ARPA-E Rare Earth and Critical Materials Workshop
Breakout Session: Supply

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DEVELOPMENT OF BREAKTHROUGH ELECTROCHEMICAL TECHNOLOGIES FOR RARE-EARTH ELECTROWINNING

Antoine Allanore & Donald R. Sadoway
Massachusetts Institute of Technology

ARPA-E Workshop
December 6, 2010
Arlington, VA, USA
What is Sadoway Group expertise?

Achievement: Molten Oxide Electrolysis

Rare-Earth Extraction by electrolysis

Sadoway Group contribution
Sadoway Group

- Development of breakthrough electrochemical technologies for environment preservation

- Fields of application:
  - Energy storage: solid polymer & liquid metal battery
  - Extraction of metals at high temperature (Molten Salts)

- Provide the basic science (thermodynamics, electrochemistry) supporting the technique, demonstrate its feasibility, support its scaling-up to pilot scale
  - 2 recent spinouts: ① Titanium extraction ② Liquid Metal Battery

- Infrastructure:
  - Furnaces from 300 to 1800°C; power-supplies up to 10kW
  - Own metallography lab
Achievements in metals extraction

- **Molten Oxide Electrolysis:**
  - electrolyte = mixture of molten oxides (acidic & basic oxides), operative from 900 to 1800°C
  - “like dissolves like” = all raw oxide materials can be dissolved in a suitable electrolyte
  - very high-temperature = liquid product = industrially useful

Steel production (1600°C)
- Raw iron ore
- Fe₂O₃
- SiO₂
- Al₂O₃

- **molten electrolyte**
  - O²⁻
  - SiO₂
  - Al₂O₃
  - MgO
  - CaO
- Fe³⁺

- **cathode (-)**
- Fe (l)

- **anode (+)**
- O₂

- Lean process - few unit operations
- No GHG emissions
- Easy alloying

Titanium production (1750°C)
- Raw TiO₂
- **carbon anode (+)**
- CO
- **molten electrolyte**
  - TiO₄⁴⁻
  - CaO

- **cathode (-)**
- Ti (l)
- 4

- ΔG
- CO₂
- carbothermic reduction impossible
Rare Earth Electrowinning?

• An established technique
  ○ <1988 electrowinning demonstrated in molten salts, fluorides or chlorides, up to small pilot-scale for Ce, La, Nd, Pr, starting from purified salts of RE (chlorides)

• Advances in electroextraction in last 20 y
  ○ 1990 - Molten Oxide Electrolysis proposal “Sadoway process” demonstrated since then for Fe, Ti, Cr, Ni, Mn, Si
  ○ 1998 - Demonstration of oxide deoxidation in CaCl₂ (FFC process & Ohno-Suzuki process: electrochemical-calciothermic)

• Recent interest for electrolysis of RE
  ○ 2009 - Research on electroextraction of lanthanides in molten salts relaunched for nuclear waste treatment in France in LiF - CaF₂

Sadoway, D.R “Fused Salt Electrolysis of Rare Earth Metals,” Rare Earths, R.G. Bautista and M.M. Wong, editors, TMS, Warrendale PA, 1988, pp. 345-353
Rare Earth Electrowinning?

- **Proposal**
  - Investigate the possible application of recent developments to direct electrowinning of RE ore
  - Thermodynamic assessment and update (database spotty)
  - Comparison of the potential of new routes (chloride, fluorides, oxides, etc...)
  - Small-scale tests to validate thermo & demonstrate feasibility
- **Questions**
  - What raw materials?
  - What products:
    - state (solid or liquid)
    - purity specification (alloying w/transition elements is easier)
ARPA-E Workshop
Rare Earth & Critical Materials

Supply / Material Processing Breakout Session
Dec. 6, 2010
Rare Earth Recovery

- **Mineral-Selective Reagents for Beneficiation & Recovery**
  - Magnetic & Electrostatic Separation

- Selective Flocculation

- Flotation Reagents
  (collectors & modifiers)

Engineered Complexation Controls Surface Chemistry & Selection
Rare Earth Recovery

- **Extractive Metallurgy**
  - Solvent Extraction
  - Ion Exchange
  - Leaching
  - Precipitation & selective crystallization
  - High temperature processing
Magnetic Separation in Suspension

Conventional Magnetic Separation Technology

- Magnetic Carrier – Magnetizes the impurities
- Reagent - Facilitates selective agglomeration and extraction

Chemically Enhanced Magnetic Separation

Selective Chemical aggregation of impurities and surface treated NanoMagnetite

Enhanced Magnetic separation

Step increase in Impurities removal by Judicious Combination of NanoTechnology and Magnetic Separation
Complex Mineralogical Systems

- Processing schemes are complex due to the...
  - similarity of rare earth material & surface properties
  - varied nature of gangue minerals
  - plethora of aqueous species
• Many current recovery processes for rare earths are very complex
• Reducing this complexity can result in improvements in efficiency – better recovery, less waste
Rare Earth and Critical Materials

- Novel extraction, processing, and recycling technologies

**Taylor - Novel Molten Salt Electrolysis Process**

- Based upon a recent KIEM PhD thesis on the production of boron metal from boron oxide (patent applied – Gomez and Taylor)
- Development of an electrolyte that contains a salt that may be more readily reduced than the RE oxide; but is less noble than the RE metal desired.
- May decrease environmental concerns due to the decreased use of halides.
- May allow a more economic method to reduce rare earth metal oxides
Taylor - Recycle of Rare Earth Magnets

- Remelting in a controlled atmosphere furnace with liquid/liquid extraction using magnesium or zinc metal.
- By using magnesium, the neodymium will be dissolved forming a Mg-Nd alloy.
- In the case of molten zinc, neodymium and iron will be dissolved forming a Zn-Nd-Fe alloy.
- Magnesium and zinc are later removed by distillation.
- May be an economic method for recycling some RE magnets.
**Rare Earth and Critical Materials**

- **Novel extraction, processing, and recycling technologies**

---

**Taylor - Dry Milling and Recovery Circuits for Rare Earth Metals**

- Replace wet grinding, flotation and acid leaching with dry grinding, dry concentration and pyrometallurgical extraction.
- Evaluate using density, conductivity and magnetic susceptibility for dry concentration.
- Evaluate direct carbo-chlorination and separation of the minerals to chloride products.
- May eliminate much of the water quality issues in mineral processing and extraction of RE metals from minerals.

---

**Table:**

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Specific gravity</th>
<th>Magnetic Response</th>
<th>Electrostatic Response</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bastnasite</td>
<td>5</td>
<td>Paramagnetic</td>
<td>Non conductor</td>
</tr>
<tr>
<td>Monazite</td>
<td>4.9-5.5</td>
<td>Paramagnetic</td>
<td>Non conductor</td>
</tr>
</tbody>
</table>

---

**Diagram:**

Carbo-chlorination of Nd$_2$O$_3$

---

G. S. ANSELL DEPARTMENT OF METALLURGICAL & MATERIALS ENGINEERING
Rare Earth and Critical Materials
- Novel extraction, processing, and recycling technologies

**Anderson – Selective TREO Ion Exchange Adsorption**

- Replace solvent extraction reagents and multiple series mixer settler units.
- Replace ion exchange organic substrates thereby eliminating, shrink, swell, crosslink and pressure drop issues.
- Eliminate complex elution regimes
- Evaluate selective active agents for discrete adsorption and concentration of TREO’s from aqueous phase.
- Evaluate and establish protocol for attachment of active agent to a silica substrate.

![Ion Exchange Resin On Silica Substrate Schematic](image_url)

Anchored nitrogen atoms not involved
N/Pd = 1

Anchored nitrogen atoms involved
N/Pd = 2
Rare Earth and Critical Materials
- Novel extraction, processing, and recycling technologies

Anderson – Hydrometallurgical
Direct Precipitation of Rare
Earth Metals.

- Replace pyrometallurgical fused salt reduction.
- Replace intermediate salt production and handling.
- Direct hydrometallurgical production of high purity Rare Earth Metals
- Predicated on selective IX adsorption followed by elution and concentration.
- Evaluate and optimize using ionic, non ionic, galvanic and electrolytic reduction and direct recovery.
Separation of Lanthanides
- Potential Research Directions

Presenter: Glen Fryxell

Contributors: Gregg Lumetta, Randall Scheele, Chuck Soderquist and Shane Addleman

Pacific Northwest National Laboratory
Many other metals will dissolve concurrently with the RE, and must be either recovered or disposed of.

