For nuclear energy to remain a sustainable energy source, there must be assurance that an economically viable supply of nuclear fuel is available.

Seawater contains more than 4 billion tonnes of dissolved uranium.

This unconventional uranium resource, combined with a suitable extraction cost, can potentially provide a price cap and ensure centuries of uranium supply even with aggressive world-wide growth in nuclear energy applications.

The challenge is low concentration of uranium in seawater: 3.3 ppb.

In the late 1990’s, Japanese researches developed braid adsorbent for mooring collection systems.

Most (~69%) technology costs came from adsorbents materials.
The Office of Nuclear Energy in the U.S. Department of Energy assembled a multidisciplinary team from the U.S. national laboratories, universities, and research institutes in 2011.

The team has taken advantage of recent developments in (1) high performance computing, (2) advanced characterization instruments, and (3) nanoscience and nanomanufacturing technology to enable technical breakthroughs. The technology driven, sciences based R&D efforts are focused on:

- Synthesizing novel nanoscale adsorbent materials with architectures tailored for specific chemical performance;
- Applying quantum beam technologies to understand dynamic chemical processes at the atomic and molecular levels;
- Simulating and predicting structural and functional relationships using modern computational tools.
DOE Seawater U Recovery Program – Strategy & Goals

- **Investment Strategy:**
  To develop advanced adsorbents that can simultaneously enhance U sorption capacity, selectivity, kinetics, and materials durability to reduce the technology cost and uncertainties.

- **Program Goals:**
  To develop lab-scale uranium recovery technology demonstration under marine conditions, and
  To work with potential commercial/industry partner(s) to establish technology pricing threshold.

DOE Seawater U Recovery Program Team

- Marine Sciences Lab
- Pacific Northwest Nat’l Lab
- Lawrence Berkeley Nat’l Lab
- Univ California -Berkeley
- Los Alamos Nat’l Lab
- Univ of Idaho
- Univ of Chicago
- Woods Hole Oceanographic Inst
- CUNY Hunter College
- Univ of Maryland
- Oak Ridge Nat’l Lab
- Univ of Miami
- Univ of Texas Austin
- Univ of Alabama
Seawater U Recovery Program
Major R&D Thrust Areas

Adv. Adsorbent Novel Nano-Synthesis
Adv. Adsorbent Radiation Induced Graft Polymerization
Marine Testing & Performance Assessment
U Coordination & Computer-aided Ligand Design and Screening
Thermodynamic, Kinetics, & Structure Characterization
Long-term Durability & Reusability
Technology Cost Analyses & Deployment Modeling

Understand Uranyl Binding Mechanism

- Uranium exists in seawater as the uranyl ion \( \text{UO}_2^{2+} \) bound to carbonate \( \text{UO}_2(\text{CO}_3)_3^{4-} \).
- The uranyl ion binds to two adjacent amidoxime ligands on the adsorbent material to form a chelate complex.

X-ray diffractions of amidoximate-uranyl complexes show \( \eta^2 \) binding

Computer-aided Ligand Design and Screening

INPUT
Molecular fragments defining geometry of binding interaction(s)

Computing Tools
Structure generating module
Scoring module

OUTPUT
List of optimal structures


Characterization of Structures & Interaction Kinetics

Closed (cyclic imidedioxime) vs Open (bis-amidoxime) Amidoxime Ligands

H₂A > H₂B

Kinetics of U(VI) interactions with Amidoxime related ligands

Steering Uranium from Seawater: Binding Strength and Modes of Uranyl Complexes with Glutarimidedioxime


Dalton Trans., 2013, 42, 14621-14627. X. Sun, C. Xu, G. Tian, L. Rao, Complexation of glutarimidedioxime with Fe(III), Cu(II), Pb(II), and Ni(II), the competing ions for the sequestration of U(VI) from seawater
Thermodynamic Enthalpy Measurements

