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OVERVIEW OF FUEL RESOURCES PROGRAM – SEAWATER URANIUM RECOVERY SPONSORED BY THE U.S. DEPARTMENT OF ENERGY

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IAEA Symposium on Uranium Raw Material
for the Nuclear Fuel Cycle

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Seawater Uranium Recovery Rationale & Background

- 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.

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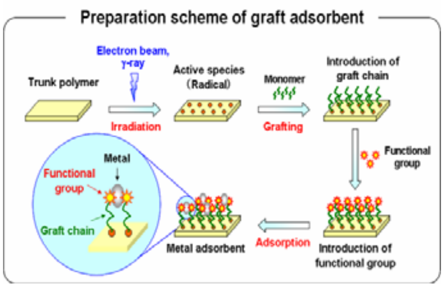
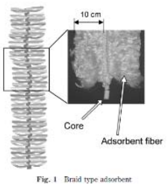
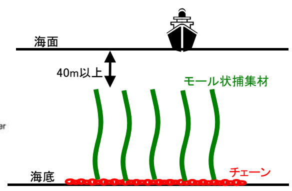
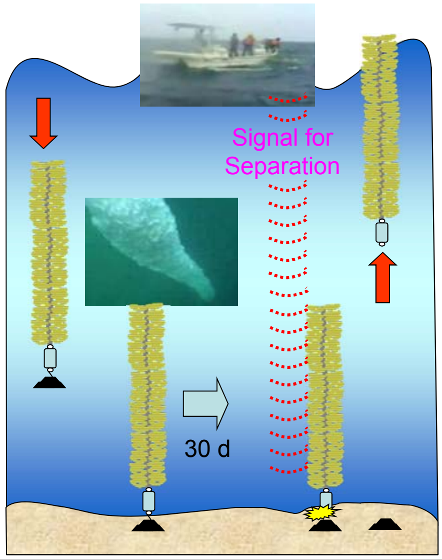
Braid Adsorbent Deployment
- Dr. M. Tamada of JAEA









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DOE-NE
Seawater U Recovery Program

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.**

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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.

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DOE Seawater U Recovery Program Team