- Includes thorium, uranium, and their daughters.

Tailings and insoluble matter may be hazardous or radioactive and must be managed accordingly

- New technologies could be applied to minimize the mass of the hazardous fraction.
Lanthanide separation by solvent extraction

- Lanthanide cations extracted from aqueous solution into an organic phase using a lipophilic complexing agent (HDEHP)

- Separation of one element (X) from another (Y) is dependent upon the distribution ratio ($D$) for each:

$$D = \frac{[\text{ElementX}]_{\text{org}}}{[\text{ElementX}]_{\text{aq}}}$$

- Low separation factors (SF) require many stages to effect the separation
  - This is the current situation for the lanthanides

HDEHP

Ln distribution ratios for extraction from 0.5 M HCl with 0.75 M HDEHP in toluene. Taken from Peppard et al. J. Inorg. Nucl. Chem., 1957, 4, 334-343.
Potential Research Directions

- Increase separation factors between adjacent lanthanide through, for example:
  - Design of selective extractants using molecular recognition principles
  - Manipulation of chemical speciation to exploit differences in properties such as
    - Solubility
    - Volatility
    - Extraction kinetics

- Explore separations using surface-functionalized nanoporous sorbents
Improving separations through ligand design

- New extractants are needed to increase the separation factors between the different lanthanide elements; especially Pr/Nd.
- Previous work at PNNL has shown that improved metal ion binding can be achieved by linking complexing groups in a pre-organized manner that favors the target ion(s).

Traditional malonamide must rearrange to chelate to lanthanide or actinide ion.

Molecularly constrain amide oxygen atoms into the correct geometry for metal ion binding.

Bicyclic diamide displays exceptionally high affinity for Am(III) and Eu(III).

This ligand design approach could potentially be used to develop new extractants that selectively differentiate between the different lanthanide elements.

$10^7$ increase in extracting power.
Counter-current solvent extraction development and testing capabilities

Lab-scale (2-cm rotor) centrifugal contactors instrumented for real-time monitoring of process solution composition and other process parameters

- Raman (nitrate, nitric acid, uranyl ion)
- Vis/NIR (neodymium, plutonium, neptunium)
- Flow meters
- Balances (mass of process vessels)

On-line monitoring allows for more rapid flowsheet development and testing

- Reduces need for time-consuming laboratory analyses

Extension to processing plant allows optimization of plant operation and control
Differences in thermal reactivity and physical properties can be used for separations:

- Treatment of mixed (U,Pu)O₂ by NF₃ at 500°C can be used to separate U from Pu.
- Similar strategies could be useful for lanthanides.
Chemically selective nanoporous sorbents

- **High binding capacity** comes from coupling the extremely high surface area of the support with dense surface coverage of the monolayer coating.
- **Fast sorption kinetics** arise from the rigid, open pore structure which leaves all of the binding sites available all of the time.
- **Chemical specificity** dictated by monolayer interface; easily modified for a wide range of target species.
- Particle size can be tailored to fit application/engineering needs.
- Sorbent can be stripped and regenerated many times.
- Have been tailored to bind lanthanide cations.

Nanoporous sorbents binding Hg.

Thiol monolayer lining the pore surface of mesoporous silica. The mercury (shown in blue) binds to the sulfur atoms (sulfur atoms are shown in yellow).

RARE EARTH SUPPLY/DEMAND SITUATION

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Many of the slides for this presentation were taken from talks presented by the following persons at recent conferences or workshops on the rare earth crisis

Dudley J. Kingsnorth  Industrial Minerals Company of Australia, Pty. Ltd.
James B. Hedrick  U.S. Geological Survey – retired
Mark A. Smith  Molycorp Minerals
Anthony N. Mariano  Consultant
Chen Zhanheng  Chinese Society of Rare Earths
Yasushi Watanabe  Geological Survey of Japan
REE PRODUCTION TRENDS

Monazite-placer era | Mountain Pass era | Chinese era → ?

Source: USGS Fact Sheet 087-02 updated with recent USGS Minerals Yearbook
REE MINERAL RESERVES

88 million metric tons of contained rare-earth oxide (REO)

- China: 30.9%
- United States: 14.9%
- Others: 25.2%
- CIS: 21.8%
- Malaysia: <1%
- Australia: 6.0%
- India: 1.3%

Enough Rare Earths for >600 years at current production levels
## RESERVES
**(in percent)**

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Australia</td>
<td>3</td>
<td>6.1</td>
<td>6.0</td>
</tr>
<tr>
<td>China</td>
<td>70</td>
<td>51.3</td>
<td>30.9&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>India</td>
<td>4</td>
<td>2.7</td>
<td>1.3</td>
</tr>
<tr>
<td>CIS</td>
<td>2</td>
<td>0.5</td>
<td>21.8</td>
</tr>
<tr>
<td>Malaysia</td>
<td>--</td>
<td>&lt;1</td>
<td>&lt;1</td>
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<tr>
<td>USA</td>
<td>20</td>
<td>15.0</td>
<td>14.9</td>
</tr>
<tr>
<td>Other</td>
<td>1</td>
<td>24.4</td>
<td>25.2</td>
</tr>
</tbody>
</table>

Total (M metric tons) 26 84 88

<sup>a</sup>The actual tonnage of the known Chinese reserves increased by almost 300% from 1980 to 2010.
China: RE Export Transition

- 1970s: Rare earth mineral concentrates.
- 1980s: Mixed rare earth chemical concentrates.
- Early 1990s: Separated rare earth oxides and metals.
- Late 1990s: Magnets, phosphors, polishing powders.
- 2000s: Electric motors, computers, batteries, LCDs, mobile phones.
REE WORLD MINERAL PRODUCTION IN 2008

124,000 metric tons of contained rare-earth oxide (REO)

Black market: 10 to 15% of reported production, mostly smuggled out of China
## REGIONAL PROPORTION OF RARE EARTH RESERVES IN CHINA (REO,%)  

<table>
<thead>
<tr>
<th>SOURCE</th>
<th>COMMENT</th>
</tr>
</thead>
<tbody>
<tr>
<td>BaoYunebo Mine</td>
<td>Rare earth content has decreased</td>
</tr>
<tr>
<td>Shandong</td>
<td>8%</td>
</tr>
<tr>
<td>Sichuan</td>
<td>3%</td>
</tr>
<tr>
<td>South of China</td>
<td>Ore deposits will be exhausted of rare earths in 10-15 years</td>
</tr>
<tr>
<td>Others</td>
<td>3%</td>
</tr>
</tbody>
</table>
RARE EARTH IMPORTS
Principal sources by weight in 2008

- CHINA: 93.0%
- JAPAN: 1.5%
- FRANCE: 2.6%
- AUSTRIA: 0.8%
- RUSSIA: 0.5%
THE RARE EARTHS MARKET TODAY

- Estimated demand in 2010: 125,000t REO
- Average price: US$20/kg REO;
  - LaCe $40/kg REO
  - Nd, Pr $70/kg REO
  - Dy $200/kg REO
  - EuTb $550/kg REO
- Total value: US$ 3 billion pa
- Constraints on Chinese exports are creating opportunities for non-Chinese projects
- Many non-Chinese rare earths projects being evaluated
U.S. MINES

- Carbonatites
- Peralkaline Igneous Deposits
- Vein Deposit
- Magnetic Ore Deposit

Locations:
- Nd Lemhi Pass
- LREE Bear Lodge
- HREE Pajarito
- HREE Bokan MT
- HREE Mineville

References:
- Nd Lemma Pass LREE
- Bear Lodge HREE
- Pajarito HREE
- Bokan MT
## U.S. MINES

### Expected Dates for the Beginning of Mining

<table>
<thead>
<tr>
<th>Location</th>
<th>Company</th>
<th>Date</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mountain Pass, California</td>
<td>Molycorp</td>
<td>2011</td>
</tr>
<tr>
<td>Bokan Mountain, Alaska&lt;sup&gt;a&lt;/sup&gt;</td>
<td>Ucore Uranium (Canada)</td>
<td>2014</td>
</tr>
<tr>
<td>Bear Lodge, Wyoming</td>
<td>Rare Element Resources</td>
<td>2015</td>
</tr>
<tr>
<td>Lemhi Pass, Idaho</td>
<td></td>
<td>&gt;2015</td>
</tr>
<tr>
<td>Pajarito, New Mexico&lt;sup&gt;a&lt;/sup&gt;</td>
<td></td>
<td>&gt;2015</td>
</tr>
<tr>
<td>Pea Ridge Mine, Missouri&lt;sup&gt;b&lt;/sup&gt;</td>
<td></td>
<td>&gt;2015</td>
</tr>
<tr>
<td>Mineville, New York</td>
<td></td>
<td>&gt;2015</td>
</tr>
</tbody>
</table>

