U.S. DEPARTMENT OF ENERGY | Nuclear Energy

Characterization and Deployment Studies and Cost Analysis of Seawater Uranium Recovered by a Polymeric Adsorbent System

Erich Schneider
The University of Texas at Austin

Gary Gill
Pacific Northwest National Laboratory

Presented at: URAM-2014
IAEA, Vienna, Austria
June 26, 2014

U.S. DEPARTMENT OF ENERGY
Nuclear Energy

Overview

- **The 4.5 billion tonnes of uranium in seawater exceed conventional resources by a factor of ~1,000:**
  - the Uranium from Seawater Program is developing novel materials that surpass the **sorption capacity, selectivity, kinetics and durability** of the best existing technology.

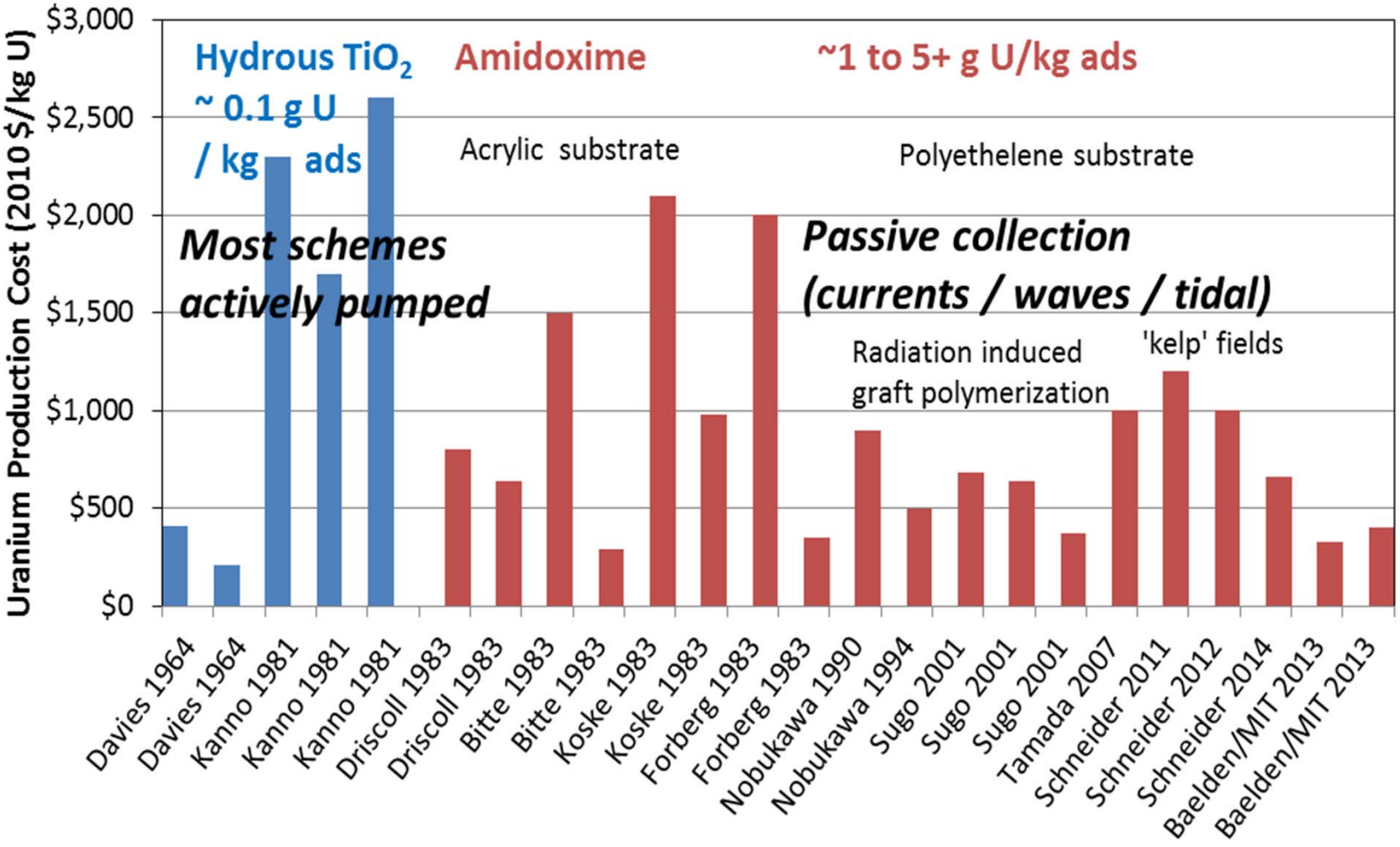
- **Parallel to the R&D effort are ongoing assessments of:**
  - adsorbent performance and durability in authentic ocean environments via a vigorous **marine testing** program;
  - the **cost, in $/kg U,** and **energy return on investment (EROI)** of the technology.

- **By identifying the highest-impact components of the system, cost and EROI analyses can guide the technology R&D campaign.**

