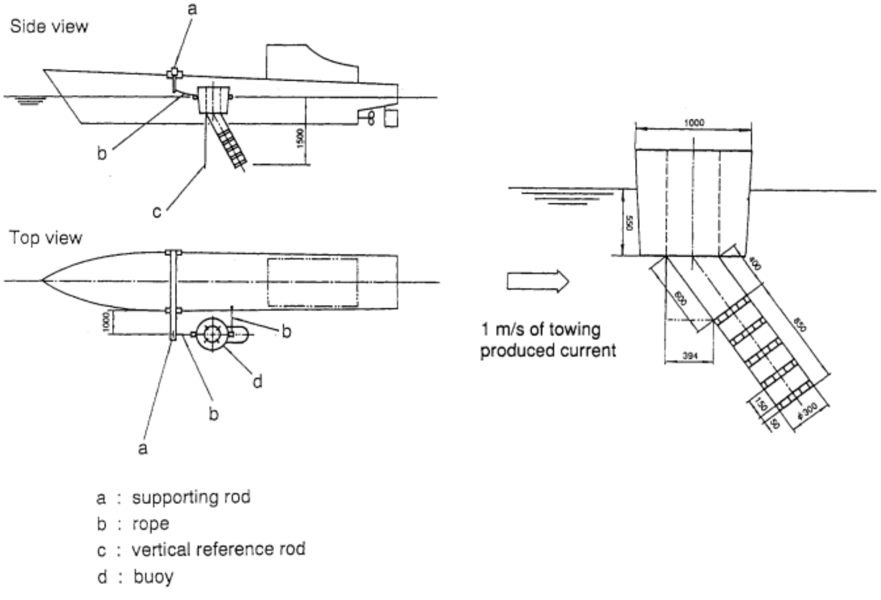


Figure 10. Forberg's Floating Platform (Forberg, Lagstrom and Valla 1983)

1990's

In the 1990's, research continued to focus on amidoxime as the primary ligand for recovering uranium because of a significantly higher capacity (Sugo, et al. 2001) with the most intense activity shifting to Japan. The Japanese system used an amidoxime ligand attached to a high-density polyethylene (HDPE) substrate (Sugo, et al. 2001). This material pioneered by the Japanese constitutes the foundation for the current process described later in this paper.

The early estimates for amidoxime on an acrylic substrate came from (Nobukawa, Tamehiro, et al. 1989) and (Nobukawa, Michimoto, et al. 1990) presented in (Sekiguchi, et al. 1994). This work documented a shift from packed beds containing small adsorbent balls to fiber adsorbent in beds (strings of adsorbent.) Nobukawa proposed a mooring system where a series of beds packed with fibrous amidoxime adsorbents are suspended in the ocean current and uranium is collected during passage of seawater through the beds. The beds hung from boats presented in Figure 11. The adsorption capacity was assumed to be 3.2 g U / kg Ads. in 40 days. Nobukawa estimated the cost as 55,000 yen / kg U in 1990 dollars or $900 / kg U in 2010 dollars (Sekiguchi, et al. 1994) . (These sources are in Japanese with English abstracts that include the capacity and the production cost.)



(a) boat for towing

(b) adsorption unit

Figure 11. Nobukawa's Mooring Scheme (Sekiguchi 1994)

(Nobukawa, Kitamura, et al. 1994) went on to report results of field with updated adsorbent performance and present a second set of cost estimates. He employed the same amidoxime ligand on an acrylic fiber adsorbent that was used in his earlier work (Nobukawa, Tamehiro, et al. 1989) The field experiments explored the effect of seawater velocity on adsorption by moving adsorbent through seawater (hanging braids from a boat) versus allowing adsorbent to sit at sea (hanging from a bouy.) The results showed increased adsorption with higher velocities. Nobukawa noted the adsorbent floated inside the cages which allowed for increased permeability. This fiber based adsorbent (Nobukawa 1989) was packed into metal cages and hung from boats as shown in Figure 12.

The cost estimate of $495 / kg U (2010 dollars) assumed 4.6 g U / kg adsorbent at 60 days of mooring with boats towing adsorbent. This cost is low relative to other cost estimates, but the very optimistic adsorption capacity was never observed experimentally: Nobukawa linearly extrapolated the 60 day capacity based on a few days of data. The paper does not mention the number of reuses or loss per use assumed for the cost analysis.

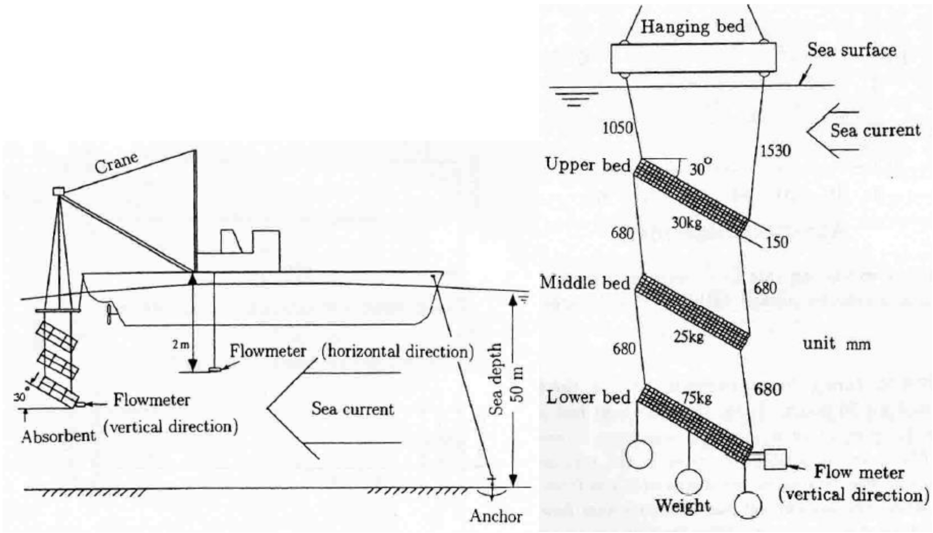


Figure 12. Nobukawa scheme for hanging adsorbent beds off boats (Nobukawa, Kitamura, et al. 1994)

Around the same time of Nobukawa's estimates from the late 1980s to the early 1990s, (Uezu et al., 1988; Saito et al., 1990) was researching amidoxime ligands attached to high density polyethylene adsorbent (Sekiguchi, et al. 1994). Although the results were published without any cost estimates, it appeared to be the first instance of radiation-induced graft polymerization in creation of a ligand for uranium recovery from seawater. The process also used acrylonitrile onto a porous polyethylene hollow fiber to produce amidoxime from the cyano group. Uezu reported the capacity as 0.27 g / kg U in 25 days. The difference between this adsorbent and the amidoxime-HDPE adsorbents discussed next was the structure of the HDPE: Uezu used a hollow fiber versus a solid fiber.

2000 TO TODAY

The first cost estimate for the amidoxime-HDPE adsorbent came from (Sugo, et al. 2001). (Sugo 2001) employed the amidoxime ligand grafting process previously discussed, Uezu's, one that utilized electron beam irradiation to open grafting sites on the HDPE. Sugo was also the first investigator to report an experimentally observed durability for the amidoxime adsorbent. Based upon five elution-adsorption cycles, Sugo found that the adsorbent lost 5% of its capacity per reuse. Sugo observed that increasing the surface area of the fibers and mooring in higher temperature seawater both led to increased adsorption. He set mooring campaign length to 60 days and assumed20 uses of adsorbent before it is disposed.

Although experimental results to date only supported a 60 day uranium uptake of 2 g U / kg adsorbent, the cost analysis used 6 g / kg ads. It assumed that the adsorbent fibers were packed into metal cages and suspended about 10m beneath the ocean surface using weights and floats. Each adsorbent bed weighed slightly over 1 tonne containing 125 kg of adsorbent, around 320,000 beds in the ocean a year to recover 1,200 tonnes of U. The beds are shown in Figure 13.

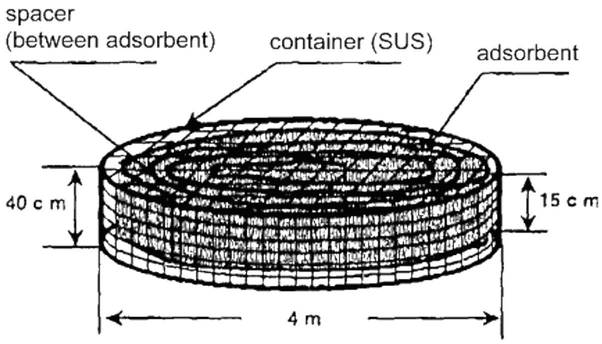
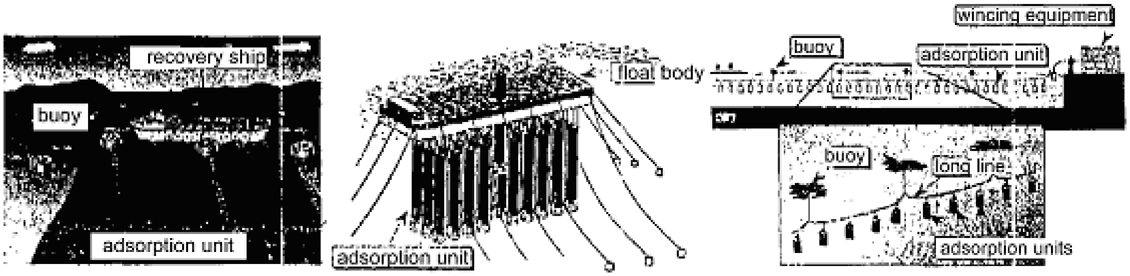


Figure 13. Adsorption bed loaded with adsorbent (Sugo, et al. 2001)

Three mooring systems were proposed for the adsorbent beds: a buoy method, a floating body method, and a chain-binding method, shown in Figure 14. The buoy method hung 100 adsorption beds from a buoy. Given the duration of the recovery and elution operations, Sugo recognized that in order to produce the target of 1,200 tonnes U per year, the inventory of adsorbent had to be 40% larger than the amount in seawater at any given time. The second proposed method was a system of floating bodies that acted as a large buoy or platform. Each body had 54,000 adsorbent beds and a crane atop the body winched up the beds. Recovery ships were used to move adsorbent to and from shore. The final strategy was a chain based ‘ski lift’ strategy. Adsorbent beds are attached to chains and move continuously from shore to sea and back. Buoys keep the adsorbent at a fixed height in seawater. The total chain loop length to produce 1,200 tonnes U/year was found to be 320 km or 200 miles. The costs for each mooring strategy are presented below. Table 1 highlights the costs.