<sup>a</sup>Deposits listed in green print are heavy rare earth deposits

<sup>b</sup>Iron mine being reopened in 2012.
Applications For Rare Earth Elements

Electronics
- Display phosphors (CRT, PDP, LCD)
- Medical imaging phosphors
- Lasers
- Fiber Optics
- Optical temperature sensors

Catalysts
- Petroleum refining
- Chemical processing
- Catalytic converter
- Diesel additives
- Industrial pollution scrubber

Glass
- Polishing compounds
- Optical glass
- UV resistant glass
- Thermal control mirrors
- Colorizers/Decolorizers

Other
- Water Treatment
- Fluorescent lighting
- Pigments
- Fertilizer
- Medical Tracers
- Coatings

Ceramics
- Capacitors
- Sensors
- Colorants
- Scintillators

Magnets
- Motors
- Disc drives & disk drive motors
- Power generation
- Actuators
- Microphones & speakers
- MRI

Metal Alloys
- Hydrogen storage (NiMH batteries, Fuel cells)
- Steel
- Lighter flints
- Aluminum/ Magnesium
- Cast iron
- Superalloys

Rare Earths
4f ELECTRON ENERGY LEVELS
(In the absence of a crystal field)
SUBSTITUTION

Difficult, if Not Impossible

Most critical applications – phosphors, magents
  Depend on the 4f electronic levels (each lanthanide is different) and crystal environment
    Eu – color TV
    Nd – lasers
    Nd, Sm – permanent magents
    Tb – fiber optics
    La, Y, Gd – absence of 4f level – optical & electronic

Applications of unseparated rare earths
  Depend upon the valence state and average atomic size of the rare earths in the mixture
    petroleum cracking catalysts
    alloy additives – Mg, Al, cast iron

Mixed valence applications
  CE(III)-CE(IV) – glass polishing, UV resistant glass, catalytic converters
SUBSTITUTION – YES or NO EXAMPLES

YES
Mischmetal for La in Ni metal hydride batteries
Rouge (Fe oxides) for CeO$_2$/Ce$_2$O$_3$ in glass polishing
(However Ce is not in short supply – excess)

PARTIAL SUBSTITUTION
Pr for Nd in NdFeB magnets; 4Nd atoms per 1Pr in original ore
Y – high temperature superalloys – used for ~30 years
Al, Cr, could be utilized instead of Y

NO (People have been looking – but no luck)
Eu – red color in TV; used for ~50 years, yet no substitute
Nd – permanent magnets; used for ~27 years, , yet no substitute
Sm – permanent magnets; used for over 30 years, , yet no substitute
Ce – 3-way catalytic converters (automotive exhaust) – used for ~30 years – yet no substitute
Rare Earths Project Essentials

- Compliant resource/reserve
- Rare earth minerals amenable to concentration
- Continuous pilot plant to demonstrate/provide:
  - Ability to produce products to customer specifications
  - Data for bankable feasibility study
  - Data for environmental impact statement, including radioactive waste management
  - Viability of project for investors and banks
- Access to labour, power, water and chemicals
- Realistic marketing strategy
- Adequate funding including working capital ($\leq 500\ M\$)
- Realistic construction and start-up schedule
THE OUTLOOK FOR 2015

• Supply will be tight.
• ‘Balance’ will still be an issue; so prices for Nd, Tb, and Dy will remain strong.
• Potential large surplus of Ce.
• China will not ‘starve’ the ROW of rare earths.
• Several new projects should be on-stream
• Demand: 190-210,000tpa RWO – **will be met.**
WILL THE CHINESE CUT THE PRICE OF RARE EARTHS IN THE FUTURE?

WHAT RARE EARTH PRODUCTS?
Concentrates (mixed REO)
Individual oxides
Semi-finish RE materials, e.g. Nd, La, Dy; compounds for phosphors; magnet materials

BUT NOT FINISHED PRODUCTS
• magnets for electric motors
• CFL
• cell phones, etc.

NOT LIKELY
South China clays will be depleted in 10 to 15 years
Chinese economy is growing so fast they will need all of Chinese rare earths by 2015 at the latest
Chinese do not want to use their vast, but finite, resources to supply the rest of the world (ROW) high tech products
GSCHNEIDNER’S FORECAST

USING
Dudley Kingsnorth projections
Published information from non-Chinese companies planning on mining RE ores

PREDICTION
There will be a 13% surplus of REO on the market between 2015 and 2020
Because of over production, weak companies will go out of business, the strong will survive.
RECOMMENDATIONS
INDUSTRY

Strong US Government Support
Start-up RE mining, primary production of REs
beneficiation, separation, oxide producers

IT IS HAPPENING

Future near term action of support
Premanufacture RE materials
Nd, La, compounds for phosphors
Manufacturers of products containing rare earths
electric motors, batteries, cell phones, monitors, CF lamps
Loan guarantees in House bill, which passed just before the recess for the election.

Companies
Vertically integrate
full spectrum of RE processing and manufacture

Alliances
companies involved in the supply train (mining to products)
Training students
undergraduate, graduate, post-doctorate
chemistry, chemical engineering, material science &
ingengineering, physics

Research projects funding
NSF, DOE, DOD, NIST

National Research Center for Rare Earths and Energy
Education institution with a strong tradition on REs
Link with industry
Subsidiary branches at other universities
Recycling grinding swarf from rare earth sintered magnet production

• **Press to Shape (P-T-S )**
  – High yield
  – Inferior properties
  – Not currently used by Chinese

• **Blocks and slicing**
  – blade thickness of 0.025+/-.
  – rectangular pieces,
    • the yields range from a high of ~92% to a low of ~45%

• **EDM (arcs or cylinders)**
  – From rectangular blocks
    • Low yield
      – Large chunks
        » milled and fed back into the process
    • Cut thickness 0.012+/-
      – Swarf is nanoparticulate.
Swarf Properties

*low value*

- Slicing swarf
  - Fine particles
    - Highly oxidized
    - Contaminated
      - Cutting fluid
      - Abrasive residue
    - Mixed chemistries

- EDM swarf
  - Nanoparticles
    - Suspended in fluid
    - Contaminated with wire brass

- Must be reprocessed to be usable
  - Chemistry vastly different from ore
Opportunity

• Two stage recycling
  – Develop simple process to be carried out by magnet processor to concentrate RE into a uniform high value product
  – Develop separations process to be carried out at RE processor to reclaim rare earth oxides

• RE separation simplified
  – Only Pr, Nd, Sm, and Dy should be in stream
Acetate

8 Fe(III) → 8 Fe(II)

U(VI), TC(VII), Au(III)
sorbed or accumulated by bacterial species
(La, Eu, Yb, Sm, Sc, Er, Lu, Ce, Pr & Nd)


Adaptive Evolution for Higher Current Production Led to Faster Fe(III) Reduction, Greater Pilin Production and Higher Conductance

Electrode-Selected Strain KN400

- 10-fold higher power output
- higher power output per cell
- more pili
- fewer outer surface cytochromes
- higher biofilm conductance

Other Strategies
- Genetic Modification
- Antibodies to Metals

Instead of the addition of soluble Electron donor, Use of Electrodes as An Electron Donor for In Situ Uranium Bioremediation Offers the Potential for Simple, Controlled Delivery of Electron Donor to the Subsurface…

Electrons provided by the electrode serve as an electron donor to stimulate reduction of uranium which becomes immobilized on the electrode and in soil.

Electrode-stimulated Anaerobic Bioremediation Zone

Uranium electrosorbs to electrode surface

Treated Water

...and a Strategy for Easily Removing the Reduced Uranium From the Subsurface

Forward Looking Statements and Other Important Cautions

This presentation contains forward-looking statements that represent Molycorp's beliefs, projections and predictions about future events or Molycorp’s future performance. Forward-looking statements can be identified by terminology such as “may,” “will,” “would,” “could,” “should,” “expect,” “intend,” “plan,” “anticipate,” “believe,” “estimate,” “predict,” “potential,” “continue” or the negative of these terms or other similar expressions or phrases. These forward-looking statements are necessarily subjective and involve known and unknown risks, uncertainties and other important factors that could cause Molycorp’s actual results, performance or achievements or industry results to differ materially from any future results, performance or achievement described in or implied by such statements.