Marine Sciences Lab
Pacific Northwest Nat'l Lab

Univ of Idaho

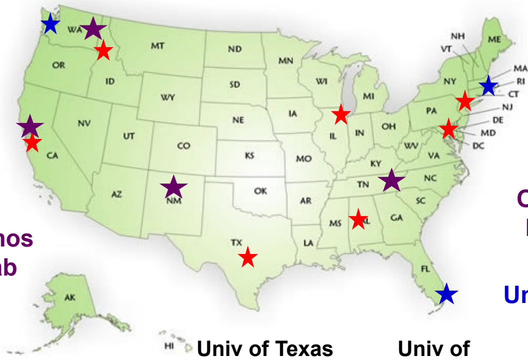
Univ of Chicago

Woods Hole Oceanographic Inst

Lawrence Berkeley Nat'l Lab

Univ California -Berkeley

Los Alamos Nat'l Lab



CUNY Hunter College

Univ of Maryland

Oak Ridge Nat'l Lab

Univ of Miami

Univ of Texas Austin

Univ of Alabama

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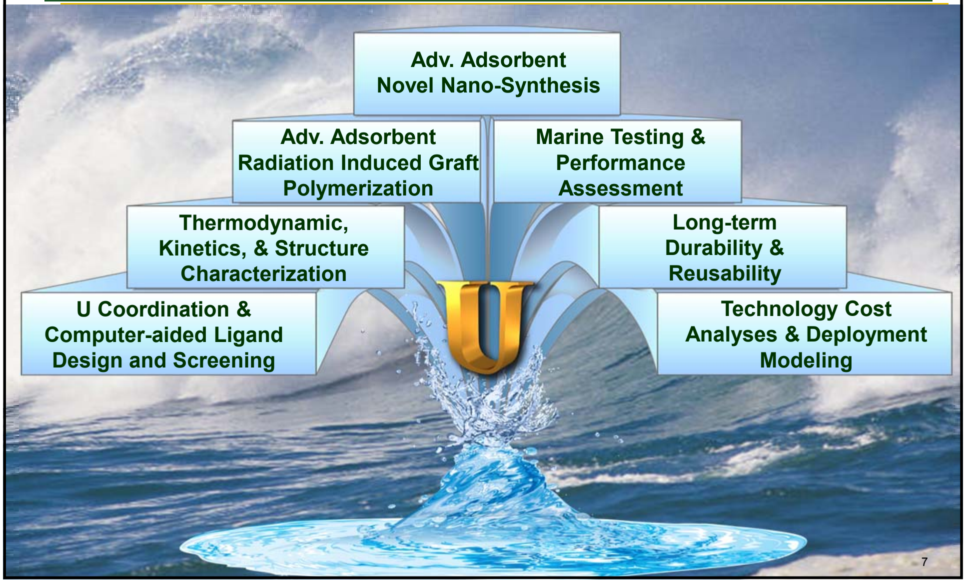
Seawater U Recovery Program Major R&D Thrust Areas



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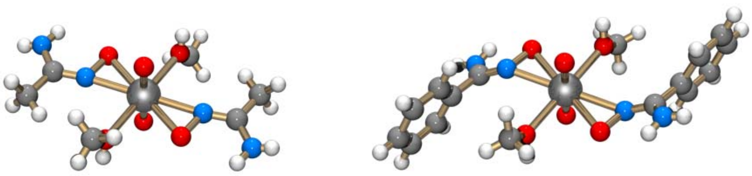
Understand Uranyl Binding Mechanism

- Uranium exists in seawater as the uranyl ion (UO_2^{2+}) bound to carbonate
  $UO_2(CO_3)_3^{4-}$
- 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 η^2 binding



"How Amidoximate Binds the Uranyl Cation", Vukovic, S.; Watson, L. A.; Kang, S. O.; Custelcean, R.; Hay, B. P. Inorg. Chem. **2012**, 51, 3855-3859.

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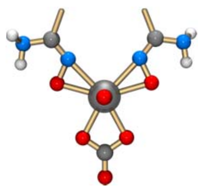
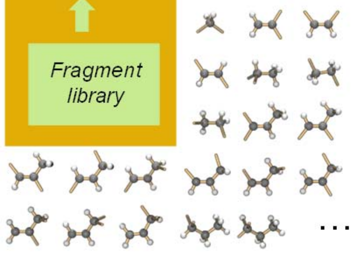
Computer-aided Ligand Design and Screening

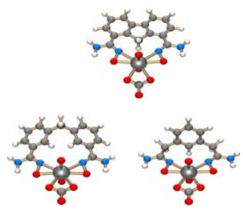
INPUT | **Computing Tools** | **OUTPUT**

Molecular fragments defining geometry of binding interaction(s) → *Structure generating module* → *Scoring module* → List of optimal structures

Fragment library → *Structure generating module*







Vukovic, S.; Hay, B. P. "De Novo Structure-based Design of Bis-amidoxime Uranophiles" *Inorg. Chem.* 2013, *52*, 7805-7801

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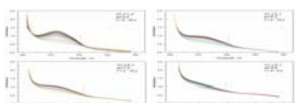
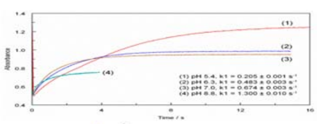
Characterization of Structures & Interaction Kinetics

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

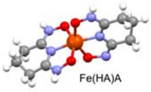
Kinetics of U(VI) interactions with Amidoxime related ligands

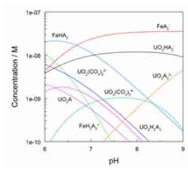




Competition of U(VI) binding site

$Fe^{3+} > UO_2^{2+} \approx Cu^{2+} > Pb^{2+} > Ni^{2+}$





Dalton Trans., 2012, 41 (38), 11579. G. Tian, S. J. Teat, Z. Zhang, L. Rao, Sequestering 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