U.S. DEPARTMENT OF ENERGY
Nuclear Energy

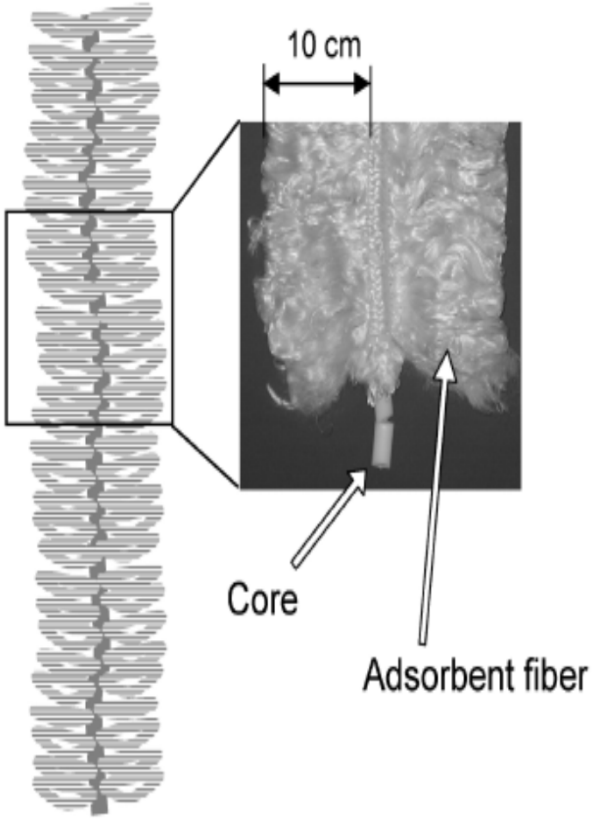
Overview:
Historical perspective

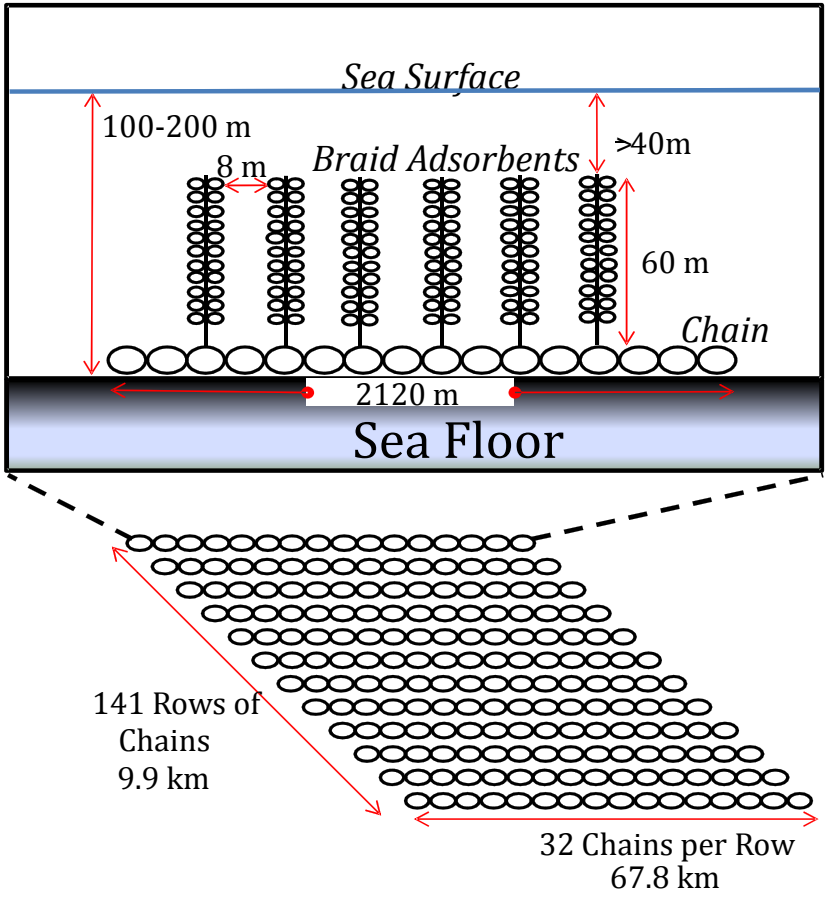
Figure. Historical estimates of the cost of recovering U from seawater



U.S. DEPARTMENT OF ENERGY
Nuclear Energy

Overview: **deployment strategy**



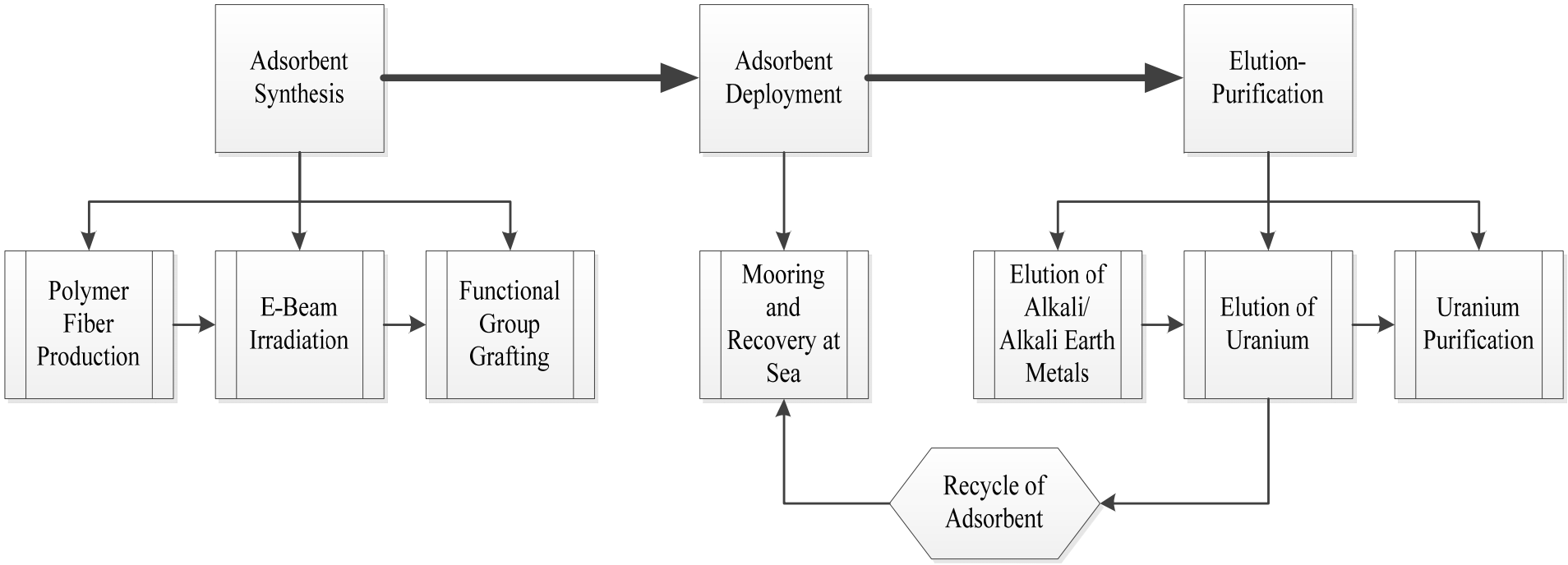


(Sized for recovery of 1,200 tU/year)

Left figure from M. Tamada et al., 2006. Cost Estimation of Uranium Recovery from Seawater with System of Braid Type Adsorbent. Transactions of the Atomic Energy Society of Japan, pp. 358-363.