Factors that may cause actual results to differ materially from expected results described in forward-looking statements include, but are not limited to: Molycorp’s ability to secure sufficient capital to implement its business plans; Molycorp’s ability to complete its modernization and expansion efforts and reach full planned production rates for rare earth oxides and other planned downstream products; uncertainties associated with Molycorp’s reserve estimates and non-reserve deposit information; uncertainties regarding global supply and demand for rare earths materials; Molycorp’s ability to maintain appropriate relations with unions and employees; Molycorp’s ability to successfully implement its “mine-to-magnets” strategy; environmental laws, regulations and permits affecting Molycorp’s business, directly and indirectly, including, among others, those relating to mine reclamation and restoration, climate change, emissions to the air and water and human exposure to hazardous substances used, released or disposed of by Molycorp; and uncertainties associated with unanticipated geological conditions related to mining.

For more information regarding these and other risks and uncertainties that Molycorp may face, see the section entitled “Risk Factors” beginning on page [14] of the prospectus described below. Any forward-looking statement contained in this presentation or the prospectus reflects Molycorp’s current views with respect to future events and Molycorp assumes no obligation to publicly update or revise these forward-looking statements for any reason, or to update the reasons actual results could differ materially from those anticipated in these forward-looking statements, even if new information becomes available in the future, except as otherwise required by applicable law.

This presentation also contains statistical data and estimates obtained by Molycorp from industry publications and reports generated by third parties. Although Molycorp believes that the publications and reports are reliable, it has not independently verified such data.

**THIS PRESENTATION USES THE TERM “RESOURCES” TO DESCRIBE THOSE QUANTITIES OF REE’S THAT ARE POTENTIALLY RECOVERABLE FROM ACCUMULATIONS YET TO BE DISCOVERED. BECAUSE OF THE UNCERTAINTY OF COMMERCIALITY AND LACK OF SUFFICIENT EXPLORATION DRILLING, THE RESOURCES CANNOT BE CLASSIFIED AS RESERVES. INVESTORS ARE ADVISED THAT THE SEC DOES NOT RECOGNIZE RESOURCES. ONLY PROBABLE AND POSSIBLE RESERVES MAY BE DISCLOSED TO INVESTORS IN AN SEC FILING. RESOURCES HAVE A GREAT AMOUNT OF UNCERTAINTY AS TO THEIR EXISTENCE. THERE IS NO CERTAINTY THAT ANY PORTION OF THE RESOURCES WILL BE DISCOVERED AND, IF DISCOVERED, WHETHER THEY COULD BE DEVELOPED ECONOMICALLY. THEREFORE, INVESTORS ARE CAUTIONED NOT TO ASSUME THAT ALL OR ANY PART OF MOLYCORP’S RESOURCES EXIST, OR THAT THEY CAN BE DEVELOPED ECONOMICALLY. ACCORDINGLY, INFORMATION CONCERNING DESCRIPTIONS OF RESOURCES CONTAINED IN THIS PRESENTATION IS NOT COMPARABLE TO INFORMATION INCLUDED IN SEC FILINGS.**

The issuer has filed a registration statement (including a prospectus) with the SEC for the offering to which this communication relates. Before you invest, you should read the prospectus in that registration statement and the other documents the issuer has filed with the SEC for more complete information about the issuer and this offering. You may get these documents for free by visiting EDGAR on the SEC Web site at www.sec.gov. Alternatively, the issuer, any underwriter or any dealer participating in the offering will arrange to send you the prospectus if you request it by calling toll-free [877-731-6659].
Reestablish key Western Rare Earth Supply Chains

- Produce a full suite of high purity products
- Exceed all environmental requirements
- Be globally cost competitive
Mountain Pass Challenges

- Two Minerals: Bastnasite & Monazite
- 15 Elements: Complicated Separations
- Balancing Production with an eye on the individual commercial markets for all.
- Exceed Customer Needs
- Maintaining a competitive position vis-à-vis China.
Meeting the Challenges

- Develop IP protected, value added uses for RE materials
  - Ensure RE products are not stockpiled
- Develop innovative Plant processes that:
  - Produce new products
  - Increase recovery
  - Reduce costs
- Help Customers Understand RE Requirements
Rare Earths in Actinide Separations

Candido Pereira
Chemical Sciences & Engineering Div.
Argonne National Laboratory

Rare Earth and Critical Materials Workshop
December 5, 2010
Arlington, VA
Can rare earth supply be extended through improved separation and recovery technologies?

- Improve efficiency of recovery from existing sources and low-grade sources
  - Target specific rare earths to achieve separations from mixtures or low-grade ores
  - Improve separation among RE using new technologies or improved extraction methods

- Develop technologies to efficiently recover REE from non-traditional sources
  - Harvest REE as a by-product from other metal recovery operations
  - Recycle REE elements from manufactured materials
    - catalysts, powders, batteries, lamps, glasses, etc.
  - Recovery options and needs may parallel those of low-grade sources
    - Composition variation, transportation, segregation, collection issues

- Knowledge base developed for other materials processing may be adaptable to REE recovery
  - Nuclear fuel processing and recycle
  - Thorium processing
Typical used nuclear fuel includes a significant fraction of REE

- Nuclear separations target recovery of selected actinides from a complex feed
  - Rare earths comprise the largest fraction of fission products
  - RE fraction is dominated by lighter metals
  - Current industrial-scale processes (PUREX) are based on solvent extraction but do not target fission product separations

- Advanced recycle options under development parallel those used for REE
  - Solvent extraction and pyrochemical processes have been primary focus of development

- Stringent processing requirements
  - Limit material losses
  - High purity requirements on final product
  - Recovery of minor components from complex feed
  - Stringent controls on releases (off-gases, process water, secondary chemicals)

---

**Typical Used LWR Fuel Composition (as metal, excl. U)**

<table>
<thead>
<tr>
<th>Component</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gp I&amp;II</td>
<td>12.2%</td>
</tr>
<tr>
<td>Noble Metals</td>
<td>10.5%</td>
</tr>
<tr>
<td>Noble Gases</td>
<td>12.2%</td>
</tr>
<tr>
<td>Tran. Metals</td>
<td>12.9%</td>
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<tr>
<td>Other</td>
<td>7.3%</td>
</tr>
<tr>
<td>TRU</td>
<td>21.5%</td>
</tr>
<tr>
<td><strong>Rare Earths</strong></td>
<td><strong>23.5%</strong></td>
</tr>
</tbody>
</table>

**Rare Earth Metal Distribution**

<table>
<thead>
<tr>
<th>Rare Earth Metal</th>
<th>Distribution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y</td>
<td>4.1%</td>
</tr>
<tr>
<td>La</td>
<td>11.7%</td>
</tr>
<tr>
<td>Ce</td>
<td>22.9%</td>
</tr>
<tr>
<td>Pr</td>
<td>10.6%</td>
</tr>
<tr>
<td>Nd</td>
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</tr>
<tr>
<td>Pm</td>
<td>0.2%</td>
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<tr>
<td>Sm</td>
<td>7.7%</td>
</tr>
<tr>
<td>Eu</td>
<td>1.7%</td>
</tr>
<tr>
<td>Gd</td>
<td>2.02%</td>
</tr>
<tr>
<td>Tb</td>
<td>3.3E-02</td>
</tr>
<tr>
<td>Dy</td>
<td>2.1E-02</td>
</tr>
<tr>
<td>Ho</td>
<td>3.1E-03</td>
</tr>
<tr>
<td>Er</td>
<td>1.2E-03</td>
</tr>
<tr>
<td>Tm</td>
<td>1.1E-06</td>
</tr>
<tr>
<td>Yb</td>
<td>7.1E-07</td>
</tr>
<tr>
<td>Lu</td>
<td>7.8E-05</td>
</tr>
</tbody>
</table>
Advanced used nuclear fuel separation schemes are designed to recover actinides for recycle.

- Several approaches are under development for different elemental separations:
  - Solvent extraction
  - Pyro-electrochemical
  - Ion Exchange
  - Gaseous processing

- Trivalent-actinide-lanthanide separation is the most difficult in a comprehensive treatment process:
  - Advanced aqueous processes have proven feasible for separation at the lab scale
    - TALSPEAK, SANEX
  - Pyrochemical processes have also been demonstrated for the separation

- Some separation among REE has been observed but not targeted.

```
UREX+3a Process

UREX → U, Tc

NPEX → U/Pu/Np

TRUEX → Non-RE FPs

TALSPEAK → Ln, Y

Am/Cm
```
INL Lanthanide Separations Chemistry Activities

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Process Science and Technology
Idaho National Laboratory (INL)
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November, 2010
Outline

What are the Strategic and Critical Minerals/Metals?