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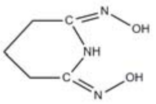
Thermodynamic Enthalpy Measurements

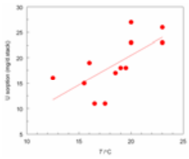
Amidoxime "A"



Reaction	logβ	ΔH, kJ/mol	ΔS, J/(K·mol)
$UO_2^{2+} + A^{2-} = UO_2A$	17.8 ± 1.1	-59 ± 8	142 ± 19
$H^+ + UO_2^{2+} + A^{2-} = UO_2(HA)^+$	22.7 ± 1.3	-71 ± 6	197 ± 14
$UO_2^{2+} + 2A^{2-} = UO_2A_2^{2-}$	27.5 ± 2.3	-101 ± 10	188 ± 24
$H^+ + UO_2^{2+} + 2A^{2-} = UO_2(HA)A^-$	36.8 ± 2.1	-118 ± 6	309 ± 14
$2H^+ + UO_2^{2+} + 2A^{2-} = UO_2(HA)_2$	43.0 ± 1.1	-154 ± 25	307 ± 59

(1) $UO_2(CO_3)_3^{4-} + 2\ H_2A = UO_2(HA)A^- + 3\ HCO_3^-$ **ΔH = +16.7 kJ/M**

(2) $Ca_2\ [(UO_2)(CO_3)_3] + 2\ H_2A = UO_2(HA)A^- + 3\ HCO_3^- + 2\ Ca^{2+}$ **ΔH = + 30 kJ/M**



Enthalpy studies suggest an "overall" endothermic reaction under seawater conditions

➡ U sorption would be enhanced at higher temp

Dalton Trans., 2013, 42 (16), 5690. G. Tian, S. J. Teat, L. Rao, Thermodynamic studies of U(VI) complexation with glutardiamidoxime for sequestration of uranium from seawater

Dalton Trans., 2014, 43 (2), 551. X. Sun, G. Tian, C. Xu, L. Rao, S. Vukovic, S. O. Kang, B. P. Hay, Quantifying the binding strength of U(VI) with phthalimidedioxime in comparison with glutarimidedioxime: Implications in the extraction of U(VI) from seawater with amidoxime-based sorbents

Chem. Eur. J., 2014, in press. F. Endrizzi, L. Rao, Formation of Ca^{2+} and Mg^{2+} Complexes with $(UO_2)(CO_3)_3^{4-}$ in Aqueous Solution: Effect on the Speciation of U(VI) and its Extraction from Marine Environments.

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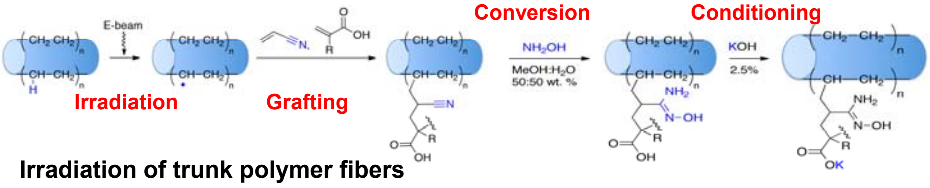
Radiation-induced Grafting Polymerization Technology



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

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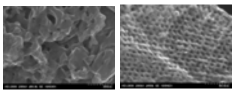
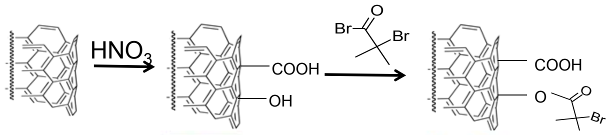
Novel Nano-Synthesis:
High Surface Area Nanoporous Carbon Materials

