Chien Wai, principal investigator, displays the yellowcake uranium extracted using methods developed in NEUP-supported projects.
Photo courtesy of LCW Supercritical Technologies.

Seawater Yields Yellowcake Uranium

by Kate Meehan for DOE's Nuclear Energy University Program

Dipping a bundle of yarn into the ocean and pulling out uranium sounds easy enough. This method of extracting uranium from seawater, an effort led by Chien Wai, emeritus chemistry professor at the University of Idaho, has created quite a splash with its promising results. But while the process itself may be fairly straightforward, reaching this point of success has taken a significant amount of time and effort.

Uranium is a silvery-white metallic chemical element that occurs naturally in low concentrations in soil, rock and water. For many years, uranium was used primarily as a colorant for ceramic glazes and for tinting in early photography. Its radioactive properties were not recognized until 1866, and its potential for use as an energy source was not manifested until the mid-20th Century. Today, uranium is used to power commercial nuclear reactors that produce electricity and to produce isotopes used for medical, industrial and defense purposes around the world.

Traditionally, uranium has been mined the same way other heavy metals are extracted from the earth. In addition to environmental concerns, this method has a limited time span, as various agencies estimate that current methods of uranium mining will only provide around 100 more years of capacity for the world's nuclear power plants.

The potential for extracting uranium from seawater, by contrast, is almost limitless. Seawater contains approximately three parts per billion of uranium, a seemingly tiny amount. Yet with a total ocean volume of approximately 1.3x109 km^3, there are over 4 billion tons of uranium in seawater—about 1000 times the amount known to exist on land. Environmentally sustainable separation and recovery of uranium from seawater has been an ongoing research area supported by the Department of Energy's Office of Nuclear Energy (DOE-NE).

The low concentration of uranium in seawater (as well as its stable chemical form, uranyl tris-carbonato complex, or $UO_2(CO_3)_3$) makes the extraction of uranium extraction extremely difficult. Scientists, mainly in Japan, have been tackling this challenge since the 1980s. These scientists determined that amidoxime-based polymer adsorbents have the greatest potential, thanks to their mechanical strength and high uranium loading capacities.

To continue this area of study, Wai applied for—and received—support from DOE's Nuclear Energy University Program (NEUP) back in 2011. This was in addition to ongoing support from DOE's Small Business Innovation Research (SBIR) program for LCW Supercritical Technologies. Wai is CEO of LCW Supercritical Technologies, a company focused on bringing this new technology to market. Both avenues of funding from DOE have helped bring Wai's idea to fruition.

The first phase of his research was carried out over a two-year period and was then followed by a second, three-year NEUP research and development project. Over the course of these studies, Wai worked with both national laboratory partners and his home university. Oak Ridge National Laboratory (ORNL) developed an adsorbent and provided it to Wai, who then carried out most of the work at his lab at the University of Idaho. Uranium adsorption, elution and sorbent reuse tests were performed using a recirculating seawater flume system available at the Pacific Northwest National Laboratory (PNNL) Marine Sciences Laboratory located in Sequim, Washington.

ORNL's polymer adsorbent utilizes high-surface-area polyethylene fibers as the backbone material and shows very high uranium adsorption capacities. It is prepared through an intensive process of radiation-induced grafting and treatment with a strong potassium hydroxide (KOH) solution to make it effective for uranium adsorption in seawater. Hydrochloric acid has traditionally been used to elute uranium from the adsorbent, which must then be treated with KOH again to recondition the adsorbent. For his NEUP projects, Wai mainly used a variety of this adsorbent referred to as AF1.

In Wai's study, AF1 had an initial uranium adsorption capacity of about 3.7 g U/kg after 42 days of seawater exposure. After the acid elution and the KOH reconditioning process, the uranium adsorption capacity of the recycled adsorbent dropped drastically to about 0.5 g U/kg. Wai theorized that a combination of factors during the elution and reconditioning process causes physical and chemical changes to the material that reduce its uranium adsorption capacity. Spectroscopic techniques (FTIR and SEM) support this contention, as Wai observed a decrease in amidoxime groups as well as physical damage to the fiber structure of the material.