U.S. DEPARTMENT OF ENERGY
Nuclear Energy

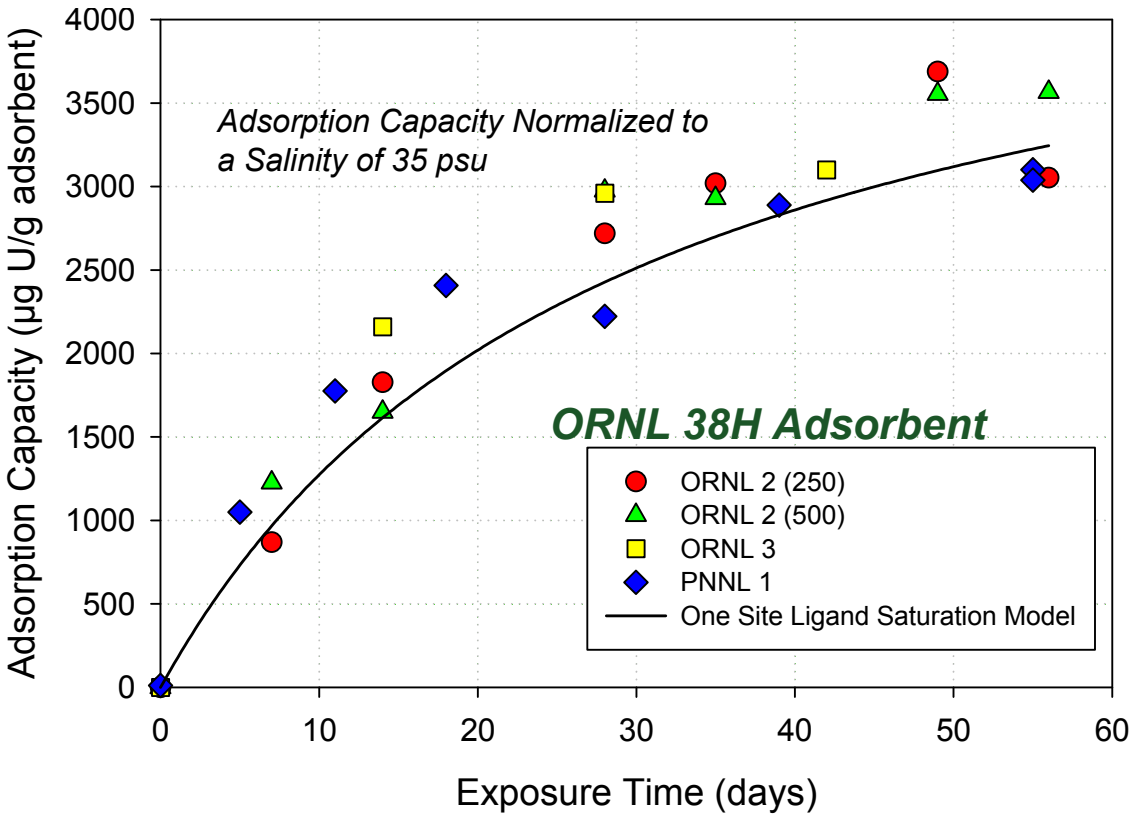
Overview: **system components**



- **engineering cost estimation techniques:**
  - block or process flow diagrams and equipment lists;
  - code of accounts (COA) tables at the 2 digit level;
  - cost (and uncertainty) of itemized & non-itemized inputs.

U.S. DEPARTMENT OF ENERGY
Nuclear Energy

Marine Testing
Time Series Capacity Measurements with ORNL 38H Adsorbent



Saturation Capacity:

4.89 ± 0.83 g U/ kg adsorbent at 35 psu

Half saturation time:

28 ± 10 days

Uptake at 60 days:

3.33 ± 0.68 g U/ kg adsorbent

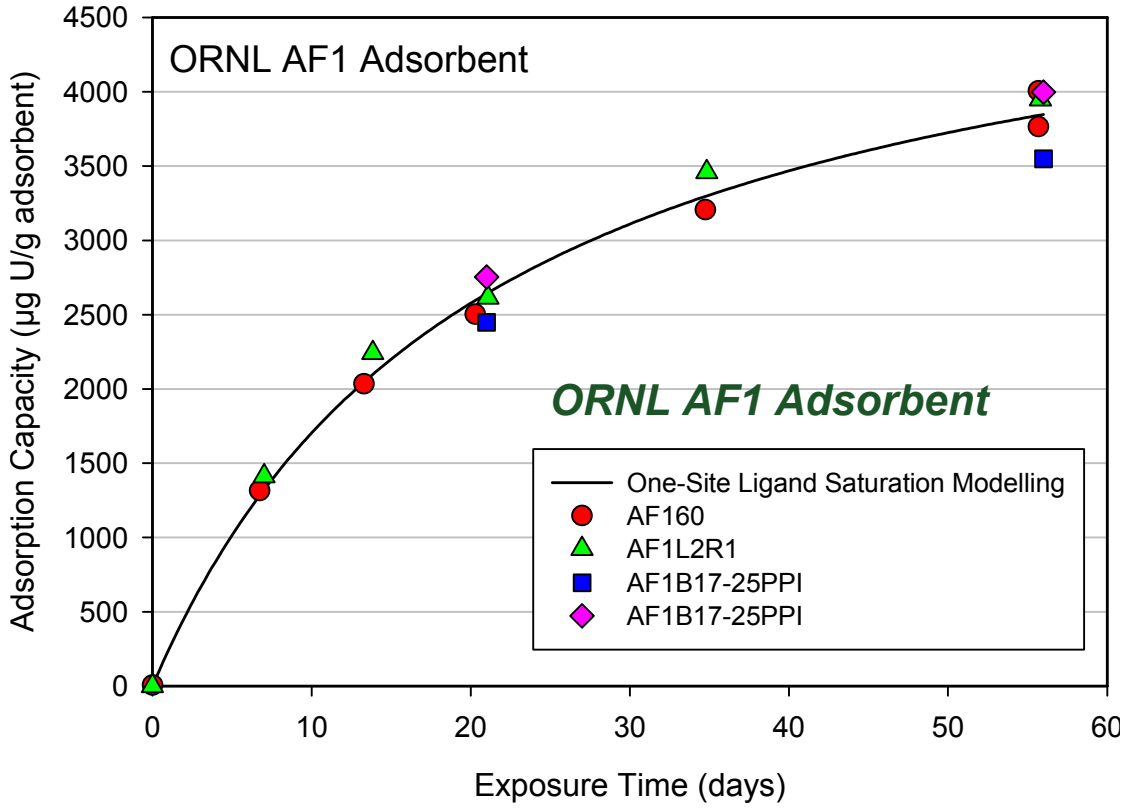
One Site Ligand Saturation Model:

$$y = \frac{\beta_{max} t}{K_D + t}$$

y = uranium uptake [g U/kg ads]
β_{max} = saturation capacity [g U/kg ads]
K_D = half saturation time [days]
t = exposure time [days]

U.S. DEPARTMENT OF ENERGY
Nuclear Energy

Marine Testing
Improvements Continue: ORNL AF1 Adsorbent



Saturation Capacity:

5.30 ± 0.20 g U/ kg adsorbent at 35 psu

Half saturation time:

21 ± 2 days

Uptake at 60 days:

3.92 ± 0.19 g U/ kg adsorbent

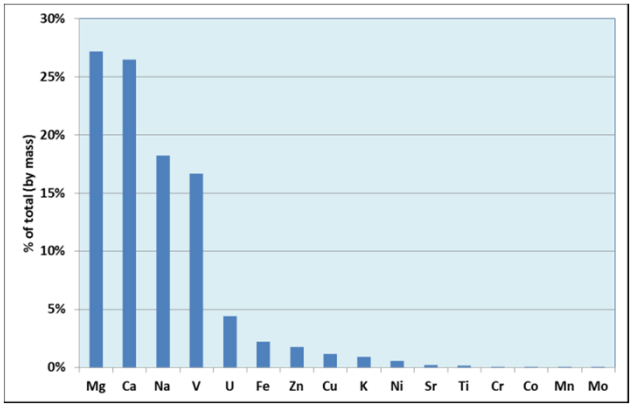
- 38H adsorbent qualified in 2013, AF1 series in 2014
- Reference cost analysis based on 38H