(a) Buoy method (b) float body method (c) Chain-binding method

Figure 14. Sugo’s Three Mooring Strategies (Sugo, et al. 2001)

Table 1. Mooring Strategy Cost (Sugo, et al. 2001)

Mooring Strategy	Cost (2010 $/kg U)
Buoy method	$676
Floating body method	$632
Chain-binding method	$362

Although Sugo presented novel mooring strategies, his cost analysis parameters -- 20 uses of adsorbent with 6 g U / kg adsorbent – were not borne out by the measured performance data.

The Japanese Atomic Energy Agency Japan (JAEA) and the Atomic Energy Research Institute (JAERI) built upon Sugo's work by introducing free standing braided adsorbent systems versus large structure based mooring strategies (M. Tamada, et al. 2006). Tamada noted that the mooring costs associated with the large structures were dominating the overall system costs and introduced the braids as a means of reducing the mass of material the ships needed to convey. Using the radiation grafted polyethylene amidoxime fibers, the adsorbent performance was taken to be 2 g U / kg adsorbent in 60 days and the adsorbent was used six times with 5% loss per use. The mooring strategy was to tie 60m long adsorbent braids to chain that had been anchored to the seabed and allow the braids to float to the surface, like a kelp field. Work boats would winch up the chain in order to moor and recover the adsorbent braids, and the braids would be taken back to shore for elution and preparation for redeployment. Figure 15 shows the mooring operation. Tamada estimated this cost as $1,000 / kg U.

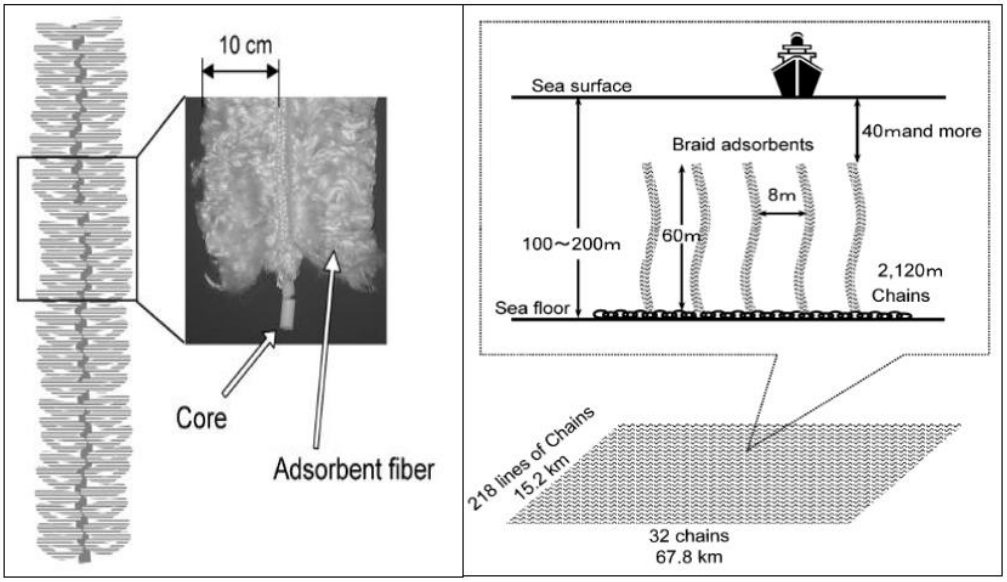


Figure 15. Braid Adsorbent and Mooring System (Tamada et al., 2006)

Oak Ridge National Laboratory in conjunction with The University of Texas at Austin evaluated and updated this cost estimate and model (Sachde 2011) (Schneider and Sachde 2013). The evaluation developed an independent cost estimate for the chemical process and adsorbent performance as in (Tamada 2006). Some modifications to the process published by JAEA were made; for instance, ORNL researchers had found that a hydrophilic group, not present in (Tamada 2006) but noted in other Japanese publications, was necessary in order to attain capacities approaching those claimed by JAEA. The US cost estimate also added financial modeling reflecting a private venture in the US, accounted for adsorbent degradation, and included adsorbent and chemical disposal costs. The estimated uranium production cost for the JAEA system was $1,220 / kg U. Accounting for a 5 percent per-recycle adsorbent capacity degradation rate had greatest impact on cost of the changes mentioned above. The assumption was based upon experimental results in (Sugo, et al. 2001)

(Schneider and Sachde 2011) also estimated uncertainties in a detail not seen in previous or past estimates. They considered three types of uncertainties: decision variables such as 1,200 tonnes U per year, value parameters such as discount rate, and empirical quantities such as equipment cost. They combined uncertainties in a Monte Carlo analysis. The 2-sigma (95%) confidence interval on the uranium production cost was \$689/kg U to \$2850/kg U. The reason for the large uncertainty was led by the adsorbent capacity expected value of 2 g U / kg ads. and it's standard deviation of 0.5 g / kg. If the adsorption capacity performance was better-quantified, so that it could be said with certainty that the capacity is 2 kg U/t ads, then the 95% confidence interval would refine to \$1030/kg U to \$1430/kg U. If degradation rate of adsorbent reuse of 5% was known with no uncertainty versus 2.5% standard deviation, the interval would shrink to \$1110/kg U to \$1350/kg U, holding all else constant and the previous change of certainty of capacity. This analysis showed the importance of fully quantifying the performance of the technology and reiterated the technology is still in the early stages of development.

In 2011, a US group led by ORNL began to develop a series of adsorbents that built upon the Japanese amidoxime-HDPE textile. The University of Texas at Austin (UT) group collaborated with ORNL to provide cost estimates for these adsorbents. In 2012, (Schneider and Lindner 2012) built upon seawater experiments and kinetics modeling (Tsouris, et al. 2012) that demonstrated a 60-day uranium uptake of 2.76 g U/ kg ads. The cost estimate incorporated changes to the adsorbent grafting chemistry to more accurately describe the ligand production chemistry. The update also included a new mooring strategy: the adsorbent elution and regeneration processes were moved offshore, taking place a large boat called a 'mothership.' This modification reduced the size and cost of the work boats being used to service the adsorbent field. A supply ship carried product, spent chemicals, and spent adsorbent from the mothership to shore and replenished the mothership with fresh chemicals and replacement adsorbent.

(Schneider and Lindner 2012) explored disposal options for adsorbent: selling the adsorbent as scrap, reusing the adsorbent material (high density polyethylene (HDPE) substrate), or reusing the adsorbent fiber (the spun HDPE as opposed to the raw material.) They also accounted for economies of scale in the production of chemicals whose markets would be significantly impacted by implementation of the uranium recovery from seawater system. Finally, they included cost reductions from sale of a potential co-product, vanadium. It was later noted that vanadium is an unlikely co-product since it is very difficult to elute from the amidoxime adsorbent without damaging the ligand. They mentioned lanthanides and precious metals as likely other co-products, but noted additional experiments at larger scales would need to confirm yields. They published the cost estimate at $1,000 / kg U and considered sensitivity cases as summarized below in Table 2.

Table 2. Summary of Options and Updates (Schneider and Lindner 2012)

Category	Item	Percent Change
ORNL Adsorbent & Performance	Assumes reference conditions except adsorption capacity of 2.76 ('Flow Combined') and the ORNL process for adsorption production.	-- (-19% change from the reference case)
Offshore Elution and Purification		-7%
Adsorption Capacity Scenarios	2.76 g U / kg ads.	-
	3.26 g U / kg ads.	-15%
	3.88 g U / kg ads.	-28%
End Use Options Scenarios	Sell as scrap	-6%
	Reuse HDPE	-7%
	Reuse HDPE and Braiding	-8%
Reuse Chemicals Scenarios	Reuse hydroxylamine, dimethylsulfoxide, and methanol	-25%
Economies of Scale	-	-11%
Incineration Cost for Hazardous Chemicals	-	+14%
Co-products	-	-3%

* Rounding to two significant figures accounts for the difference.

The most recent publication was (Schneider and Lindner 2014). This updated the capacity to 3.09 g U / kg ads.) based on measurements at PNNL of new, high surface area fibers prepared at ORNL. The reduced radius of the new fiber increases its surface area to mass ratio which improves the amount of ligand contacted with the water per unit mass of adsorbent. The update also revised chemical usage for ligand grafting and high density polyethylene fiber production. The heavy, stainless steel chain in previous estimates, (M. Tamada, et al. 2006), which was costly to purchase and maintain, was replaced by a high strength, advanced lightweight co-polymer material rope. The overall system cost from (Schneider and Lindner 2012) was $640 / kg U.

Another recent cost estimate for uranium recovery from seawater came from Massachusetts Institute of Technology (MIT.) They published a report exploring two new mooring strategies, a 3D adsorbent net and symbiotic system of adsorbent attached to wind turbines. (Baelden 2013) Their analysis assumed the same amidoxime adsorbent analyzed in (Schneider and Sachde 2013): 2 g U / kg ads., HDPE (high density polyethylene) substrate. The MIT team assumed that the number of uses could be increased to 18 from 6 and the adsorption capacity loss per reuse was reduced to 4.4% from 5%. The motivation for their work was the high cost for mooring in (Schneider and Sachde, The Cost of Recovering Uranium from Seawater by a Braided Polymer Adsorbent System 2013) and the relatively low number of reuses of the adsorbent.

The net system utilizes one large ship to perform the recovery, elution and mooring functions. As shown in Figure 16 and Figure 17, the ship is designed to winch up the adsorbent, elute uranium, regenerate the adsorbent, and lower it back into place in a single continuous campaign. The savings are largely a result of reducing the number of ships and including the elution on board the ship. Also, by assuming that the adsorbent braid trunks will bear the tensile load in the 3D net, MIT eliminates most of the chain present in the JAEA and ORNL designs. MIT also claimed that a scaled-down onboard elution capacity, attained by increasing the frequency of trips to shore, led to a further cost reduction. MIT placed the cost of the 3-D net scenario at $325 / kg U.