INL and Energy Resource Management

Current INL Activities

• Solvent Extraction Activities
• Supercritical Fluid Extraction Activities
• Coupled Ionic Liquid Supercritical Fluid Extraction Activities
• Pyroprocessing Activities
• Ion Exchange Activities
• Industrial Water Recycle/Recovery Activities

Future INL Activities

• Solvent Extraction
• Supercritical Solvent + Ionic Liquids Extraction
• Ion Exchange

Summary
What are the Strategic and Critical Minerals? “Critical” is in the eye of the beholder!

Strategic and Critical Minerals:

**USGS Definition:**
- RE’s, PGM’s, etc.
- In, La
- Mn, Ce
- Nb, Pr
- Ru, Nd
- Os, Pm
- Rh, Sm
- Ir, Eu
- Pd, Gd
- Pt, Tb
- Au, Dy
- Ag, Ho

**Strategic and Critical Metals:**

**DoD Definition:**
- High purity Be
- Al
- Cu
- Raw Steel
- Co
- Ni
- Ti
- An’s

INL has worked on various aspects of all of these “Strategic” elements in the past for a variety of agencies and companies.
Western Inland Energy Corridor: A Key to Energy Security

World-class Energy Resources
- Fossil (conventional and unconventional)
- Renewable
- Nuclear

Trillions of barrels of oil equivalent, local and secure

Regional Economic Development Opportunity — $Trillions
- Carbon / environmental management, efficiency
- Innovative and risk reducing

Need to do it right

“We should expand oil production by tapping into extraordinary potential of oil shale. In one major deposit — the Green River Basin of Colorado, Utah, and Wyoming — there lies the equivalent of about 800 billion barrels of recoverable oil. That's more than three times larger than the proven oil reserves of Saudi Arabia. And it can be fully recovered — and if it can be fully recovered it would be equal to more than a century's worth of currently projected oil imports.”

—President George W. Bush, June 18, 2008
Today’s Focus is on Rare Earth Elements
INL’s 2 Principal Areas of Interest

Mineral Processing and Elemental Recovery Efficiency plus Environmental Conservation Issues

- Elemental purification
- Elemental separation
- Water purification
- Water recovery
- Reagent recovery
- Waste handling

Recycling/Recovery Processing and Efficiency/Cost Effectiveness

- Elemental purification
- Elemental separations
- Water purification
- Water recovery
- Reagent recovery
Solvent Extractions and Extractants for Lanthanides

John R. Klaehn, Ph.D.
Mark D. Ogden, Ph.D.
What is solvent extraction?

The distribution of a solute between two immiscible liquid phases (liquid-liquid) in contact with each other. Below, the distribution ratio \( D \) is the ratio of the total concentration of the substance in the organic phase \([A]_{\text{org}}\) to the total concentration in the aqueous phase \([A]_{\text{aq}}\), if the volumes are 1:1.

\[
D = \frac{[A]_{\text{org}}}{[A]_{\text{aq}}}
\]
Mechanisms of Solvent Extraction

The most common types of lanthanide extractions are by the following:

**Metal Complexing**

\[ M^{z+} + zA^- \rightleftharpoons MA_z \]

Neutral, coordinatively saturated metal complex in organic phase

**Ion Exchange**

(Anion or Cation)

\[ M^{z+} + nL^- + pRNH^+L^- \rightleftharpoons (RNH^+)_{p}ML_{n-p} \]

Anion Type shown

Organic phase with anion exchanger and metal complex in organic phase

**Adduct Forming**

\[ M^{z+} + zA^- bB \rightleftharpoons MA_zB_b \]

Coordinatively saturated metal complex and B in organic phase

Formation of saturated metal complex through adduct former B in aqueous phase

Lanthanide Extractants (Chemical Structures)

Liquid Ion Exchange

**Dithiophosphinic Acid**
**INL Patented Minor Actinide Extractant**

Am$^{3+}$/Eu$^{3+}$ Separation Factor = 100,000

---

Adduct Forming

**Key points:** Manage Stability and 3$^{rd}$ Phase
Key Points for Lanthanide Extraction and Separation

→ **Stability** – no decomposition products to interfere with the separation

→ **Extraction efficiencies are not as important** – Continuous contactors (20-200X) are needed for effective lanthanide separations of neighboring elements.

→ **Solubility characteristics** – No 3rd phases during extraction process

**INL Advantages**

→ **INL can design and synthesize a variety of phosphinic acids** ($R_2PO_2H$; $R_2POSH$; $R_2PS_2H$) from multiple alkyl and aromatic ligands (R groups)

→ **INL key synthetic advantages**
  Regiochemistry is maintained with a wide array of possible alkyl and/or aromatic functional groups, even asymmetric (two different groups on phosphorus).

✓ **All the key properties can be independently addressed:**
  $pK_{a}$, Stability, and Solubility characteristics

**Disadvantages**

→ INL hasn’t investigated **selective** lanthanide extraction using their phosphinonic acids.
Introduction

Purpose: The future for AFCI (Advanced Fuel Cycle Initiative) and GNEP (Global Nuclear Energy Partnership) poses unique processing issues for the separation of various radioactive nuclides.

- Actinides(III) and Lanthanides(III): very difficult separation. (Dithiophosphinic acids (DPAHs) are good for An(III); however, DPAHs are varied for Ln(III) binding/chelation.)

To improve this separation one has to address multiple aspects of the extractant simultaneously:

- $pK_a$ of the dithiophosphinic acid
- Solubility characteristics
- Stability under typical acid extraction conditions
Extraction Conditions at the Idaho National Laboratory (INL)

- The pH is very low
  - aqueous nitric acid (~1M HNO₃)
- Oxidative environment (HNO₃)
- Radiolytic environment
- Aqueous vs. Organic solubility of the extractant

Extractants need to survive low pH and still give An(III)/Ln(III) separation!
Synthetic Pathway to Dithiophosphinic Acids (DPAH)

- 2 step synthesis (industrial synthetic process, Cytec Industries, Inc.)
- Many of the aliphatic DPAHs can be obtained commercially
  (Cytec Industries Inc.): Cyanex® 301 has been well investigated.
- Problem: Not very acidic ($pK_a$ is high)
- Problem: Must be purified from a mixture of products (~70% from manufacturer)

Main Problem with Cyanex® 301

- Prone to rapid degradation during the solvent extraction process
Expanded Higgin’s Reaction by Modolo et. al.¹ as an Actinide Extactant

¹ US Patent # 6,312,654

\[ \text{P}_2\text{S}_5 \xrightarrow{\text{Chlorobenzene, Heat}} \text{Bis(chlorophenyl)-dithiophosphinic Acid} \]

Yields are 50-70%²
No regio substitution control
Thermodynamic control only

**Advantages of Higgins Reaction**
One step synthesis

**Disadvantages of the Higgins Reaction**

- Non-regioselective; therefore, products will contain a mixture of *para* and *ortho* compounds. (thermodynamic products)

- Synthesis will be very difficult with electron withdrawing (ring deactivating) functional groups on benzene.

- Exclusive *ortho* or *meta* phenyl substituted dithiophosphinic acid products will not be viable.
Rational Design of the Dithiophosphinic Acids (DPAH)

Use the best parts

- Cyanex® 301 is good for An(III)/Ln(III) extraction - even without synergist! (Ionova, et al.)

- Diaryl substituted DPAHs are stable in 3.0M nitric acid and stable under radiolysis (Modolo, et al.)