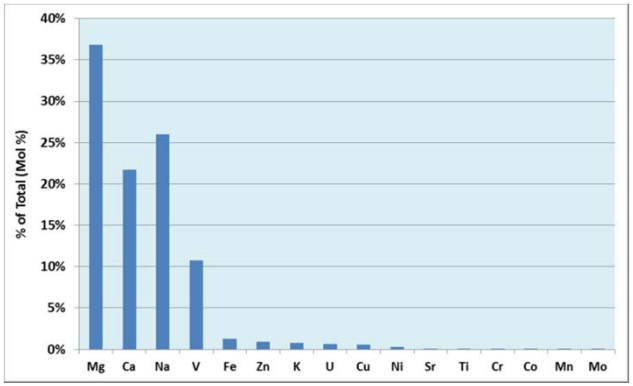
U.S. DEPARTMENT OF ENERGY
Nuclear Energy

Marine Testing
Element Selectivity

Element	Adsorption Capacity (µg/g adsorbent)	% of Total (by mass)
Mg	24302	27%
Ca	23664	26%
Na	16266	18%
V	14918	17%
U	**3949**	**4.4%**
Fe	1949	2.2%
Zn	1589	1.8%
Cu	1035	1.2%
K	800	0.89%
Ni	492	0.55%
Sr	197	0.22%
Ti	117	0.13%
Cr	33	0.037%
Co	31	0.034%
Mn	24	0.026%
Mo	11	0.013%
Sum	89376	100%

Element	Adsorption Capacity (µmol/g adsorbent)	% of Total (by mol %)
Mg	1000	37%
Ca	590	22%
Na	708	26%
V	293	11%
Fe	34.9	1.3%
Zn	24.3	0.89%
K	20.5	0.75%
U	**16.6**	**0.61%**
Cu	16.3	0.60%
Ni	8.37	0.31%
Sr	2.25	0.083%
Ti	2.45	0.090%
Cr	0.631	0.023%
Co	0.520	0.019%
Mn	0.431	0.016%
Mo	0.119	0.004%
Sum	2718	100%



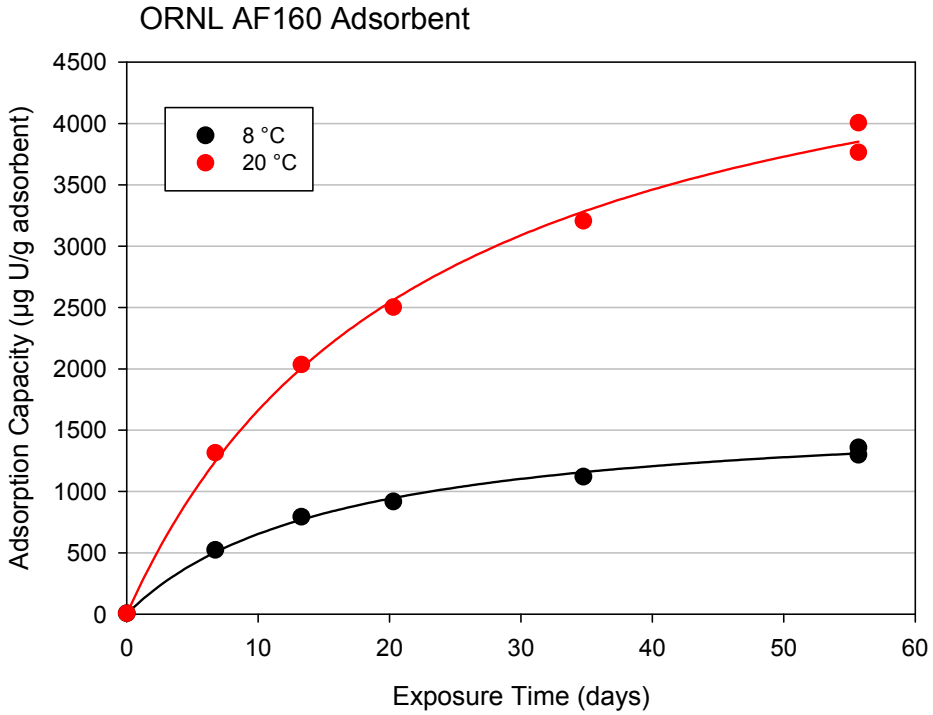


- *The amidoxime-based adsorbent is not element specific*
- *Opportunities exist to acquire other key elements*

U.S. DEPARTMENT OF ENERGY
Nuclear Energy

Marine Testing
Uranium Binding with Amidoxime – Temperature Dependence

- Uranium exists in seawater as the uranyl ion (UO_2^{2+}) bound to carbonate - $\mathbf{UO_2(CO_3)_3^{-4}}$
- The uranyl ion binds to two adjacent amidoxime ligands on the adsorbent material to form a chelate complex



*Thermodynamic modeling predicts the interaction between the uranyl ion and the amidoxime ligand to be **endothermic** in seawater; hence higher temperatures should yield enhanced adsorption capacity*

Tian, G.; Teat, S. J.; Zhang, Z.; Rao, L. "Sequestering uranium from seawater: binding strength and modes of uranyl complexes with glutarimidedioxime", Dalton Trans. 2012, 41, 11579-11586