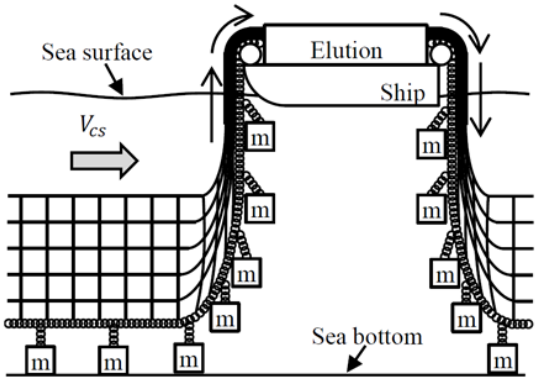


Figure 16. Side View of 3D Net Mooring and Recovery System (Baelden 2013)

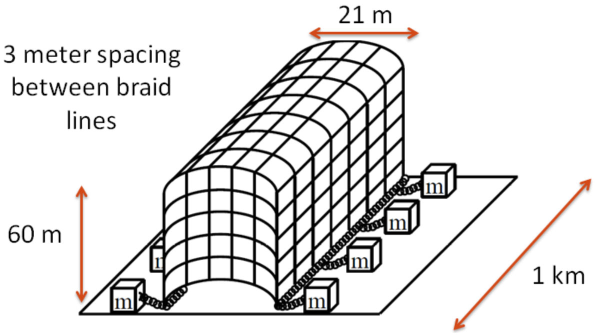


Figure 17. Section of the 3D Net (Number of braided lines is reduced and braided lines inside the net are not shown for clarity) (Baelden 2013) (Arrows and lengths are added for clarity.)

The 3D net posed some technical feasibility concerns. The rate at which the ship winches the adsorbent to the surface allowed insufficient time for the continuous elution-regeneration system to be realistic. The adsorbent net is processed at a rate of 10 meters/minute, implying that adsorbent elution and regeneration is completed in under one minute given the size of the chemical reactors. An additional potential issue is the mooring and replacement of spent adsorbent net. Each 3 km long x 21 m wide net is a single closely coupled structure. The cost analysis does not allow for repair of damaged or fouled adsorbent net or replacement of adsorbent that has reached the end of its lifetime.

The MIT team also produced a cost estimate for a symbiotic system of braids and elution stations attached to offshore wind turbines. The system used the same adsorbent braids described in (M. Tamada, et al. 2006) and (Schneider and Sachde 2013). The wind turbines power the winching system that conveys the adsorbent through seawater as well as the co-located elution reactor. The system was sized to produce ~1 tonne U/yr per wind turbine. As such, it would require 20 100-m long adsorbent 'loops' with a total belt length of 4,000m so that each turbine would carry 60 tonnes of adsorbent. An illustration of this system is shown in Figure 18.

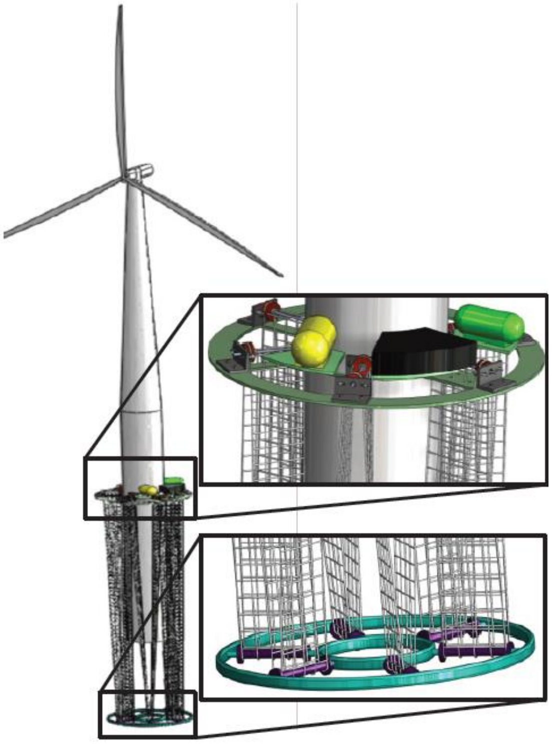


Figure 18. Symbiotic Mooring Scheme. For easiness to see, only 6 loops of belt instead of 20 are drawn in the figure. (Baelden 2013)

The cost of uranium recovery for the symbiotic wind turbine system was estimated to be $400 / kg U. Certain challenges are faced by this design. Drag forces on adsorbent might be considerable given the large braid lengths needed to attain the desired production rate and the fact that the braids are not free-floating as in (M. Tamada, et al. 2006) and (Schneider and Sachde 2013). Also, the continuously-operating elution and regeneration system may face the same timing and plausibility issues as arose with the 3D net scheme.

SUMMARY

The literature review explored cost estimates for uranium recovery from seawater through the 1960s to today. Some studies from the 1960's, (Davies 1964), produced notably low cost estimates, even including inflation. However, not all of the economic model assumptions or methods were clearly stated for the study. A detailed critique was not possible because the components of the cost (adsorbent, mooring, and elution) are omitted from the source. The work in the 1970's continued to focus on hydrous titanium oxide and packed bed adsorbents. Much of the work published in the 1970s focused on the engineering challenge of bringing large volumes water in contact with adsorbent, so proposals often involved the pumping of great quantities of water through large structures. The 1980's marked the first publications focusing on the amidoxime adsorbent, initially in packed beds. Offering a substantially larger adsorption capacity (and adsorption capacity driving the economics for all systems), the discovery of the amidoxime ligand for uranium recovery from seawater ended the use of hydrous titanium oxide. The 1980's work still used pumps to move water through beds as the method for exposing adsorbent to seawater. Work in the 1990's improved on the amidoxime grafting process and saw the development of a free form fiber adsorbent substrate. The fibrous material for the adsorbent allowed adsorbent to be deployed in a free-standing way, with no need for containers or packed beds. This change drove strategies where ocean water did not need to be actively pumped or moved; the costs and energy use associated with pumping had been seen to effectively cripple the economic viability of the technology. Adsorbent could now float in water and passively collect uranium, at the expense of a reduced rate of uranium adsorption and consequent need to extend immersion times. The 2000's to today have seen continued improvements in amidoxime ligand production chemistry and fibrous polymer substrate. This allowed for increased adsorption capacity, as more ligands are exposed to the water per mass of fiber. The most recent studies built upon the free form fiber adsorbent to create additional mooring schemes that used even less energy and resources. Finally, the methodological rigor and level of detail of the cost estimates increased with use of more comprehensive and in depth models.

The general conclusions of the body of research reviewed here are as follows:

-passive systems are more cost effective than systems that involve pumping;

-longer adsorption campaigns have higher yields;

-small diameter fibrous adsorbents have higher capacities than beads or precipitates that require packaging;

-adsorption capacity is the largest driver of cost;

-durability and number of uses are another major cost driver;

-a higher capacity does not necessarily mean a lower cost. If the ligand or substrate is more expensive to produce, the overall cost may increase relative to a similar system with a lower adsorption capacity but cheap materials;

-many different substrates exist, with the HDPE being the most widely-used.

For a recovery system to be economically viable, the ratio of adsorption capacity in g U / kg ads to the cost of producing the adsorbent material should be as large as possible. The mooring strategy needs to be passive and consume minimal energy. That means relying on the natural motion of the seawater rather than induced movement of the adsorbent or seawater to collect uranium. A final note is that none of the reviewed systems would be economically competitive against current terrestrial mining. Uranium from seawater will likely remain a ‘backstopping’ technology for some time to come. Table 3 summarizes the results and key metrics for each study reviewed.

Table 3. Cost estimates for uranium recovery from seawater

Source	Year	Cost Estimate (2010 $)	Capacity (g U / kg ads.)	Adsorbent	Substrate	Substrate structure	Mooring Strategy	Uses of adsorbent	Degradation (%/use)	Co-products	Length of Campaign (Days)
Davies	1964	$410	0.26	Hydrous Titanium Oxide	Solid insoluble resin beads - glass wool	Packed beds with support	Tidal usage of lagoons	Not Listed	Not Listed	None listed	20
Davies	1964	$210	0.26	Hydrous Titanium Oxide	Solid insoluble resin beads - muslin	Packed beds	Tidal usage of lagoons	Not Listed	Not Listed	None listed	7
Kanno	1981	$3,400	0.196	Hydrous Titanium Oxide	Precipitate and is prepared by sifting onto a mesh	Packed beds	Pumping and fixed bed of adsorbent, on-shore parallel	20	0.10%	None listed	10
Kanno	1981	$2,300	0.200	Hydrous Titanium Oxide	Precipitate and is prepared by sifting onto a mesh	Packed beds	Pumping and fixed bed of adsorbent aligned breakwater	20	0.10%	None listed	10
Kanno	1981	$1,700	0.200	Hydrous Titanium Oxide	Precipitate and is prepared by sifting onto a mesh	Packed beds	pumps	20	0.10%	None listed	10
Kanno	1981	$2,600	0.2	Hydrous Titanium Oxide	Precipitate and is prepared by sifting onto a mesh	Packed beds	cubes in water with offshore	20	0.10%	None listed	10
Driscoll	1983	$800	0.094	Amidoxime	Acrylic Fiber	Small Radius Fibers	pumps and offshore platform	Not Listed	Not Listed	None	7

Table 3 (continued)