(1) \[ \text{UO}_2(\text{CO}_3)_3^{4-} + 2 \text{H}_2\text{A} \rightarrow \text{UO}_2(\text{HA})\text{A}^- + 3 \text{HCO}_3^- \quad \Delta H = +16.7 \text{ kJ/M} \]

(2) \[ \text{Ca}_2[(\text{UO}_2)(\text{CO}_3)_3] + 2 \text{H}_2\text{A} \rightarrow \text{UO}_2(\text{HA})\text{A}^- + 3 \text{HCO}_3^- + 2 \text{Ca}^{2+} \quad \Delta H = +30 \text{ kJ/M} \]

Enthalpy studies suggest an “overall” endothermic reaction under seawater conditions

Radiation-induced Grafting Polymerization Technology

Irradiation of trunk polymer fibers
Forms reactive free radicals on polyethylene fiber
(energy sources, dosage, rate)

Grafting of monomers
Polymerization of acrylonitrile and hydrophilic methyl acrylic acid (solvent/additives; co-monomers/ratio)

Functional group conversion - amidoxime
Hydroxylamine to form amidoxime and imidedioxime groups

Conditioning
Swells adsorbent, forms micropores and converts adjacent AO groups to imidedioxime

Impact on altering polyethylene fiber diameter and morphology

Non-round shaped fibers (0.24 - 30 μm dia.) have 2 - 60X higher surface area than 20 μm dia. round fibers
Novel Nano-Synthesis:
High Surface Area Nanoporous Carbon Materials

Carbon Surface Functionalization

Activated Woven Carbon Cloth
1100 m²/g

High Surface Area Mesoporous Carbon
10 nm pore diameter
500-700 m²/g

New and innovative nanomaterials with optimum pore sizes and tailored configuration for ultra-selective U binding ligands


ORNL Adsorbents Garner 2012 R&D 100 Award

“HiCap Adsorbents from Oak Ridge National Laboratory (ORNL) and Hills Inc. have demonstrated an adsorption capacity for a variety of metals, including uranium, that is five to seven times the highest performing conventional adsorbent. This performance is made possible with high surface area, continuous polyethylene fibers of small-diameter, round, or non-round shape. These greatly increase the amount of metals recovered, in a much shorter time.”

ORNL Team Members – Costas Tsouris, Xiao-Guang Sun, Richard Mayes, Christopher Janke, Yatsandra Oyola, Sheng Dai, Chris Bauer, Tonomori Saito

Recent developments of the braided materials by the ORNL team
Lab-scale Adsorbent Screening and Uptake Modeling

Develop sorption models to:
- Determine sorption rate-limiting step
- Quantify the transport and reaction rates
- Predict the effects of seawater flow velocity, temp, pH, etc. on U uptake for cost and energy assessment

Both batch and flow-through exps were used for laboratory screening tests

Parallel to the R&D efforts, U recovery cost analyses, in $/kg U, are conducted to assess the technology potentials.

The objective of cost analyses study:

- Identify highest-impact components of the system
- Guide / prioritize R&D efforts to reduce the technology cost
- Establish technology price threshold

<table>
<thead>
<tr>
<th>Year</th>
<th>Cost (yen/kg U)</th>
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</thead>
<tbody>
<tr>
<td>2006 JAEA</td>
<td>88,000</td>
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<tr>
<td>2011 US</td>
<td>1,230</td>
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<tr>
<td>2013 US</td>
<td>610</td>
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SUMMARY

- DOE NE has assembled a multidisciplinary team in 2011 to better understand the potential of the seawater uranium recovery technology.
- U.S. investment strategies include:
  - Developing novel adsorbent materials using high performance computing, advanced characterization instruments, and nanoscale and nanomanufacturing technology;
  - Achieving a molecular-level understanding of ligand coordination modes, sorption mechanisms, kinetics, and thermodynamics.
- Economic analyses have been used to guide the technology development and to highlight what parameters have the largest impact on the technology cost.
- Continue improving sorption capacity, selectivity, kinetics, and materials durability is expected to further reduce the technology cost.