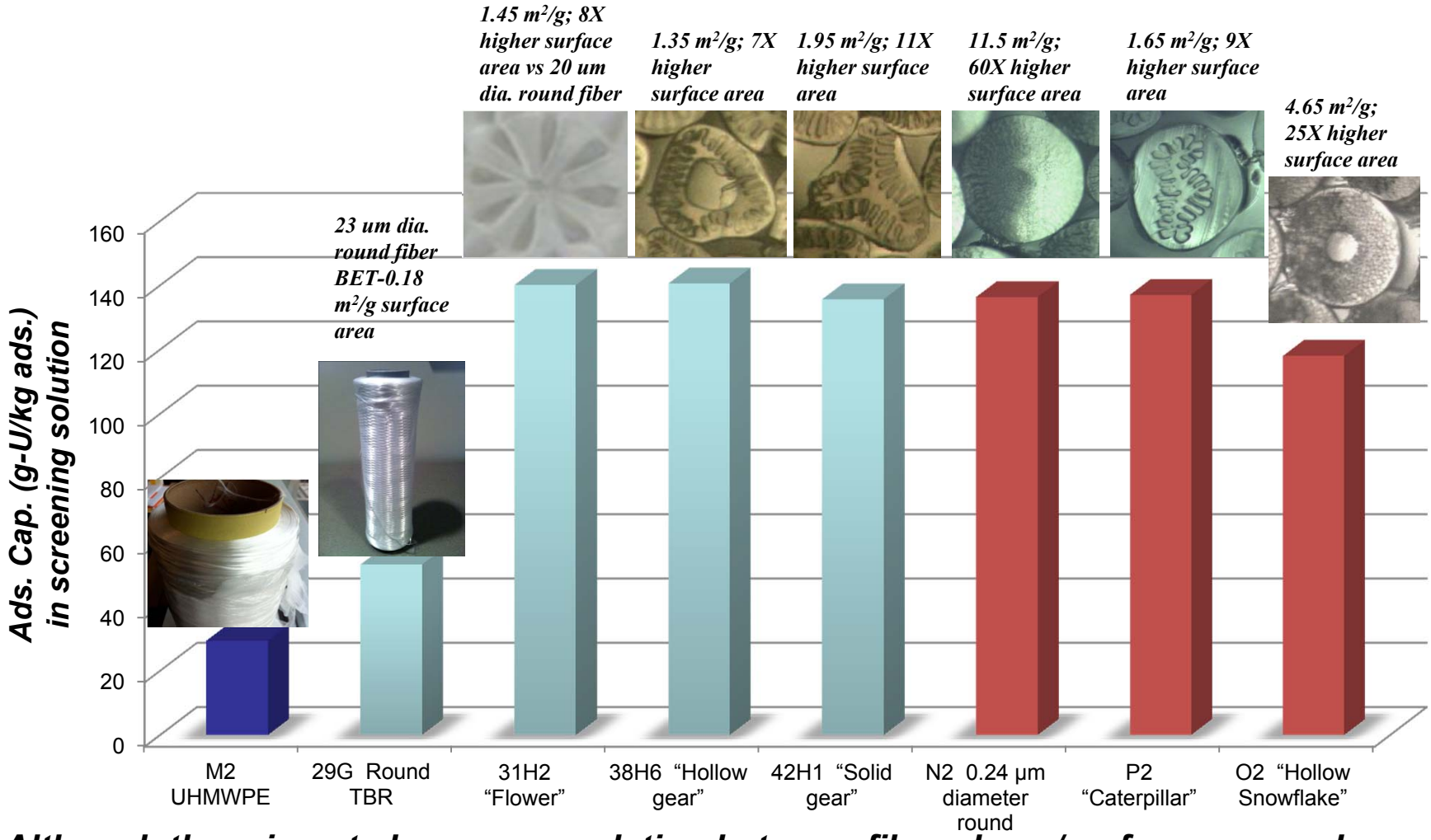
Adsorption Capacity = f(T)

Adsorption Rate ≠ f(T) ?

Half saturation rate doesn't vary w/ temperature

U.S. DEPARTMENT OF ENERGY
Nuclear Energy

Process & Design Optimization
Fiber Shape and Surface Area

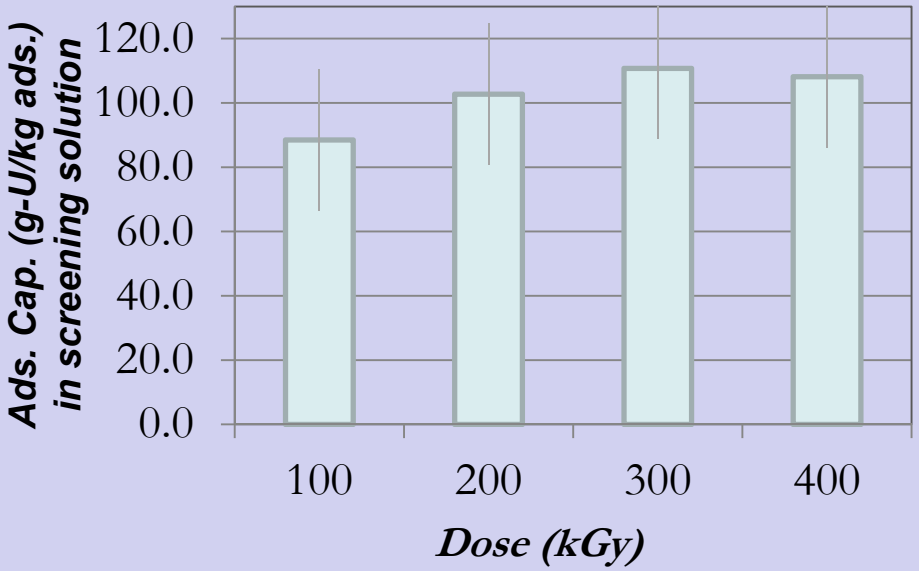


Although there is not always a correlation between fiber shape/surface area and capacity, higher surface area fibers have demonstrated significantly higher capacities vs round fibers

U.S. DEPARTMENT OF ENERGY
Nuclear Energy

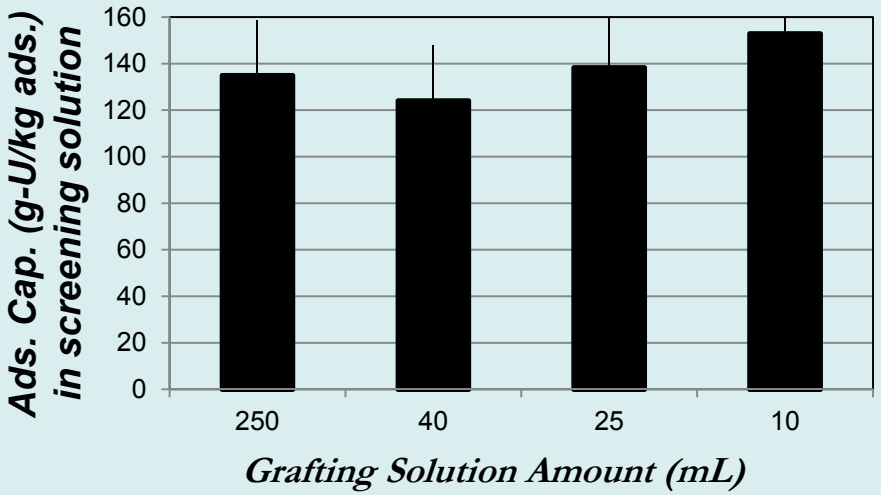
Process & Design Optimization
Selected Elements of Grafting Process

Dose [kGy] from E-beam to HDPE fibers



Free radical concentration saturates at ~ 200-300 kGy on our HDPE fibers and their capacities are comparable from 200-400 kGy

Grafting solution [mL] used per 0.5g of fiber



Reducing the amount of grafting solution from 500 mL/g of fiber to 20 mL/g of fiber did not change the adsorption capacity

U.S. DEPARTMENT OF ENERGY
Nuclear Energy

Cost analysis: **current reference U production cost**

- Reference uptake (ORNL **38H6** adsorbent tested at PNNL): **3.33 +/- 0.68 g U/ kg ads (at 60 day immersion)**

- With **6 uses of adsorbent** at **5% capacity loss per reuse**, the mean U production cost estimate has declined from **$1230/kg U** (2011 DOE estimate for JAEA technology) to **$606 / kg U**.