Driscoll	1983	$640	0.094	Amidoxime	Acrylic Fiber	Small Radius Fibers	pumps	Not Listed	Not Listed	Molybdenum and Vanadium	7
Bitte	1983	$1,500	7.2	Amidoxime	Acrylic	Fluidized beds	boats/floating structures with pumps	10	Not Listed	Not Listed	360
Bitte	1983	$290	6.5	Amidoxime	Acrylic	Fluidized beds	boats/floating structures with pumps	25	Not Listed	Not Listed	360
Koske	1983	$2,100	70%	Amidoxime	Acrylic	Granulate in structure	Floating structure that utilizes convection - Loop formation	Not Listed	Not Listed	Not Listed	Not Listed
Koske	1983	$980	80%	Amidoxime	Acrylic	Granulate in structure	Floating structure that utilizes convection - Loop formation, Compares to fluidized bed	Not Listed	Not Listed	Not Listed	Not Listed
Forberg	1983	$2,000	3.3	Amidoxime	Acrylic	Pellets in Beds	Wave powered floating structure	Not Listed	0 - "Negligible"	Not Listed	27.5
Forberg	1983	$350	5.28	Amidoxime	Acrylic	Mats, free floating	Wave powered floating structure	Not Listed	0 - "Negligible"	Not Listed	27.5
Nobukawa	1989 & 1990	$900	3.2	Amidoxime	Acrylic Fiber	Fiber in Beds	Fiber in beds hanging from boats	Not Listed	Not Listed	Not Listed	40
Nobukawa	1994	$500	4.6	Amidoxime	Acrylic Fiber	Fiber in Beds	Fiber in beds hanging from boats	Not Listed	Not Listed	Not Listed	60

Table 3 (continued)

Sugo	2001	$680	6	Amidoxime	HDPE - Radiation Grafting	Fiber	Buoy method	20	4%	Not Listed	60
Sugo	2001	$640	6	Amidoxime	HDPE	Fiber	Floating body method (large buoy)	20	4%	Not Listed	60
Sugo	2001	$370	6	Amidoxime	HDPE	Fiber	Chain-binding method in ski lift strategy	20	4%	Not Listed	60
Tamada	2007	$1,000	2	Amidoxime	HDPE	Fiber	Long free floating braids in kelp field formation	6	Not Listed	Not included	60
Schneider and Sachde	2011	$1,200	2	Amidoxime	HDPE	Fiber	Long free floating braids in kelp field formation	6	5%	Not included	60
Schneider and Lindner	2012	$1,000	2.76	Amidoxime	HDPE	Fiber	Long free floating braids in kelp field formation	6	5%	Not included	60
Schneider and Lindner	2014 (Submitted)	$640	3.08	Amidoxime	HDPE	Fiber	Long free floating braids in kelp field formation - uses small boats to recover	6	5%	Not included	60
Baelden (MIT)	2013	$330	2	Amidoxime	HDPE	Fiber	Braids in 3-D Net formation	18	4.4%	Not included	30
Baelden (MIT)	2013	$400	2	Amidoxime	HDPE	Fiber	Symbiotic System with wind turbines	18	4.4%	Not included	38

Methodology

This thesis attempts to address that concern by assessing the cost impacts of a proposed biomaterial substrate, chitin. The following section outlines the methodology of uranium recovery from seawater system using an amidoxime ligand attached to a chitin nanomat as adsorbent with the ‘off-shore’ mooring and elution strategy presented in (Schneider and Lindner 2012). It also presents a sensitivity analysis with a ‘hair-net’ strategy of a net of adsorbent braids attached to the belly of a large container ship.

The goal of the cost assessment was to obtain a uranium production cost, which can viewed as a cost benefit or return on investment analysis. The uranium production cost is a ratio of cost of producing, mooring and eluting uranium from a unit mass of adsorbent over the amount of uranium obtained by that adsorbent. Equation 3.1 shows this relationship.

$$\underset{(\$/\text{kg U})}{\text{Uranium production cost}} = \frac{\text{Cost per unit mass of adsorbent}}{\text{Uranium product per unit mass of adsorbent}} \qquad \text{(Eq. 3.1)}$$

The methodology for calculating the uranium product per unit mass of adsorbent was to sum the product for each use of a tonne of adsorbent. The product was based on adsorption capacity, number of uses of adsorbent before it was disposed, and the degradation rate of the adsorbent (measured as a percent capacity loss per use.) The product was also discounted for time. The discount rate was annually 7% (Schneider and Sachde 2011) and the degradation per use was 5% (Sugo, et al. 2001). Calculating the numerator, the cost per unit mass of adsorbent, was slightly more complicated and is the focus of the rest of this section.

A methodology for conducting cost estimations of nuclear industrial technologies was established in the (Economic Modeling Working Group of the Generation IV International Forum 2007) (EMWG) as part of the OECD (Organization for Economic and Cooperative Development.) For cost analyses at the early stages of a technology's development when the process and components are uncertain, as is the case for uranium recovery from seawater, the major equipment cost estimates were used to produce system costs through scaling factors determined through a meta-analysis of major equipment and plant costs. Each component of costs, direct and indirect, relevant to industrial technologies was considered using the code of accounts method described in (EMWG 2007) and (Remer and Chai 1993). These costs included land, taxes, fees, permitting, process equipment, electrical equipment, contingency, etc. that are not specified in detail at the preliminary top down level of assessment presented here. A life cycle discounted cash flow (LCDCF) approach was utilized to synthesize the system component costs into a uranium production cost in $/kg U. The implementation of the EMWG approach to the adsorbent technology for uranium recovery from seawater was fully documented in (Schneider and Sachde 2011) and (Schneider and Lindner 2012).

To complete the methodology set forth in the EMWG, a block flow diagram or detailed process flow diagram was developed for both the overall process and each individual step to the level of detail available. Figure 19 shows a process flow diagram.

That process was separated into sections:

- adsorbent production,
- mooring,
- elution/purification,
- disposal of adsorbent,
- product.

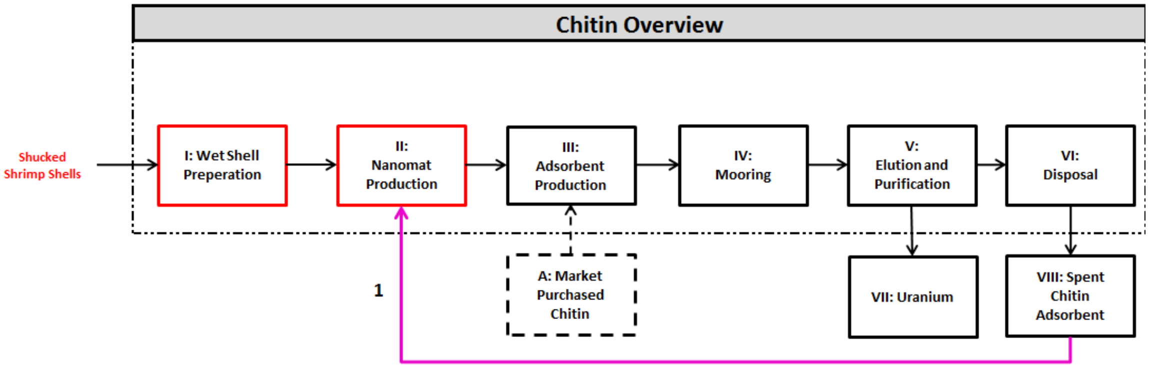


Figure 19. Overview of Uranium Recovery from Seawater with a Chitin Nanomat Based Adsorbent

The pink line labeled 1 shows a potential sensitivity analysis where spent chitin adsorbent was stripped of the amidoxime ligand with strong acid and a fresh ligand was grafted.

Adsorbent production data came from two groups of sources: for high molecular weight chitin nanomat production related processes, data was from conversations with the University of Alabama Rogers' group and Jon Bonner (Barber 2013) (Bonner 2010) (Barber, Griggs, et al. 2013) and for ligand production and chemical plant processes, data was from (M. Tamada, et al. 2006) and (Schneider and Sachde 2011). Mooring data was the same models and data in (Schneider and Lindner 2012) and material updates in (Schneider and Lindner 2014). Elution and purification data came from original sources in (M. Tamada, et al. 2006) and material and equipment cost updates in (Schneider and Sachde 2011). Disposal data was sourced from the sell spent adsorbent as scrap material and hazardous chemical disposal for some adsorbent production chemicals, outlined in (Schneider and Lindner 2012), with updates for the chitin process chemical disposal for semi-hazardous disposal from conversations with the largest U.S. chemical disposal firm, Clean Harbors (Clean Harbors 2013).

Data for equipment and chemicals came from industry analysis reports, literature reviews, or meta-analysis when available. If none of those were available, the author conducted a market size and cost meta-analysis through obtaining quotes from industrial suppliers in western markets and in eastern markets, often through the e-commerce website Ali-Baba.com.

MODEL AND PERFORMANCE PARAMETERS

The model and performance parameters outline the key metrics which are used to create the return on investment analysis, both the cost for producing uranium as well as the benefit of amount of uranium recovered, for uranium recovery from seawater.

Parameter	Value	Unit
Annual Uranium Production	1,200	metric ton/year
Adsorption Capacity	3.09	g U/ kg adsorbent
Length of Mooring Campaign	60	days
# of Adsorbent Uses	6	N/A
Recovery efficiency	100%	N/A
Adsorbent Degradation Rate	5%	% per recycle
Degree of Grafting	100%	
Ionic Liquid (IL) Reusability	0%	
IL wt. pct. in IL/Chitin solution	98%	
Chitin Nanomat Reusable	No	
Economies of Scale for Ionic Liquid	No	
Disposal of Ionic Liquid	Non-hazardous	

The first rows of values that were the same as the original Japanese estimate (M. Tamada, et al. 2006) and carried through the ORNL-UT studies (Schneider and Sachde 2011) (Schneider and Lindner 2012) with the adsorption capacity updated in (Schneider and Lindner 2014). The five rows were values unique to the chitin scenario except adsorption capacity. This analysis proceeded as if the adsorbent could reach that capacity, observed in Oak Ridge National Laboratory experiments with the amidoxime-HDPE adsorbent, holding all else constant (Schneider and Lindner 2014). A result using the amidoxime-chitin observed capacity was 0.00348 g U / kg ads. This low capacity was largely due to a low degree of grafting, 9%. Perturbing the values unique to the chitin scenario provides the basis for the sensitivity analysis as those values are seen to be the largest contributor to cost after adsorption capacity.

GRAFT PERCENTAGE

The amount of adsorbent required per year was about 65,000 tonnes. This was calculated from the system parameter of 1,200 tonnes U recovered per year, adsorption capacity of 3.09 g U / kg ads., and the number of campaigns completed per year, 6 (Schneider & Sachde, 2011). Once the amount of adsorbent was determined, the amount of chitin and chemicals required was calculated using Equation 3.2.