How? – Anionic (Nucleophilic) substitution at phosphorus

Allows a variety of possible alkyl and aromatics with functional groups, even asymmetric products (placement of two different groups at phosphorus)
Reactive Reagents: Et$_2$NP(Cl$_2$) – Protected Phosphorus
(Two Pathways for Nucleophilic Substitution: DPAH Derivatives)

```
Cl$_2$P–N(CH$_2$CH$_3$)$_2$ → 2 F$_3$C

Diethyl ether, 0 ºC → N(CH$_2$CH$_3$)$_2$

2.0M HCl in diethyl ether → Hexanes, 25 ºC

```

```
F$_3$C

LiAlH$_4$

Diethyl ether reflux

H

Flower Sulfur / S$_8$

Toluene, reflux

```

“0” did not show selective An(III)/Ln(III) separation

Separation Factor = <10 (pH = ~2.5) [Am(III)/Eu(III)]
(using INL solvent extraction methods)
“Controlled” Reagents: PCl₃ – Plain Phosphorus (Two Pathways for Nucleophilic Substitution: DPAH Derivatives)

- Very good overall yields of ~40%
- “1” shows selective An(III)/Ln(III) separation
  Separation Factor = ~100,000 (pH = ~2.5) [Am(III)/Eu(III)]
  (using INL solvent extraction methods)

-Rejects Europium!
Nine different Lanthanides [Ln(III)] were analyzed. Organic: 0.1 M (1) in FS-13
Aqueous: 0.01 M HNO₃, 0.005 M Ln(NO₃)₃, 1.0 M NaNO₃ total

Rejects many other Lanthanides!
Asymmetric DPAH Acid Derivatives Using PCl₃ – Plain Phosphorus (“controlled” reagents)

Why asymmetric? better solubility in organic solvents

“4” shows selective An(III)/Ln(III) separation!
Separation Factor = ~5,000 (pH = ~4) [Am(III)/Eu(III)]
(using INL solvent extraction methods)
Anionic Substitution: Symmetric and Asymmetric DPAH Derivatives

An(III)/Ln(III) Separation factor = <10

“0”

An(III)/Ln(III) Separation factor = ~1000

“1”

“2”

An(III)/Ln(III) Separation factor = ~5000

“3”

An(III)/Ln(III) Separation factor = ~90,000

(Dean R. Peterman – INL An(III)/Ln(III) solvent extraction methods)

Asymmetric DPAH Derivatives
Dithiophosphinic Acid (1): X-ray Structure

Where are the Fluorines?

Fluorines are in the proximity of the phosphorus (solid state)

Distances

\[ P1 - F1 = 2.968(1) \text{Å} \]
\[ P1 - F5 = 3.165(1) \text{Å} \]

Courtesy of Rigaku Americas, Inc. - Dr. Lee M. Daniels
Ammonium Dithiophosphinic Salt (1c): X-ray

Where are the Fluorines?

Fluorines are *still* in the proximity of the phosphorus! (solid state)

Distances

P1-P1 = 2.989(2)Å
P1-F4 = 3.185(2)Å

Courtesy of Rigaku Americas, Inc. - Dr. Lee M. Daniels
DPAH “1” - Stability in Nitric Acid

HNO₃ (0.100M; 0.010M; 0.005M) and NaNO₃ (1.00M)

Exposure for 57 days

³¹P NMR
Summary of the Synthetic Methods

→ Designed a synthetic pathway that employs a wide array of alkyl and/or aromatic compounds which generates an entire new class of dithiophosphinic acid (DPAH) derivatives. The synthetic route addresses several issues for An(III) extraction.

→ Key Advantages
  • *Regio*- and *Stereo*- chemistry are maintained at the functional group
  • Wide array of possible alkyl and/or aromatic functional groups, even *asymmetric* (two different groups on phosphorus).

→ ALL the key properties can be addressed:
  • $pK_a$
  • Stability
  • Solubility characteristics

→ Current DPAH derivatives with o-CF3 ("1"; "2") show promise for effective An(III)/Ln(III) separation.
Continuing Work: Synthesis and Characterization

- Synthesize asymmetric DPAH derivatives using o-CF3
- More X-ray determinations with DPAH compounds
- Multinuclear NMR studies for “proximity” effects
- IR and Raman for extraction studies
Acknowledgements

This work was supported by the United States Department of Energy and the Laboratory Directed Research and Development (LDRD) program at the Idaho National Laboratory (INL) through contract DE-AC07-05ID14517.

Byron M. White & William F. Bauer – ICP/MS analysis

Special thanks for the X-ray Determination by Dr. Lee M. Daniels: Rigaku Americas Corp. using the new SCXmini.
Supercritical Fluid Extraction of Lanthanides

Mark D. Ogden, Ph.D.
INL
What is a Supercritical Fluid (SCF)?

A supercritical fluid is any substance at a temperature and pressure above its critical point (Fig. 1).

Above the critical point the supercritical fluid:
- can effuse through solids like a gas.
- dissolve materials like a liquid.

Close to the critical point, small changes in pressure or temperature result in large changes in density; allows many properties of a supercritical fluid to be "fine-tuned"

*Fig. 1 P-T phase diagram for a pure substance*. Dotted line indicates conditions needed to maintain critical density above $T_c$.

*Note that this diagram cannot be used to represent a real chemical reaction system which necessarily involves several components.*
Supercritical Fluid Extraction (SFE)

- majority of supercritical experiments are carried out in SC CO₂
- non-polar nature
- most solid ionic metal salts do not dissolve directly (i.e., overcome lattice forces).
- modifiers or complexants are used to increase solubilities of metal ions in the SCF phase

**Fig. 2.** Set-up to determine metal solubilities and speciation in SCF

- A useful rule-of-thumb is that if a substance dissolves in *n*-hexane, it will probably dissolve in SC CO₂ and vice versa.
Extraction Complexes in SC CO$_2$

1. Dissolution of rare earth material in concentrated nitric acid
2. Contact with SC CO$_2$ containing extractant ~ usually tributylphosphate (TBP)
3. Metal nitrate TBP complex soluble in SC CO$_2$
4. Water soluble in SC CO$_2$ acts as modifier
5. Combining another extractant only increases extraction modestly
Supercritical Fluid Extraction Research at INL

INL Advantages

INL already has developed capabilities in supercritical fluids:

- Supercritical fluid synthesis of novel catalytic compounds
- Supercritical fluid spectroscopy
- Supercritical CO₂ based extractions

INL Currently beginning to explore different SF matrices

- Extractions not explored in more polar SC fluids e.g. NH₃, MeOH, H₂O
- Polarity of SC phase can be modified by combining SC fluids; CO₂, MeOH, H₂O, NH₃
  - Polarity and density of supercritical phase can then be “tuned” to effect dissolution and separation much like solvent gradient elution in chromatography
- Combining ligands to increase extraction and separation in polar SF phases need to be tested
  - INL has a key synthetic advantage in development and design of ligands
- Combining SFE with chromatographic stationary phases to effect greater separations
Ionic Liquids Coupled with Supercritical Fluid Extraction for the Lanthanides

Brian Harris
Bill Bauer, Ph.D.
INL
Alternate Methods for Ln and An Class Separations

- **Room Temperature Ionic liquids (RTIL)**
  - Liquid at $T << 100^\circ C$
  - Very low volatility
  - Polar but hydrophobic organic solvents
  - High conductivity
  - Wide Electrochemical window

- **Supercritical Carbon Dioxide (sc-CO$_2$)**
  - Moderate $T$ and $P$ ($T_c = 31^\circ C$, $P_c = 73$ atm, $\rho_c = 0.47$ g/mL)
  - Easily tunable solvating properties via $T$ and $P$
  - Isolation by depressurization maximizes volume reduction
The Concept

- **Differential dissolution/extraction of Ln and An in RTIL**
- **Additional separation via selective back-extraction into sc-CO$_2$**
- **Adjustable parameters**
  - RTIL
  - Electrochemical parameters
  - Sc-CO$_2$
  - Synergist
- **Overall volume reduction**

RTIL: BMIM$^+$ cation with Tf$_2$N$^-$ or PF$_6^-$

[Diagram showing the concept with RTIL, Synergist, and sc-CO$_2$]
Preliminary Results

- Ln and An both extracted directly from soil (Rocky Flats) or acidic solution into RTIL with TPB(HNO$_3$)$_x$(H$_2$O)$_y$ as synergist – preference tends toward An
- Initial back extraction into sc-CO$_2$ slightly favors Ln over An
- Preliminary extractions of Bastnaesite ore
  - Ln and An have some direct solubility in RTIL
For Ln Separations

- Exploring the use of soft donor and other ligands as a means to vary the solubility of the Ln in the aqueous, RTIL and SC-CO$_2$ phases
- Possible ligands include
  - TPEN - N,N,N',N'-Tetrakis(2-pyridylmethyl)ethylenediamine
  - TTA - 2-Thenoyltrifluoroacetone
  - HFA – Hexafluoroacetylacetone
  - TODGA – N,N,N',N'-tetra(n-octyl)diacglycolamide
  - TBODA – N,N,N’ tetrabutyl-3-oxapentanediamide
Pyroprocessing Activities

Alan Wertsching
INL
**Pyroprocessing – Electrorefining**

- INL Materials and Fuels Complex

INL’s activities include metals electrorefining and purification.