U.S. DEPARTMENT OF ENERGY
Nuclear Energy

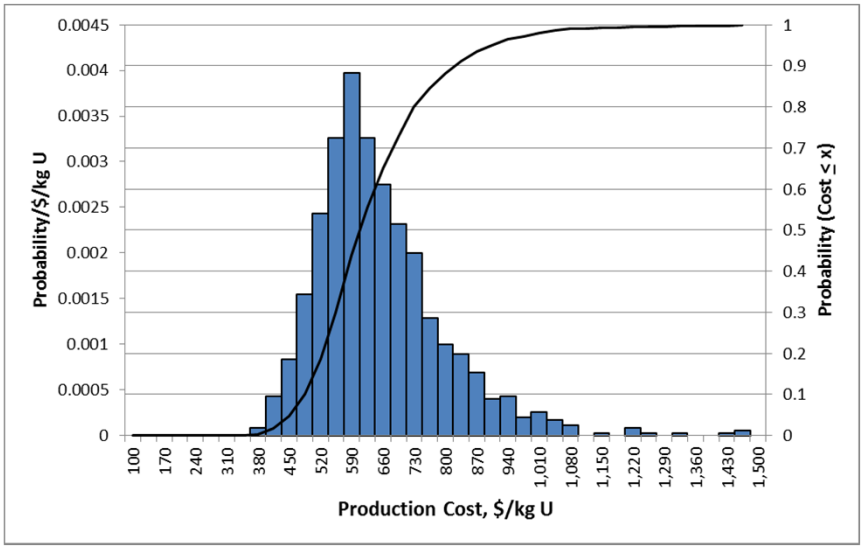
Cost analysis: **cost components**

Table. Components of $606/kg U production cost

	Capital Investment	Operations
	Contribution to Production Cost ($/kg U)	Contribution to Production Cost ($/kg U)
Adsorbent Production	**58**	**290***
Mooring and Deployment	**102**	**121**
Elution and Purification	**13**	**22**
TOTAL	**173**	**433**

** includes initial chemical and material inventories.*

- **There are uncertainties associated with**
  - **Input costs and system design** (e.g., chemical and commodity costs)
  - **adsorbent performance** (fresh capacity, durability)
- **They give rise to a 95% confidence interval of [$420, $1,000] around the $606/kg U expected cost**



U.S. DEPARTMENT OF ENERGY
Nuclear Energy

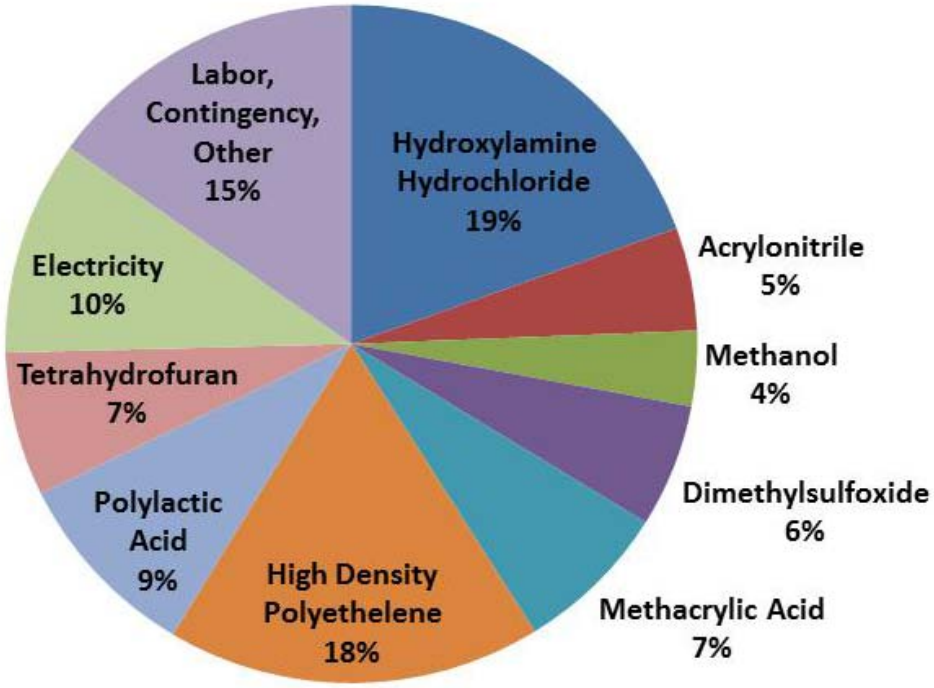
Cost analysis: **adsorbent production cost components**

Operating costs associated with adsorbent production *account for $290/kg U or 48% of the $606/kg U production cost:*

Table. Chemical requirements per unit mass of high density polyethylene (HDPE)

Chemical	Tonnes per tonne of HDPE
Acrylonitrile (AN)	0.7
Hydroxylamine	1.12
Methanol	0.53
Dimethylsulfoxide (DMSO)	0.88
Methacrylic Acid (MAA)	0.18
Polylactic Acid (PLA)	0.40
Tetrahydrofuran (THF)	0.10

Figure. Components of adsorbent production cost (materials, labor, utilities)