Adsorbent mass = Chitin nanomat mass + Ligand (Amidoxime) mass (3.2)

The relationship between the mass of chitin versus the mass of ligand is governed by the graft percentage or degree of grafting (DoG). DoG is weight change of the fiber before and after ligand is grafted. Equation 3.3 shows this relationship.

$$\boldsymbol{Degree\ of\ Grafting}\ (\%) = \frac{\boldsymbol{W_G - W_O}}{\boldsymbol{W_O}} * \mathbf{100} \qquad (3.3)$$

where

W_G = Weight of grafted chitin nanomat (65,000 tons)
W_O = Weight of ungrafted chitin nanomat (32,500 tons)

Experiments at the University of Alabama using the chitin nanomat based adsorbent and grating the amidoxime ligand showed a degree of grafting of 9%. That degree of grafting compared 100% assumption in Tamada 2006 and Schneider 2011, 2012, and 2014. The relatively low degree of grafting had implications on the adsorption capacity seen in the next section.

ADSORBENT CAPACITY

Laboratory experiments using the chitin nanomat based adsorbent with the amidoxime ligand in filtered seawater conducted at Pacific Northwest National Laboratory (PNNL) showed adsorption capacity of 0.00348 g U / kg adsorbent or 3.48 ppm (Gill 2013). That compares to 3.09 g / kg for the high density polyethylene (HDPE) based adsorbent tested in the same system and set of experiments at PNNL (Schneider and Lindner 2014). Both adsorbents used the amidoxime ligand. The HDPE adsorbent was prepared by chemists and chemical engineers at Oak Ridge National Laboratory. The Japanese amidoxime-HDPE adsorbent achieved 2 g U / kg ads. (M. Tamada, et al. 2006) Other adsorbents with similarly low capacity that had been considered for further development were the biosorbers Rhizopus Arrizus and Penicillium Chryzogenum (Borzekowski, Driscoll and Best 1982).

The low degree of grafting meant less ligands were available for adsorption which in turn produced a low adsorption capacity. For reasons of producing a practical cost assessment result, the cost assessment proceeded as if the chitin nanomat could obtain 100% degree of grafting and the same adsorption capacity as the amidoxime/HDPE system. Sensitivity analysis was conducted and presented in the results showing the impact of a 9% degree of grafting and 3.48 ppm U capacity.

WET, SHUCKED SHELL TO SHELL POWDER

The first step in the adsorption production process was to transform wet, shucked shell to shell powder. The wet shell was modeled as taken from shrimp and crab shucking shops as a waste product. The shells were then pressed with a screw press, dried, and ground. Figure 13 shows a process flow diagram for the facility that accomplishes this step.

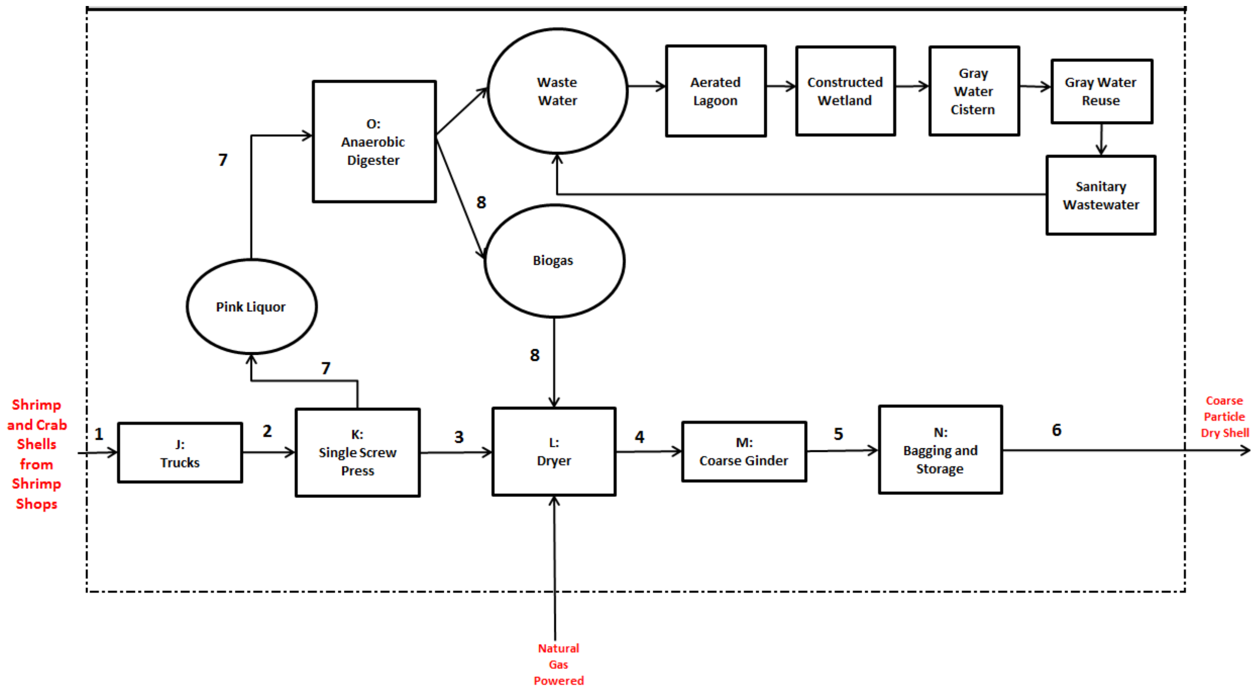


Figure 20. System process for wet, shucked shell to shell powder facility

A currently operating plant at Bayou La Batre, Alabama was used as a model. Its capital and operating costs were scaled using a standard industrial modeling exponent of 0.67. Equation 3.4 shows this relationship.

$$So = Ro * \left(\frac{Sa}{Ra}\right)^{0.67} \qquad (3.4)$$

where
So = Scaled Plant Cost ($)
Ro = Reference Plant Cost ($)
Sa = Scaled Plant Capacity (tonnes)
Ra = Reference Plant Capacity (tonnes)

At scale, the system would require 130,000 tonnes/year of dry shell needed. That compared to 2,500 tonnes/year dry shell capacity at the AL facility. The capital cost of the actual facility was \$5.176 million dollars (Bonner 2013). Plant operating labor and electricity costs were calculated the same way with scaling as the plant capacity with a yearly plant electricity usage of 8,790 GJ (Bonner 2013). The plant had 1 manager and 5 workers including a dump truck driver (Bonner 2013).

The wet, shucked shell input to the plant was a waste product from the local shrimp and crab market. Fishermen caught the shellfish and delivered them to 'shell shops.' These shops removed the meat from the fish and disposed of the waste. The cost of disposing this waste was \$120,000 in a landfill for the 5,400 tonnes of wet shell waste per year. The wet waste contained 46% dry weight which was 25% chitin on average.

The plant produced potentially valuable waste from tailings of the screw press that is mostly proteins, minerals, and ions from shellfish. Figure 14 shows the screw press in action. The filtrate or tailings from that was dried using an anaerobic digester producing a nutrient rich compost or manure that could be sold as a fertilizer.

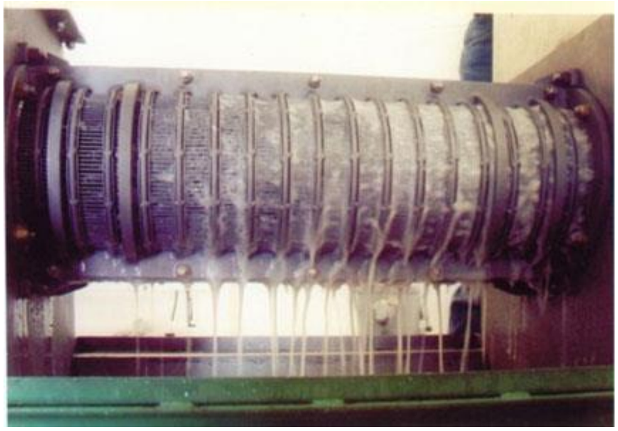


Figure 21. Screw press at shucked, wet shell facility. The first step in the process of creating shell powder. (Bonner 2010)

CHITIN NANOMAT PRODUCTION

Chitin nanomat production was based on a process developed by chemists at University of Alabama (Barber, Griggs, et al. 2013). Previous work in producing chitin nanomats was costly and energy intensive. The researchers at Alabama used an innovative approach to create high molecular weight chitin nanomats by dissolving the shell powder, a mix of chitin (25%) and proteins (75%), in an ionic liquid, 1-ethyl-3-methylimidazolium acetate, and electrospinning the mixture into a water bath to separate proteins from chitin. Ionic liquid was defined as a salt with a melting point below 100°C. Alabama's method produced high molecular weight chitin chains. These chains had bonding sites that the ligand, an amidoxime group, was chemically grafted in the next and final step of the adsorbent production. Figure 22 shows the electrospinning process.

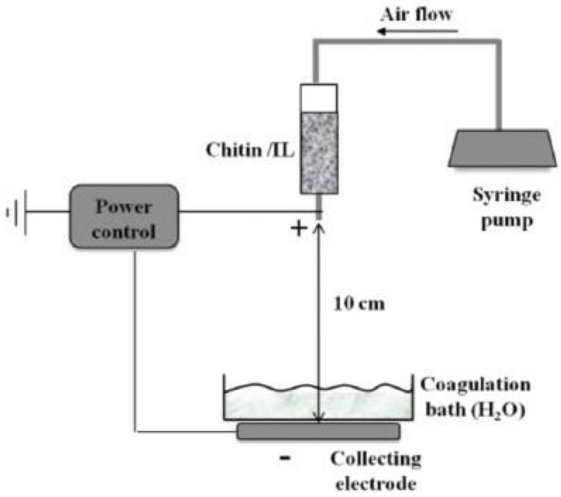


Figure 22. Electrospinning Process (Barber, Griggs, et al. 2013)

This process is presented in process flow diagram format in Figure 23.