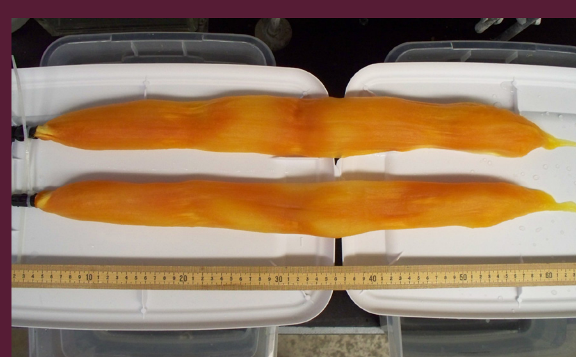
Wai's main objectives with his NEUP research included adsorption capacity, durability for reuse, and affordability, as these factors determine the economic feasibility for future commercial extraction of uranium from seawater. To this end, Wai aimed to develop a new, milder elution process that would result in minimal damage to the fiber adsorbent. During his five years of NEUP funding, Wai explored a number of different methods, including carbonate elution and supercritical fluid elution, before settling on a bicarbonate elution technique. Wai describes his new process, which uses sodium bicarbonate (baking soda), as "very effective" for removing uranium from the adsorbent.

In real seawater experiments carried out at PNNL, the fiber attracted heavy metals as well as natural organic matter, which was not removed by the bicarbonate elution. Wai added a dilute base (0.5M NaOH) soaking step to the process, which

Just Add Seawater

Tests at Pacific Northwest National Laboratory's Marine Sciences Laboratory have focused on recreating actual ocean conditions. The purpose is to better understand environmental factors that can degrade acrylic yarn as well as provide accurate estimates of uranium adsorption. The adsorbent is added by attaching it to a flume where raw sea water is circulated for approximately one month (photo: top right). At that time, the yarn is removed from the system, measured and packaged to be sent to Wai's lab in Moscow, Idaho (photo: bottom right).

Wai emphasizes that this research is in the preliminary stages. To increase production for large-scale industrial application, which would be needed to supply U.S. nuclear reactors, the system would have a large footprint. Wai estimates that several square miles would be needed to deploy enough yarn to collect the necessary levels of uranium.



removed organic matter as well as some of the transition metals. After this process, the initial uranium adsorption capacity of the recycled adsorbent remained virtually unchanged; however, uranium adsorption started to decrease with subsequent reuse. Wai theorized that the fiber material is probably not stable over long-term exposure to seawater.

To combat this, during the first phase of his DOE SBIR award, Wai developed his own highly efficient polymer adsorbent (LCW fiber) derived from acrylic yarn. The material is inexpensive, according to Wai, both to purchase and modify. Wai can start with any acrylic fiber, which can readily be found in craft stores in the form of yarn, or even in clothing stores already made into apparel.

"I went to Goodwill and picked up a sweater and a pair of gloves that were 100% acrylic," said Wai. "We can convert waste into a magical material."

In fact, if Wai could find a large enough volume of recycled fiber, he would not need to use any newly created material. The fiber is also reusable (though its life span is still under investigation), making this a truly green technology.

Once he has the acrylic fiber, Wai performs a simple chemical process to prepare it for uranium adsorption. The overall procedure is significantly cheaper than the process of radiation-induced grafting required to create fibers like AF1.

During the second phase his DOE SBIR grant, Wai's experiments yielded over 5 grams of yellowcake uranium (uranium oxide), a bit more than the size of a U.S. nickel. Yellowcake is the material used in the preparation of fuel for nuclear reactors. Right now, Wai only has the capacity for small-scale production at his lab in Moscow, Idaho, but he is looking to scale up.

Future experiments seek to test LCW fiber in an actual ocean installation. Thanks to an ongoing grant from the DOE SBIR program, Wai has continued his partnership with PNNL.

In 2019, the team will begin testing in the warm waters of the Gulf of Mexico. Since the material performs better in warmer water, Wai expects higher removal rates of uranium from the region than have been found at PNNL's home in the Pacific Northwest.

Looking forward, Wai envisions a bright future for his new technology. While uranium remains the focus, LCW fiber is also effective at removing heavy metals like lead from water. Wai sees the potential for LCW fiber to be used in a variety of ways to help with heavy metal cleanup, from a large mining site to the water filter in your kitchen. In fact, his company is currently comparing its technology to commercially available filters for drinking water.

Might we find LCW fiber on the shelf any time soon? Wai says the company is still in the testing phase. So far, experiments have established the fiber as nontoxic, but some questions still need to be answered, such as how often the fiber can be recycled and how to properly dispose of it once it has reached the end of its usefulness. Wai's company is currently looking for private investment to continue to develop and prove the efficacy of its technology, particularly in the field of industrial wastewater treatment.

With an impressive amount of success already under its belt, LCW fiber is well on its way to becoming a novel, green technology capable of providing both waste cleanup and uranium extraction in the years to come.

Related NEUP Projects:

11-3256 Innovative Elution Processes for Recovering Uranium from Seawater

13-5004 Innovative Elution Processes for Recovering Uranium and Transition Metals from Amidoxime-based Sorbents

Release Date: October 2019

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