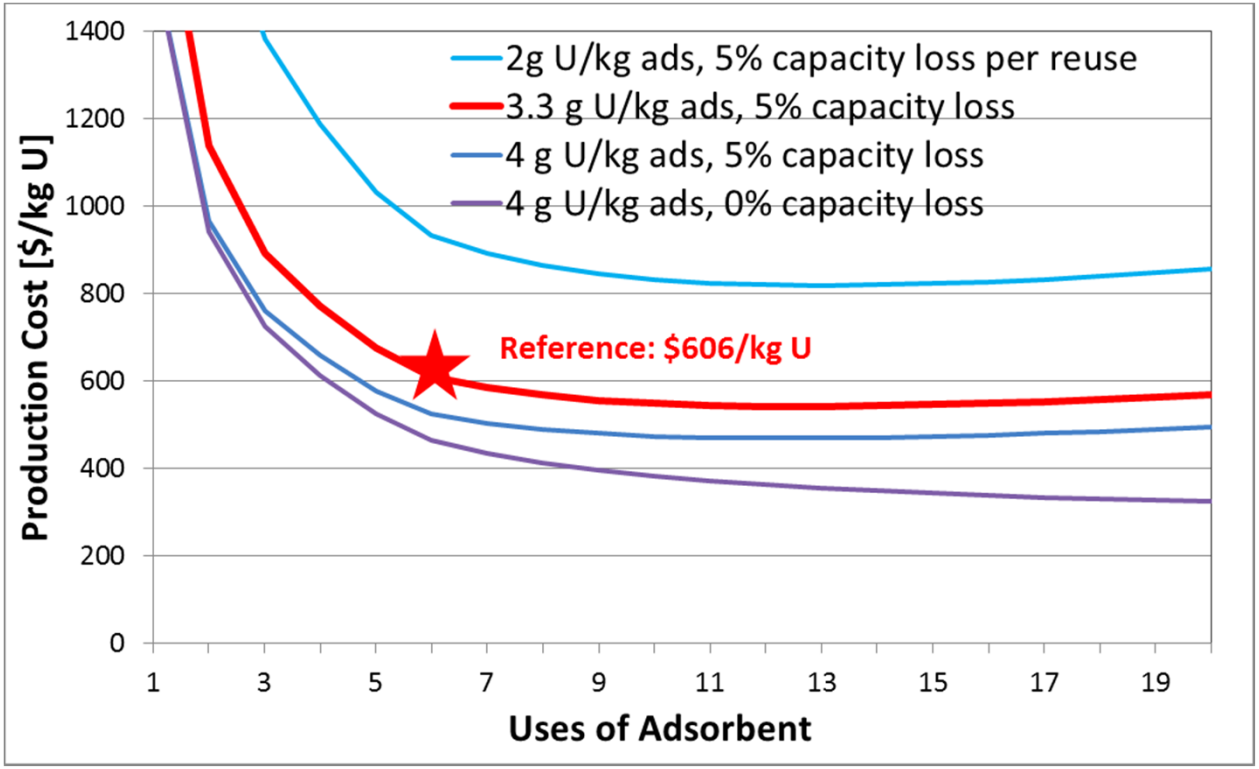


U.S. DEPARTMENT OF ENERGY
Nuclear Energy

Cost analysis: **sensitivity to capacity and durability**

- **Adsorbent capacity is the most crucial driver of U production cost:**
  - to generate the figure, capacity and recycle number were varied without modifying the adsorbent production process or other inputs.

- **Recent tests indicate that a 60-day loading of 4.0 g U/kg ads is within reach.**
  - If the adsorbent can also retain its full capacity over many recycles, the **U production cost would be cut by almost half** to ca. $350/kg U.



U.S. DEPARTMENT OF ENERGY
Nuclear Energy

Energy return on investment **definition**

- **A mass balance for a once-through nuclear fuel cycle (below) shows that the energy produced per mass of U extracted is about 170 GJ(e)/kg U.**
- **Define the energy return on investment (EROI) as**

$$\frac{\text{energy produced per mass of U [GJ(t+e)/kg U]}}{\text{energy consumed per mass of U [GJ(e)/kg U]}}$$

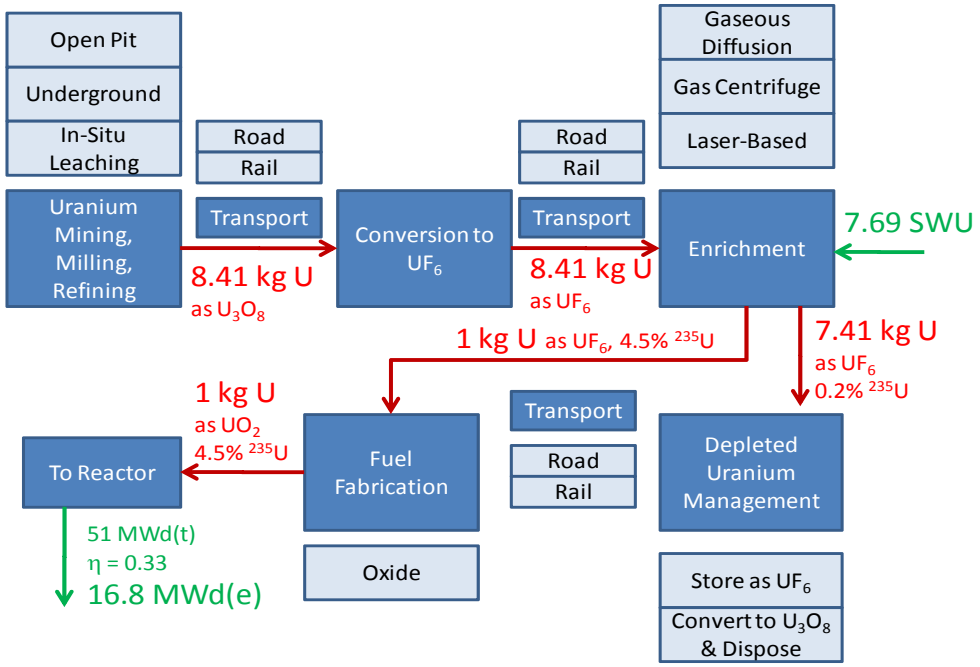


Figure: Schneider, E., Tavrides, E. and B. Carlsen, Measures of the Environmental Impact of the Front End of the Nuclear Fuel Cycle, INL Report FCRD-SYSA-2010-000104, 2010.

U.S. DEPARTMENT OF ENERGY
Nuclear Energy

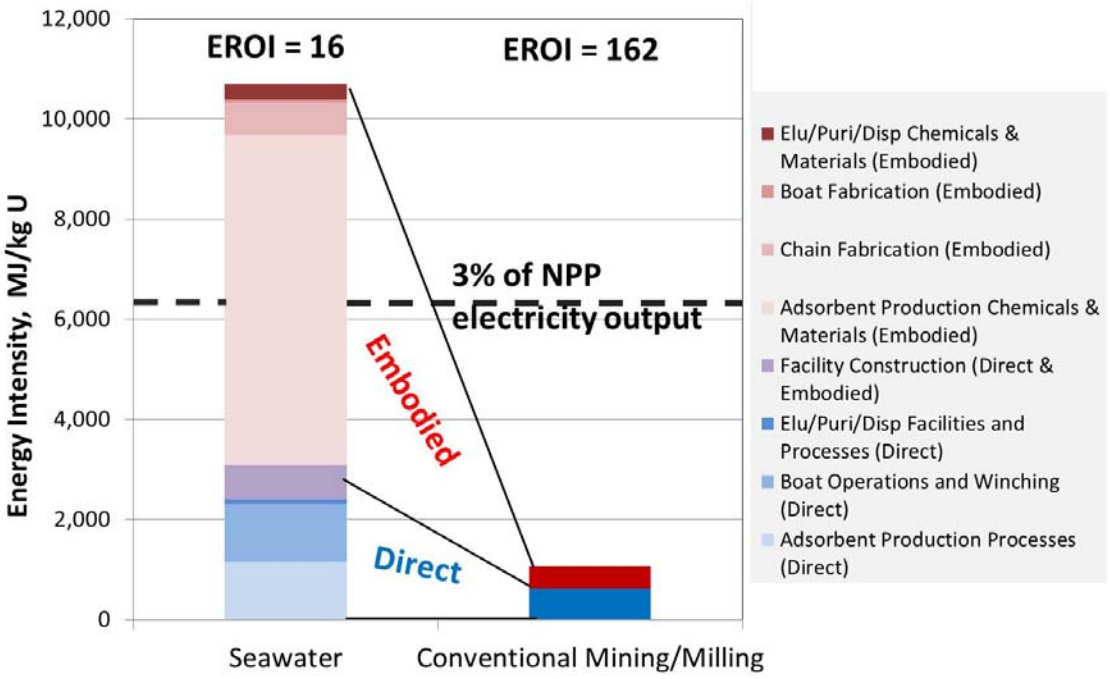
Energy return on investment
list of energy inputs