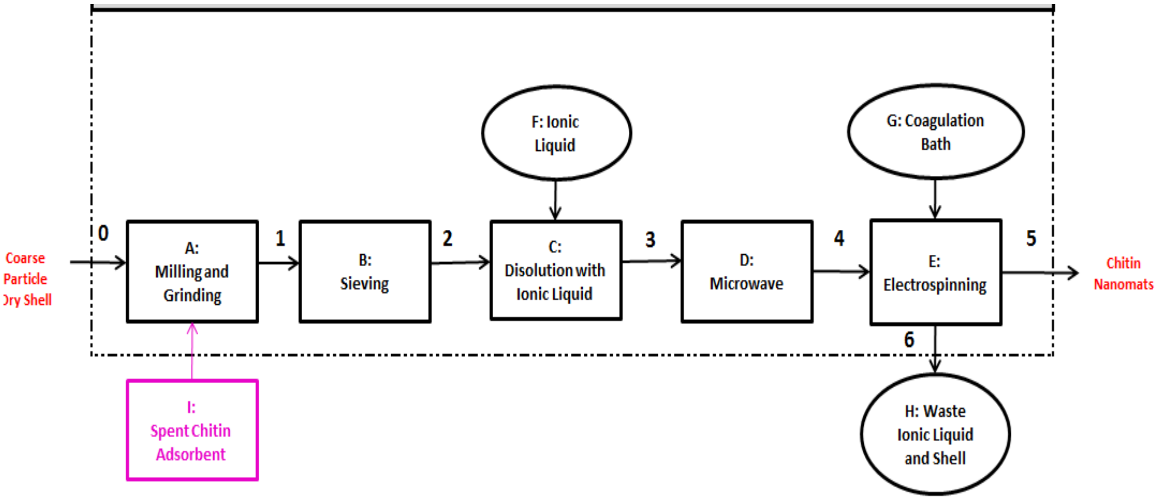


Figure 23. Process flow diagram for the nanomat production facility

The nanomat production steps were grinding the coarse shell powder into a fine powder, sieving out unwanted pieces, dissolving the powder in the ionic liquid, heating the mixture, and electrospinning the mixture. The components of the process were industrial grinders, sieves, electrospinners, and containers. The heat and electricity costs were also calculated.

The ionic liquid heating cost was conservatively calculated using an electric industrial boiler to heat the liquid by 80°C. The energy required to heat the ionic liquid was:

$$Q = m\, c\, \Delta\, t$$

Q = energy (kJ)

m = mass (kg)

c = specific heat, assumed to be the same as water (4.186 kjoule/kg °C)

$\Delta\, t$ = change in temperature, 80°C

The amount of ionic liquid required was based on a ratio determined experimentally from University of Alabama (Barber, Griggs, et al. 2013). The ratio was

98 w.t.% ionic liquid with 2 w.t.% shell powder. The shell powder was only 25% chitin. With the 32,500 tonnes of chitin needed per year and 25% chitin in dry shell powder, 6.4 million tonnes of ionic liquid were required. To heat that mass of ionic liquid, 590 million kwh of energy was necessary. With the cost of electricity per kilowatt hour at \$0.069, 2010 dollars from the Energy Information Agency via (Schneider and Sachde 2011) and an assumed 98% thermal efficiency, the total heating cost was \$41 million dollars.

The electricity cost for maintaining the voltage difference was calculated by using the baseline watts, 80 watt, and conservatively estimating plant uptime at 24hrs a day, 365 days a year to produce a kilowatt hour. That amount was multiplied by the cost of electricity per kilowatt hour, \$0.069, 2010 dollars from the Energy Information Agency via (Schneider and Sachde 2011). This value was negligible compared to the ionic liquid heating cost.

The ionic liquid was assumed to be only used once without any of the ionic liquid being able to be separated from the crash solvent (H_2O). Sensitivity analysis, shown in the results, explored the cost benefits of more favorable ionic liquid-to-chitin mixtures and recycle of some or all of the ionic liquid.

The chemical storage tank cost was calculated using an empirical based relationship found in (Peters, Timmerhaus and West, 2003) and employed in (Schneider and Sachde 2011). This relationship was based on a meta-analysis of tank costs and volume. The container for IL and H2O separation was only utilized in the sensitivity analysis where ionic liquid was recycled. The electrospinner extruded 0.078cc/min (Kato Tech Co., Ltd. 2014). Table 4 summarizes all of the equipment costs for the chitin nanomat production facility.

Table 4. Equipment for Chitin Nanomat Production Facility

Capital Equipment Item	**Cost at Scale [$]**	**Variable of Interest**
Grinder and Sieve	< $100,000	tonnes/hour, m^3 per hour, pressure, needle diameter
Electrospinner (syringe pump with voltage)	$83,000,000	
Metal Container (IL Storage)	$120,000,000	m^3
Boiler	$2,000,000	Tonnes/hour
Coagulation Bath	$120,000,000	m^3
Container for IL and H2O separation	$45,000,000	m^3 for IL recycling
Operational Cost Item	**Cost at Scale [$/yr]**	**Variable of Interest**
IL heating	$41,000,000	Based on 80^{o} C DT, water heat capacity & electric heating source

Nanomat Production Chemical Market Analysis

Water and 1-ethyl-3-methylimidazolium acetate, the ionic liquid (IL), were the only chemicals used in the chitin nanomat production. Additional chemicals were used for the ligand production discussed in the next section. The ionic liquid market was analyzed for price and market size. It was found that chemical usage associated with large-scale chitin nanomat the production would significantly increase the world demand for the chemical, so the cost was scaled using 0.6 exponent (Whitesides 2012). Equation 3.5 shows this relationship.

$$P_2 = P_1 \left(\frac{M_2}{M_1}\right)^{0.6} \qquad (3.5)$$

P_1 =Current Unit Price ($/tonne)
P_2 =Unit Price for total scaled industry ($/tonne)
M_2 =Current Industry Size+Reference Case Usage (tonnes/yr)
M_1 =Current Industry Size (tonnes/year)

Through contacting and surveying chemical suppliers in the Western market as well as the Asian market, the total world production for the ionic liquid was determined to be 300 tonnes per year. This compared to calculated reference usage of 6,300,000 tonnes per year. The ionic liquid market would be significantly impacted by the production usage. The current price of $20,000 per tonne was scaled to $300 per ton.

Hazardous Chemical Disposal

Previous analysis showed that several chemicals used in the ORNL reference process were hazardous and required special disposal (Schneider and Lindner 2012). The author explored the issue of disposability of the ionic liquid. Material safety and data sheets (MSDS) for the ionic liquid are only available in preliminary form as the chemical is not fully characterized. This was consistent with the market analysis result that the IL market and usage was underdeveloped. A quote from Clean Harbors, the largest chemical disposal firm in the United States of America, indicated that the ionic liquid is semi-hazardous and the disposal cost would be $152 per 55 gallon drum (ca. $670/tonne) (Clean Harbors 2013).

This evaluation was tentative based on the incomplete data reflected in the MSDS, so the disposal cost was *not* included in the U production cost estimate shown later in this paper. If this disposal cost were included in the model holding all else constant, the production cost would be uneconomical at twice the baseline value.

Chitin Market Analysis

A market analysis and literature-meta analysis were conducted to explore if there was enough chitin produced annually to meet the system requirements. The results of that analysis showed around 250 billion tonnes of unrefined chitin were disposed each year worldwide. The current world market for processed chitin appeared to be 1.8

million tonnes per year, but not in the form of high molecular weight nanomats. There was considerable variability on particle size and purity. The weighted average price of processed powdered chitin was $2,000 per tonne. At scale (1,200 tU/yr of production), the uranium recovery from seawater system using the amidoxime-chitin nanomat adsorbent system would require 32,500 tonnes of chitin nanomat per year. Because the analysis utilized shrimp and crab shell waste as the source for chitin, the cost for the waste was assumed to be zero.

LIGAND PRODUCTION THROUGH CHEMICAL GRAFTING

Although the ligand was the same as that used by the Japanese Atomic Energy Agency (JAEA) (M. Tamada, et al. 2006) and Oak Ridge National Laboratory (ORNL) (Kim, et al. 2013), (Tsouris, et al. 2012), the chemicals to make the ligand were unique (Barber, Griggs, et al. 2013) as the process is entirely chemical and does not rely upon irradiation to open grafting sites. The process flow diagram is shown in Figure 24. The new chemicals utilized were 4-chlorobutyronitrile, triethylamine, and ethyl acetate.

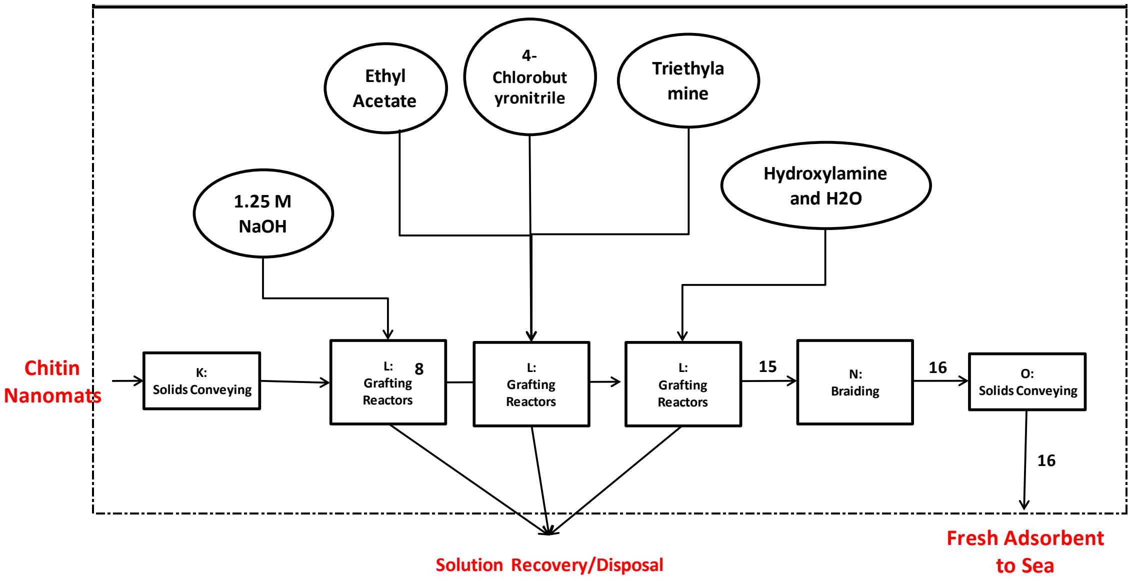


Figure 24. Process flow diagram for amidoxime ligand grafting to the chitin nanomat

Figure 25 highlights the chemical grafting process in more detail.