Typical electrorefining experiment\(^9\).

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Driver fuel</th>
<th>Blanket fuel</th>
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</thead>
<tbody>
<tr>
<td>Uranium</td>
<td>99.19</td>
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<td>Zirconium</td>
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<td>Sodium</td>
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<td>Process impurities</td>
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</tr>
</tbody>
</table>
Industrial Ion Exchange Processes for Water Treatment

Eric S. Peterson, Ph.D.
Alan Wertsching
INL
Ion Exchange & Absorption

- Removal and purification of metals and metal ions from solutions
  - Industrial wastewaters
  - Military wastewaters
  - Electronic manufacturing
  - Gas stream conditioning
  - Environmental cleanup

Processes Investigated:
- Polymer-based ion exchange resins (subsurface barriers)
- Silica-based ion exchange resins
- Naturally occurring sulfides for mercury removal
Solid Phase Extraction Media – Modified Silica Particles

Dimensions:
150µm Diameter

Silica Particle

Chelating “Head” Group

“Teather”
Ion Capture and Regeneration Mechanism

Silica/resin surface

Calcium chloride and water

2NaCl

Calcium captured ion

Regeneration

Sodium chloride or acid

CaCl₂

Regenerated Silica/resin surface

US Patent #7,312,175
Weak Binding Metal

Strong Binding Metal

Decontaminated Water

0.1 M H₂SO₄

Metal Concentrate
**Ion Exchange -vs- SPE**
- Reduced Column Size
- More IX sites per cc
- Reduced column volume
- Pressure stable bed
- Thermally stable bed
- Reduced plant footprint

“Normal” Column Chromatography
Column Systems

New Solid Phase Extraction Column
What is an Engineered Fluid Transporting Fractal?

- It is manifold constructed of a simple repeating structure
- The repeating structure is added at smaller and smaller scale to a practical end point
- The repeating structure can be exactly or statistically similar
- Reduces/eliminates turbulence in the ion exchange bed

A collaborative project with Amalgamated Research, Inc., Twin Falls, ID

US Patent # 5,534,460
Technological Significance of Engineered Fractals

- Size reduction = 90%
- Energy reduction up to 99%
- Safety improved by eliminating pressure vessels
- Improves net energy balance of biobased products
Engineered Fractal Columns are Smaller, Cheaper, and more Efficient

Overlaid fractal theory on turbulent theory using CFD (INL)

\[
\rho \frac{\partial U_i}{\partial t} + \rho U_i \frac{\partial U_i}{\partial x_j} = - \frac{\partial p}{\partial x_i} + \frac{\partial}{\partial x_j} \left( 2 \mu D_{ij} - \rho \bar{u}_i \bar{u}_j \right)
\]

where \( \rho \bar{u}_i \bar{u}_j = \tau_{ij} \)

and \( D_{ij} = \frac{1}{2} \left( \frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} \right) \)

\[
\frac{\partial \bar{c}}{\partial t} + V_i \frac{\partial \bar{c}_i}{\partial x_j} = - \tau \frac{\partial V_i}{\partial x_j} + \varepsilon \frac{\partial V_i}{\partial x_j} + \Pi_i + \frac{\partial}{\partial x_j} \left( \mu \frac{\partial \bar{c}_i}{\partial x_j} + c_0 \right)
\]

\[
\Pi_i = \frac{\rho}{\rho} \left( \frac{\partial v_i}{\partial x_j} + \frac{\partial v_j}{\partial x_i} \right)
\]

\[
\varepsilon v = 2 \mu \frac{\partial v_i}{\partial x_j} \frac{\partial v_j}{\partial x_i}
\]

\[
\rho c_w = \rho \bar{v}_i \bar{v}_j + \frac{\partial \bar{v}_i}{\partial x_j} \frac{\partial \bar{v}_j}{\partial x_i} + \rho \bar{v}_i \bar{v}_j
\]

Approx. Dimensions:
8’ dia. X 10’ high, 700 gpm

From this to this

Approx. Dimensions:
3’ X 3’ X 2’ high, 700 gpm
Industrial Wastewater Recovery and Recycling

William Greene, SpinTek
Eric S. Peterson, Ph.D.
Active Surface Membranes - Spinning

INL’s innovation involves moving the membrane away from the surface of the stainless steel frit (this photo) and embedding it into the structure of the frit to make it virtually impossible to scrape off.
### Recycled Die Lube Results

<table>
<thead>
<tr>
<th>Test Part</th>
<th>Aluminum Valve Body</th>
</tr>
</thead>
<tbody>
<tr>
<td>Material</td>
<td>ASTM, A380 Aluminum</td>
</tr>
<tr>
<td>Poured Weight</td>
<td>9.8 lbs</td>
</tr>
<tr>
<td>Injection Temperature</td>
<td>1180 – 1205 F</td>
</tr>
<tr>
<td>Test Plant</td>
<td>LCDC</td>
</tr>
<tr>
<td>Part scrap before test</td>
<td>8.4%</td>
</tr>
<tr>
<td>Part scrap during test</td>
<td>7.2%</td>
</tr>
<tr>
<td>Reduction of waste</td>
<td>1.2%</td>
</tr>
<tr>
<td>Savings (Al only)</td>
<td>1200lb of Al savings/day, $750,000/year (Al only)</td>
</tr>
</tbody>
</table>
Rotating Membrane Economic Evaluation

Overall Rotating Membrane Process Costs
Total membrane costs (per 1,000 gallons – Kgals) $13.00
Total power operating cost per Kgals $9.05
Membrane cleaning operating cost per Kgals $0.26
Misc. operating costs – per Kgals $0.56

Total operating costs per Kgal $22.87
Total daily operating cost $457.40

Annual operating cost (for 7.2 million gallons water) $164,664

Savings Ratio: 750,000/164,664 = 4.55, full pay back in 18 months
Future and Ongoing INL Activities

• **Solvent Extraction**
  • Ongoing development of novel extractants for lanthanides
  • Ongoing development of SCF systems for lanthanides

• **Supercritical Solvent + Ionic Liquids Extraction**
  • Ongoing development of ionic liquids that function in SCF regime

• **Pyro- and Electrochemical Processing** of fuels and other metals

• **Ion Exchange**
  • Ongoing industrial/government development of materials and processes for specific needs including lanthanides

• **Rotary Filtration Membranes**
  • Ongoing development of embedded membranes coupled with fouling resistant surfaces

• **Environmental Management** with respect to impact, mining, and recovery/recycling
Summary

Current INL Activities
INL’s Interests are in elemental isolation and purification
• Solvent Extraction Activities
• Supercritical Fluid Extraction Activities
• Coupled Ionic Liquid Supercritical Fluid Extraction Activities
• Pyroprocessing Activities
• Ion Exchange Activities
• Water Recycle/Recovery Activities

Future INL Activities
• Solvent Extraction
• Supercritical Solvent + Ionic Liquids Extraction
• Ion Exchange
• Water recovery/recycling
• Environmental management
Programmatic Sponsors

- **DOE Offices:**
  - Energy Efficiency
  - Fossil Energy
  - Nuclear Energy
  - Environmental Management
  - Intelligence

- **INL:**
  - LDRD

- **OGAs**
  - DoD
  - DHS
  - NSF

- **Industrial:**
  - Battelle Memorial Institute (BMI)
  - Babcock and Wilcox
  - ChromatoChem
  - Dow Corning
  - Elf Atochem
  - EXXON
  - General Electric Corp.
  - Millipore
  - Shell Oil
  - Pall Corporation
  - Shell Oil
  - SpinTek, Inc.
  - Union Carbide
    (Air Products)
  - University of Sask.

- Over 70 CRADAs executed
SOM Electrolysis $\text{MO}_x \rightarrow \text{M} + \text{pure O}_2$
- Inert anodes, no back-reaction, no ion cycling
- Scaling up production of Mg, Si, Ti, Ta, etc.