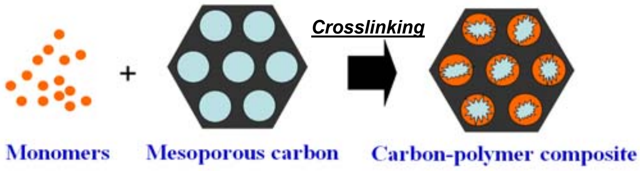
Activated Woven Carbon Cloth
1100 m²/g



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

Carbon Surface Functionalization





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

Y. Yue, R. T. Mayes, J..Kim, P. F. Fulvio, X.-G. Sun, C. Tsouris, J. Chen, S. Brown, S, Dai, Angew. Chem. Int. Ed., **2013**, 52, 13458
Y. F. Yue, X. G. Sun, R. T. Mayes, J. Kim, P. F. Fulvio, Z. A. Qiao, ZA, S. Brown, C. Tsouris, Y. Oyola, S. Dai, Science China Chem., **2014**, 56, 1510
J. Górka, R.T. Mayes, L. Baggetto, G.M. Veith, S. Dai J. Mater. Chem. A**, 2013**, 1, 3016

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ORNL Adsorbents Garner 2012 R&D 100 Award

2012 R&D 100 50th ANNIVERSARY

"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, Tomonori Saito

Recent developments of the braided materials by the ORNL team

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Lab-scale Adsorbent Screening and Uptake Modeling

Adsorbent Materials Development & Synthesis
↕
Batch Equilibrium & Kinetics Screening ↔ Transport & Kinetics Modeling
↓
Marine Testing

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

Kim, J., Y. Oyola, C. Tsouris, C.R. Cole, R.T. Mayes, J.C. Janke, S. Dai, “Characterization of Uranium Uptake Kinetics from Seawater in Batch and Flow-Through Experiments,” Ind. Eng. Chem. Res., 52, 9433-9440 (2013).
Kim, J., C. Tsouris, Y. Oyola, C.J. Janke, R.T. Mayes, S. Dai, G. Gill, L.-J. Kuo, J. Wood, K.-Y. Choe, E. Schneider, and H. Lindner, “Uptake of Uranium from Seawater by Amidoxime-Based Polymeric Adsorbent: Field Experiments, Modeling, and Economic Assessment,” Ind. Eng. Chem. Res., 53, 6076−6083 (2014).

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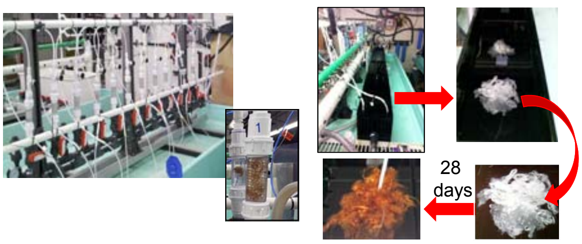
Marine Testing
Adsorbent Performance Assessment

Continuous flow through with fixed bed and flume-type devices to measure the sorption capacity and kinetics

Natural Seawater
- *Salinity*
- *Temperature*
- *Flow-rate/linear velocity*
- *Unfiltered & Filtered*
- *TOC/DOC*
- *Trace Elements*



Marine Sciences Laboratory, Sequim, Washington

To Validate Performance under Different Seawater Environments
- ***Woods Hole Oceanographic Institution, Massachusetts***
- ***Broad Key Island, University of Miami, Florida***

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Technology Cost Analyses

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**

2006 JAEA analysis+:	**88,000 yen/kg U (ca. $1,000/kg U)**
2011 US analysis++:	**$1,230/kg U**
2013 US analysis+++:	**$610 /kg U**

+ M. Tamada et al., 2006. *Cost Estimation of Uranium Recovery from Seawater with System of Braid Type Adsorbent.* Trans. Atomic Energy Society of Japan, 358-363.
++ E. Schneider, D. Sachde, 2013. The Cost of Recovering Uranium from Seawater by a Braided Polymer Adsorbent, Science and Global Security, 21, 2.
+++ Schneider, E. A., and H. D. Lindner, "Energy Balance of Uranium Recovery from Seawater," Proceedings of GLOBAL 2013: Nuclear Energy at a Crossroads, 9 pp., Salt Lake City, UT, October (2013).
Schneider, E.A. and H. D. Lindner, 2014. Unconventional Uranium Resources and Production Costs, *Transactions of the American Nuclear Society,* 110, Reno, NV, June 2014.

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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 nanoscience 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.**

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