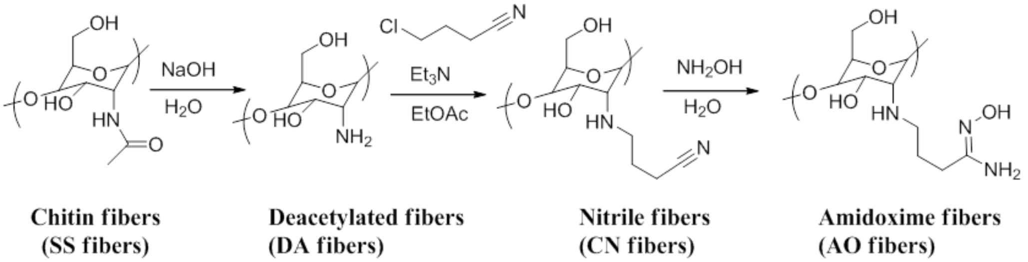


Figure 25. Ligand production chemistry (Barber and Rogers 2013)

To calculate the amounts of chemicals, the stoichiometric relationships from the chemical grafting reactions were used, with an assumption of 100% completion and no losses. The reason for the stoichiometric, 100% grafting efficiency was for ease of calculation of the chemical usage for this preliminary estimate. This also followed the previous estimates methodologies, Japanese and ORNL-UT, use of 100% efficiency for elution recovery of uranium from full adsorbent. The resulting chemical requirements and a comparison between the most recent ORNL estimate (Schneider and Lindner 2014) are listed below in Table 5.

Table 5. Chemical amounts for the ligand grafting and nanomat production

Chemical	Tonnes per tonne of HDPE	Tonnes per tonne of Chitin	Purpose of Chemical and assumption of use
Acrylonitrile	0.7	0	
Hydroxylamine	1.12	0.029	Reagent, part of ligand
Methanol	0.53	0	
Dimethylsulfoxide	0.88	0	
Methacrylic Acid	0.18	0	
Polylactic Acid	0.40	0	
Tetrahydrofuran	0.10	0	
NaOH	0	0.67	
Ethyl acetate	0	21.0*	Solvent, not depleted*
4-Chlorobutyronitrile	0	0.092 (9% Degree of Grafting) or 0.63 (100% Degree of Grafting)	Reagent, part of ligand
Triethylamine	0	0.021*	Solvent, not depleted*
Ionic Liquid	0	49.0	Solvent, consumed

Ligand Grafting Chemical Market Analysis

The ligand production chemicals were analyzed for price and market size. The only chemical market found to be significantly impacted by the production usage was the ionic liquid from the chitin nanomat production step. That is to say all of the other chemicals had well developed markets relative to the production usage amount of the chemical. Thus no other chemical prices were adjusted by economies of scale. Table 6 describes the relationship of the chemicals to the chitin nanomat.

Table 6. Adsorbent production chemical usage amount and cost

Chemical	tonnes per tonne of chitin	Cost of chemical ($/tonne)
Sodium Hydroxide	0.67	$480
Ethyl acetate	21	$890
Triethylamine	0.021	$2,000
4-chlorobutyronitrile	0.029	$12,000
Hydroxylamine	0.092	$1,500
Ionic Liquid (1-ethyl-3-methylimidazolium acetate)	49	$360

Results

Three sets of results are presented. The system, as described in the methodology, employed:

- an chitin nanomat based adsorbent
- with an amidoxime ligand
- in a kelp field mooring strategy
- combined with an offshore elution strategy

The first result is the uranium production cost using the experimentally observed degree of grafting and adsorption capacity. This result is presented in the discussion of degree of grafting's impact on adsorption capacity. The second result is the production cost with the assumption that the chitin nanomat production could achieve the same degree of grafting of 100% and adsorption capacity of 3.09 g U/ kg ads. as the current standard adsorbent (Schneider and Lindner 2014). The last set of results is the sensitivity analysis, including semihazardous disposal for the ionic liquid and ways to reduce the production cost.

URANIUM PRODUCTION COST WITH EXPERIMENTALLY OBSERVED DEGREE OF GRAFTING AND ADSORPTION CAPACITY

From experimental results at University of Alabama, the degree of grafting of the amidoxime ligand to the chitin nanomat substrate was nine percent. The previous estimates in (M. Tamada, et al. 2006), (Schneider and Sachde 2011), and (Schneider and Lindner 2012) assumed 100% degree of grafting. The implication of 9% vs. 100% is that there are fewer amidoxime ligands and thus less available bonding sites for uranium. The lower degree of grafting resulted in a reduced adsorption capacity of 0.00348 g U / kg ads compared to 3.09 g U / kg ads. in the previous estimates (Schneider and Lindner 2014).

The physical and system effects of the lower degree of grafting are highlighted in Table 7.

Table 7. Degree of grafting comparison summary and implications

	HDPE	**Chitin**
Degree of Grafting	100%	~ 9%
Bonding Sites	Inside and outside on HDPE fiber	Bonding only on surface
Grafted adsorbent is…	equal parts fiber and ligand by weight	mostly **chitin**; low weight percentage of ligand

In addition to the lower capacity, the lower DoG meant less amidoxime mass and more chitin mass. That had important sizing implications for which of the three processes of chitin nanomat adsorbent production was a larger scale. Because the substrate was more mass than the ligand, the substrate production processes occur at larger scale than the ligand grafting process. The substrate production included wet, shucked shell to shell powder and chitin nanomat production. Those had larger process scales with greater chemical and material inputs than the amidoxime ligand chemical grafting.

This had additional cost implications because the substrate was more costly than the ligand. If the substrate is more costly than the ligand, then as DoG decreases and holding uranium uptake fixed, the U production cost would increase because substrate was a larger share of the total adsorbent mass and the substrate costs more. Conversely, if the substrate was cheaper than the ligand, the opposite would be true: as degree of grafting decreased, uranium production cost decreased.

The result of using the observed capacity of 0.00348 g / kg and the 9% degree of grafting with the relative higher chitin nanomat production process was an uneconomical cost of $330 million per kg U.

URANIUM PRODUCTION COST USING AN AMIDOXIME LIGAND ON A CHITIN NANOMAT BASED ADSORBENT

While the previous result produced an impractical cost, the following result explored the assumption that the chitin nanomat production could achieve the same degree of grafting of 100% and adsorption capacity of 3.09 g U/ kg ads. as the current standard adsorbent (Schneider and Lindner 2014) produced a uranium production cost of $4,100 per kg U. This was relatively high when compared to other schemes. A comparison of results is summarized in Table 8.

Table 8. Results of recent cost analyses with a similar scheme

Scenario	Production Cost ($/kg U)
JAEA Estimate	$1,000 (M. Tamada, et al. 2006)
UT's Cost Assessment of the JAEA Estimate	$1,220 (Schneider and Sachde 2011)
ORNL Estimate	$640 (Schneider and Lindner 2014)
Chitin Estimate	$4,100

The costs by component are shown below in Table 9 and as a pie chart in Figure 26. IDC is interest during construction. O&M is operations and maintenance.

Table 9. Uranium production cost by process component

Stage in System	Cost Item	$/kg U
Adsorbent Production Costs	Capital Cost	$310
	O&M	$360
	Materials	$2,800
	Utilities	$180
Adsorbent Mooring Costs	Capital	$110
	O&M	$92
	Chemicals and Materials	$37
Elution-Purification Costs	Capital	$13
	O&M	$15
	Chemicals and Materials	$2
	Utilities	$7
Disposal and Construction Costs	Interest During Construction	$210
	Sell Value from Adsorbent	-$40
Results		$4,100

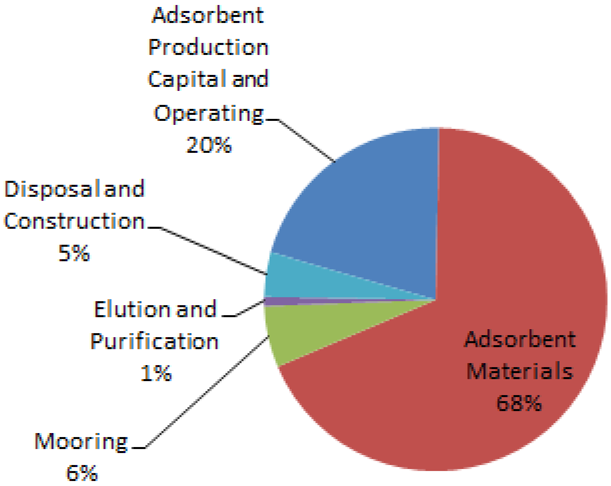


Figure 26. Component share of Final Cost

A breakdown of the adsorbent material costs by component revealed that the ionic liquid dominated the materials cost. Figure 27 shows the components of the adsorbent materials costs.

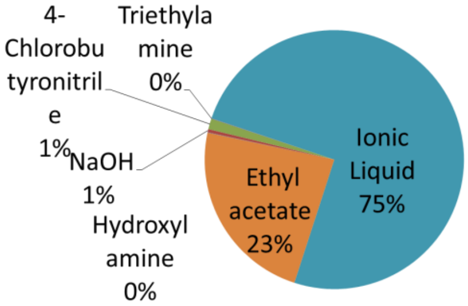


Figure 27. Adsorbent material costs by component

SENSITIVITY ANALYSIS

The sensitivity analysis explored ways to further reduce the production cost by varying the largest cost contributors. The sensitivity analysis also included the result from including the semihazardous disposal of the ionic liquid, something that did not lower the production cost. Included below in Table 10 are the relevant sensitivity analyses.