- **The table lists the direct and embodied energy inputs considered:**
  - *for each input, energy intensities [GJ/unit of commodity] were obtained;*
  - *intensities were multiplied by throughputs/capacities and summed to obtain the total energy consumption [GJ];*
  - *consumption was divided by the uranium production [kg U] for the overall energy intensity [GJ/kg U].*

Adsorbent Production	Mooring	Elution, Purification, Disposal
Production facility construction (D,E)	Chain fabrication (E)	Recovery facility construction (D,E)
Operations: melt spinning, e-beam, grafting, braiding (D)	Work boat construction (E)	Recovery facility operations (D)
Materials: polyethelene (E)	Work boat operations: daily running, winching (D)	Cementation of incinerated adsorbent (E)
Chemicals: AN, DMF, others (E)		Chemicals: Nitric acid (E)

U.S. DEPARTMENT OF ENERGY
Nuclear Energy

Energy return on investment **reference case**



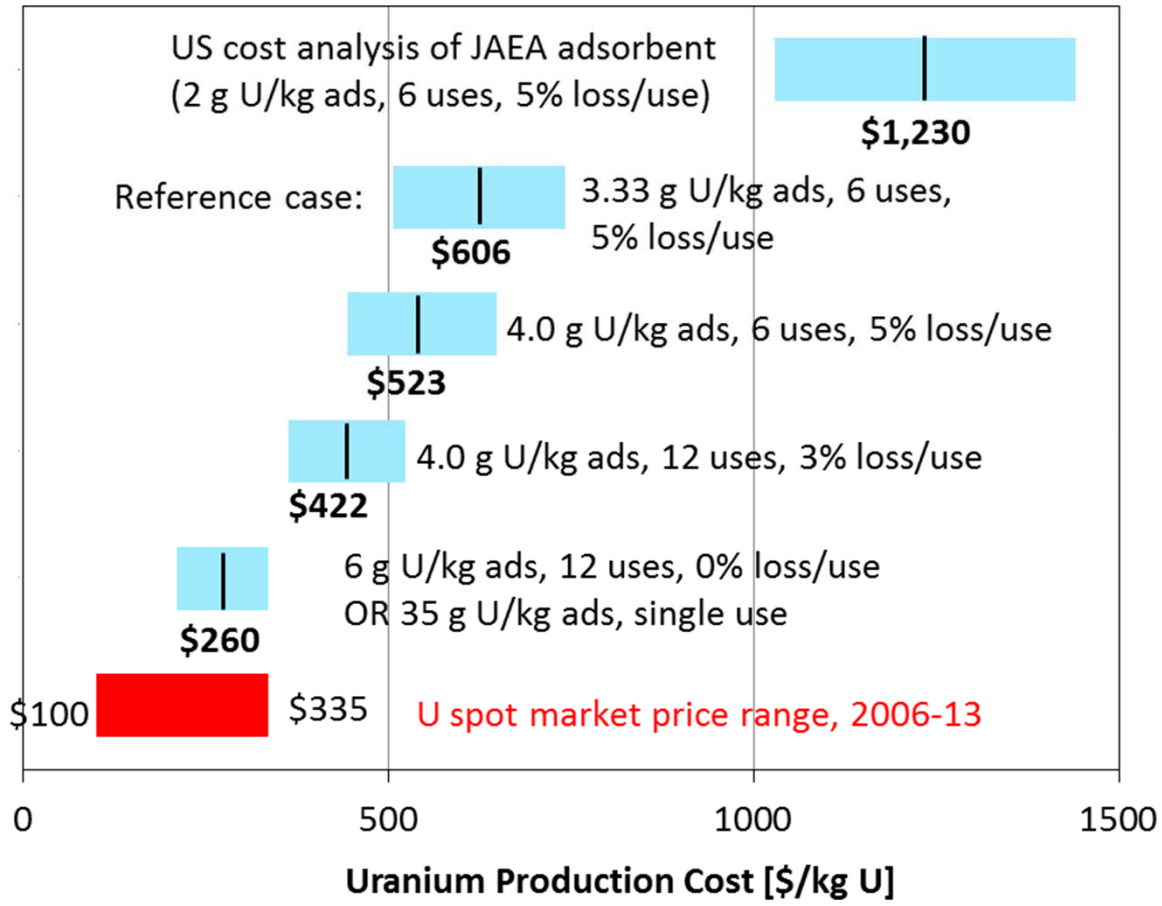
Note: 3% of NPP output is the approximate energy consumption of the rest of the nuclear electricity production chain (once through fuel cycle, reactor construction)

- **At 16, the EROI of the seawater uranium technology is a factor of 10 lower than that of conventional mining.**
  - uranium production cost and EROI are seen to differ by roughly the same factor when present-day conventional and seawater uranium recovery are compared.

U.S. DEPARTMENT OF ENERGY
Nuclear Energy

Cost analysis: **progress and objectives**

- Expected value of U production cost (black tick mark) and 95% confidence interval* (blue bar):



*considering uncertainties in input costs only.

U.S. DEPARTMENT OF ENERGY
Nuclear Energy

Conclusions

- **The cost and EROI analysis suggest a number of R&D directions aimed at high-leverage contributors to the U production cost or reducing uncertainty:**
- Capacity, durability and stability are the key cost drivers:
  - Complementary R&D areas include design of selective and durable ligands and adsorbents, as well as gentler U stripping procedures.
- Experimentation is defining minimum requirements for cost driving chemicals and improve recyclability or identify substitutes for the most costly
- Novel elution strategies have great potential to increase durability and reusability
- Textile physical properties (fiber diameter, shape, surface area to volume ratio) continue to be optimized to improve performance and fabrication cost
- Marine tests and kinetics modeling continue to improve our understanding of the time, temperature and flow velocity dependence of adsorption rate