MOxST REO(F) electrolysis process
- More efficient than metallothermic reduction
- Better current efficiency than without SOM
- Pure oxygen by-product

MOxST recycling technology
From Titanium to Rare Earths

- High current efficiency despite multiple valences
- Similar approach for multi-valent rare earths Ce, Pr
- Directly reduce calcined bastnäsite using local ore:
  \[(\text{Ce, La, Nd, Pr...})\text{OF} + \frac{1}{2} \text{CaO/BaO} \rightarrow \text{RE} + \frac{3}{2} \text{O}_2 + \frac{1}{2} \text{CaF}_2/\text{BaF}_2\]
  - Reuse fluorides in process
  - Sequential reduction?
- Far fewer steps and far less aqueous waste vs. current process

Cathode:
\[\text{Ti}^{4+} + 4e^- \rightarrow \text{Ti}\]

Anode:
\[O^2- \rightarrow \frac{1}{2}O_2 + 2e^-\]
MOxST Recycling Technology

- Nd or Nd/Dy from low-grade/heavily oxidized magnet scrap
- One-step electro-refining and reduction in molten salt
  - Refining at 1-1.5V
  - Reduction at 4-6V
  - Combine with Nd/Dy extraction
    - Add oxide(s) to bath

Electrochemical reaction equations:
- Cathode: \( \text{Nd/Dy}^{3+} + 3e^- \rightarrow \text{Nd/Dy} \)
- Scrapped anode (crucible): \( \text{Nd} \rightarrow \text{Nd}^{3+} + 3e^- \)
- SOM anode: \( O^2- \rightarrow \frac{1}{2} O_2 + 2e^- \)
Supply Breakout Session

David K. Shuh
Senior Scientist, Actinide Chemistry Group, Chemical Sciences Division
Associate Director, The Glenn T. Seaborg Center
Lawrence Berkeley National Laboratory, Berkeley, CA 94720 USA

ARPA E Workshop
Arlington, VA
6 Dec. 2010
Separations - The Siderophore Hypothesis

- Modeled after enterobactin, actinide sequestering agents are composed of catecholate and HOPO chelating subunits attached to various molecular backbones via amide linkages, to match the coordination environment of specific actinide ions.

Enterobactin

Fe Enterobactin Complex

Modeled Pu(IV) Complex
Pu Removal at Low Chelator Dosages @24h Mouse Model

3,4,3-LI(1,2-HOPO) effective two orders of magnitude below comparison dose!
(note effect of denticity on concentration dependence)
Comparative Chemical Information

Number of Crystal Structures in the Cambridge Database
(Updated November 2010)

- Fe: 27617
- La: 1922
- Ce: 1051
- Pr: 986
- Nd: 1949
- Sm: 2045
- Eu: 1879
- Gd: 1493
- Dy: 811
4f-electron Coordination Chemistry - Opportunities

- Separations and Solution Chemistry from understanding of coordination chemistry (+ thermo and kinetics)
- Electronic Structure and Bonding (f-electrons)
- New Materials and Theory
- Magnetism
- Homogenous/Heterogeneous Catalysis
- Health Science
- Next generation of scientists

Lanthanide - Actinide Trivalent Separation
Spectral Assignment by CPMD Method

Phen

Gd-Phen

Cm-Phen

T. Yaita (JAEA), D. K. Shuh (LBNL)
4f-electron Separations: Some Preliminary Thoughts About 1,2-HOPOs

• Ligands based on 1,2-HOPO are air stable and can withstand strongly acidic conditions. RE complexes using these ligands exhibit high thermal stability (up to 200 °C) and resistance to oxidative degradation.

• The stability of these complexes indicates that 1,2-HOPO ligands may be effective RE extractants and that the ligands may be successfully recycled using acidic conditions.

• The RE coordination environment can be modeled effectively using DFT (Light Atoms: B3LYP/6-31G(d,p) RE: Pseudopotential MWB).

• Rational design of ligands with increased rigidity and denticity may provide avenues for RE separation based on size and aqueous coordination number respectively (La to Lu coordination number changes from 9 to 8).

Luminescent Eu(III) 1,2-HOPO Complex
Rare (?) Earths

• Neither metals nor technology are rare (NY Times, Nov 9, 2010)
• What is Rare: Greener Technology for benign exploitation

Current extraction technologies: Mature with incremental potential

A star disruptive technology: Genetically engineered green reagents

• Surfactants, Enzymes with functional groups and dynamics
• Proven for Au, Fe, Zn P, As etc.,
• Bug factories for surfactin, acyl glutamates, Lipopeptides
• Genetically engineered microbes can adsorb on minerals
• They can produce specific metal chelating molecules

Challenges for green microbial technology for rare earths

• Mutation and genetic modular technology
• Green: energy & water consumption, chemical footprint
Microbes vs. Commercial reagents
Role of Bacillus Subtilis in extraction of Cu from talc

- Bacterial cells + Xanthate
- Bacterial cells only
- No reagents/bacterial cells

Cum. Cu Recovery, %

Cum. MgO recovery, %

QUARTZ-GROW (No envelope)

CALCITE-GROWN (Enveloped)

Polysaccharide Capsule
THE BACTERIUM *Thiobacillus ferrooxidans* ATTACHED TO PYRITE, LIBERATING GOLD (THE ROD SHAPED BACTERIA DEVOURING FLOWERS OF PYRITE, LIBERATING THE GOLD PARTICLES UNDERNEATH COULD BE SEEN)
Aptamers with specific affinity for metals

Short (15-50 bases long), single stranded oligonucleotides of RNA or DNA

High Binding affinity and specificity towards various targets; metal ions, bio-terror agent (anthrax, small pox etc.)

Challenges: Isolation from $10^{14}$ molecules, amplification

Oligonucleotide library: $10^{14}$ starting sequences
Going Forward: Greener Biobased Reagents

Twelve Principles of Green Chemistry

Greenness Scale 1.1

An index comprehensively considers production, use and disposal phases of reagents

Challenge: Cheap High volume Green Reagents
Solid Oxide Membrane (SOM) Process for the Production of Electropositive Metals (Li, Ca, Re, Mg, Ta, Ti, etc.)

Uday B. Pal and Adam C. Powell IV*

Department of Mechanical Engineering
Division of Materials Science and Engineering
Boston University

*Metal Oxygen Separation Technologies, Inc.
11 Michigan Drive, Natick, MA

Rare Earth Elements Workshop
DOE
December 6, 2010
**Schematic of the SOM Process for the Production of Electropositive Metals**

![Diagram of the SOM process](image)

**Anode**

\[ \text{O}^{2-} \rightarrow \frac{1}{2} \text{O}_2(g) + 2e \]

**Solid-Oxide Oxygen Ion Conducting Membrane (Stabilized Zirconia)**

**Cathode**

**Ionic Melt: Halides (AX) and Oxides (BO)**

\[ \text{O}^{2-}_{\text{(melt)}} \rightarrow \text{O}^{2-}_{\text{(YSZ)}} \]

\[ \text{B}^{2+}_{\text{(melt)}} + 2e^- \rightarrow \text{B} \]

- Inert to SOM
- High Ionic Conductivity
- Low viscosity
- Low volatility
- Stable

**Relevance to Rare earth element (Re) production (Source: Re}_2\text{O}_3 \text{ or Re}X_3**

CaCl\text{2}, LiCl, and CaF\text{2} are more stable than their corresponding Rare earth halides

- Ionic Melt: CaCl\text{2}-CaF\text{2}-Re\text{2}O\text{3} (Direct reduction of Re\text{2}O\text{3})
- Ionic Melt: CaCl\text{2}-ReX\text{3}-CaO or LiCl-ReX\text{3}-Li\text{2}O (Metallothermic reduction of ReX\text{3} with Ca and Li)

Less electropositive impurities can be removed prior to deposition of the desired rare earth element
Progress-to-date
SOM Electrolysis of MgO (Ionic Melt: CaF$_2$-MgF$_2$-MgO)

![Diagram of electrolysis setup]

20 KV scan (2-4 micron penetration)

![Energy spectrum graph]

Condensed Magnesium
Progress-to-date (Continued)
SOM Electrolysis of CaO (Ionic Melt: CaF₂-CaCl₂-CaO)

- Titanium production from its oxide using CaF₂-MgF₂ melts
- Tantalum production from its oxide using CaF₂-MgF₂ melts
- Silicon production from its oxide using MgF₂-BaF₂ melts
Features of the SOM Process

- Generic process for metals production
  - Source: Oxides and Halides
- Only oxide is electrolyzed; anodic reaction results in oxygen evolution and the cathodic reaction results in metals production
- High current density or production rate is possible
- Energy efficient and environmentally sound process
- Electrolyze metals having multiple valence (Ce, Pr)
- Impurity removal is possible
- Alloys can be directly produced at the cathode
- Process can be adapted for recovery or recycling of metals