Table 10. Sensitivity analysis results

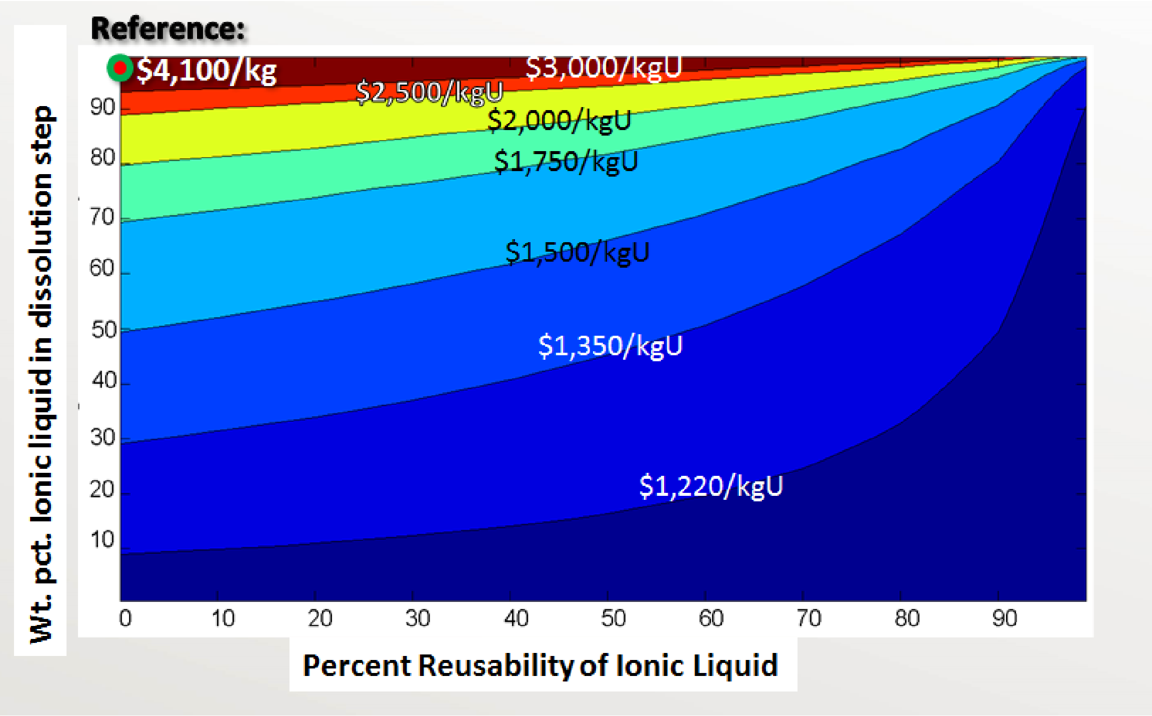
Scenario	Uranium Production Cost Change (% of previous, 100% degree of grafting estimate)
Include semihazardous disposal cost for ionic liquid	+100%
Reuse chitin nanomat as open material with open bonding sites	-67%
Reusing 80% of the ionic liquid	-51%
Reuse 80% of ionic liquid and use 20 weight percent ionic liquid with 80 w.t.% shell.	-78%

For the semihazardous disposal of the ionic liquid, because the amount of ionic liquid was so large and the disposal cost was slightly greater than the estimated cost of the ionic liquid at scale, including the IL disposal significantly increased the production cost. The semihazardous disposal cost would be $7.3 billion a year.

If the chitin nanomat could be reused after the adsorbent's life cycle was completed by removing and regrafting the amidoxime ligand, the cost would be reduced by 67%. That result was due to the largest portion of the cost coming from the chitin nanomat production step.

The final two rows of the sensitivity analysis explored the effects of a reduction in ionic liquid consumption. Results showed a scenario where the chitin nanomat production process allowed for recycling or reusing of ionic liquid. Results also showed a scenario where a greater weight percent of shell powder would be dissolved in the ionic liquid. Both of reduced the consumption of ionic liquid. If 80% of the ionic liquid can be reused, the cost was reduced by 50%. If 80% of the ionic liquid could be reused and the ionic liquid/shell powder mixture could be reduced to 20/80 weight percent, the cost of uranium production was reduced by almost 80%.

Figure 28 represents a sensitivity analysis of varying the reusability (in percent) of ionic liquid interacting with the weight percentage of ionic liquid in the IL/shell powder mixture. The green and red dot at the top left of the contour plot is the current estimate of $4,100 / kg U.



The z-values are log scale.

Figure 28. Sensitivity analysis with varying recyclability and weight percent of ionic liquid.

Results from Figure 28 suggested increasing the weight percentage of the shell powder in ionic liquid would have a significant impact on reducing the production cost and increasing the percent reusable of ionic liquid can interact with that variable to further reduce production costs.

Discussion

For the high molecular weight chitin nanomat based adsorbent with the amidoxime ligand, largest factors affecting the production cost were degree of grafting with adsorbent capacity. The relatively low degree of grafting when compared to past amidoxime-polyethylene adsorbents, 9% versus 100%, resulted in an adsorption capacity reduction by a factor of around 1,000, 0.00348 g U / kg ads versus 3.09 g U / kg ads. That low capacity produced a result that was uneconomical and unpractical. Driscoll 1983 noted adsorbent performance (capacity) was the most important factor for uranium production cost. 30 years later, that observation is still valid. Through design and improving experimental results, future research would need to focus on increasing degree of grafting and thus adsorption capacity.

The results proceeded as if the adsorbent could reach the 100% degree of grafting and a uranium uptake of 3.09 g U / kg ads. Given that assumption, the next biggest factor affecting cost was ionic liquid consumption. The ratio of 98% ionic liquid mass to 2% shell powder mass with only 25% of the shell powder containing chitin meant the system required over 6 million tonnes of ionic liquid to produce about 30,000 tonnes of chitin nanomat per year. Even scaling the ionic liquid cost to a relatively low bulk chemical cost (~$300 per tonne) when compared its current price of $20,000 per tonne, the large yearly consumption outweighed the economics of cost model. In addition, that result did not include the semi-hazardous waste disposal cost for ionic liquid. When that cost was included, the uranium production cost doubled.

As mentioned before, the high molecular weight chitin nanomat production system is an innovative process and the ionic liquid, 1-ethyl-3-methylimidazolium acetate, is a relatively new and understudied chemical. Reducing the consumption of the ionic liquid, through reusing it or increasing the weight percentage of shell mass in the solution mixture, would be paramount to improving the economics of the uranium production cost.

A final discussion note is the degradation and number of uses of adsorbent can largely impact the production cost. This study assumed 6 uses with 5% loss per use. Studies on degradation and number of optimal uses with the chitin nanomat have not been conducted. Similarly, studies on degradation and uses with the polyethylene were only conducted in Sugo 2001. An updated value could have wide positive or negative impact on the cost.

Conclusions

This paper included a literature review of past estimates of uranium recovery from seawater and a cost estimate for a new technology of chitin nanomat substrate with the amidoxime ligand. The general conclusions of the body of literature research reviewed here are as follows:

-adsorption capacity was the largest driver of cost – when a new ligand or substrate proved to have a higher capacity, research using previous adsorbent was halted

-durability measured as degradation of the adsorbent per use and number of uses were major cost drivers;

-a higher capacity did not necessarily mean a lower cost. If the ligand or substrate was more expensive to produce, the overall cost may increase relative to a similar system with a lower adsorption capacity but cheaper materials;

-many different substrates were employed, with the polyethylene being the most widely and recently used;

-passive mooring systems were more economical than systems that involve pumping seawater;

-longer adsorption campaigns yielded more uranium;

-small diameter fibrous adsorbents had higher capacities than beads or precipitates that require packaging;

-co-products could potentially reduce cost, but more research and experiments would be required.

A summary of the literature showed for a recovery system to be economically viable, the adsorption capacity should be as high as possible. The mooring strategy must be passive, consume minimal energy, and utilize the natural motion of the seawater rather than induced movement of the adsorbent or seawater to collect uranium. A final note was that none of the reviewed systems were economically competitive against current terrestrial mining from conventional sources of uranium. Uranium from seawater will likely remain a price ceiling technology for some time to come.

This paper also presented a new cost estimate that replaced polyethylene with a high molecular weight chitin nanomat while maintaining the amidoxime ligand and kelp mooring strategy. A top down approach was used to conduct the cost analysis. This same approach was recommend by OECD's Economic Modeling Working group and utilized in the recent assessments from which this assessment was based. To conduct the assessment, a process flow diagram was outlined for each step: adsorbent production, mooring, elution/purification, and adsorbent disposal. The adsorbent production was the focus of the methodology because the change from previous estimates was replacing the substrate. The adsorbent production process was wet, shucked shell to dry powder, dry powder to chitin nanomat, and chitin nanomat to adsorbent through amidoxime ligand chemical grafting.

The results showed the degree of grafting was relatively low when compared to the amidoxime-polyethylene grafting, 9% versus 100%, and the impact of that was a lower adsorption capacity by a factor of 1,000, 0.00348 g U / kg ads. versus 3.08 g U / kg ads. Hence there was an uneconomical uranium production cost.

The remainder of the work assumed that the degree of grafting and adsorption capacity performance of the amidoxime-polyethylene adsorbent could be achieved. Even under that scenario, the uranium production cost from seawater using a chitin based nanomat with an amidoxime ligand was still not economically viable. The main reason for the continued high uranium production cost was the high ionic liquid consumption with no recyclability. The high molecular weight chitin nanomat production using ionic liquid was still in the early stages of development as was the use of the ionic liquid.

A sensitivity analysis was conducted by varying the largest cost and performance drivers. The largest cost contributor was the ionic liquid, which is used as a solvent for dissolving the shell powder. Decreasing the consumption of ionic liquid per unit of shell powder dissolved had the greatest impact on reducing the production cost. Another potential cost reduction was shown by assuming the ionic liquid could be separated from the crash solvent, H_2O, and reused. If the chitin nanomat could be reused by stripping it of the spent amidoxime ligand and grafting a new one, the cost would be even more significantly reduced as the consumption of ionic liquid would be drastically reduced. Finally, if the cost of disposing the ionic liquid as a semi-hazardous chemical was included in the model, the uranium production cost from the system doubled.

On a general concluding note, many cost analysis methodologies failed to include the environmental costs and benefits. The past uranium recovery strategies all placed foreign materials in the ocean. Moving away from that was a motivating factor for considering a chitin based adsorbent. A chitin based adsorbent is biodegradable and produced from a renewable resource. It was also made from the waste product of an existing industry. Employing the adsorbent would help prevent plastics from further being placed into the ocean. Future research will show and likely improve the viability and economics for this new, developing technology.

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