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Improving Rare Earth Reuse and Recycling

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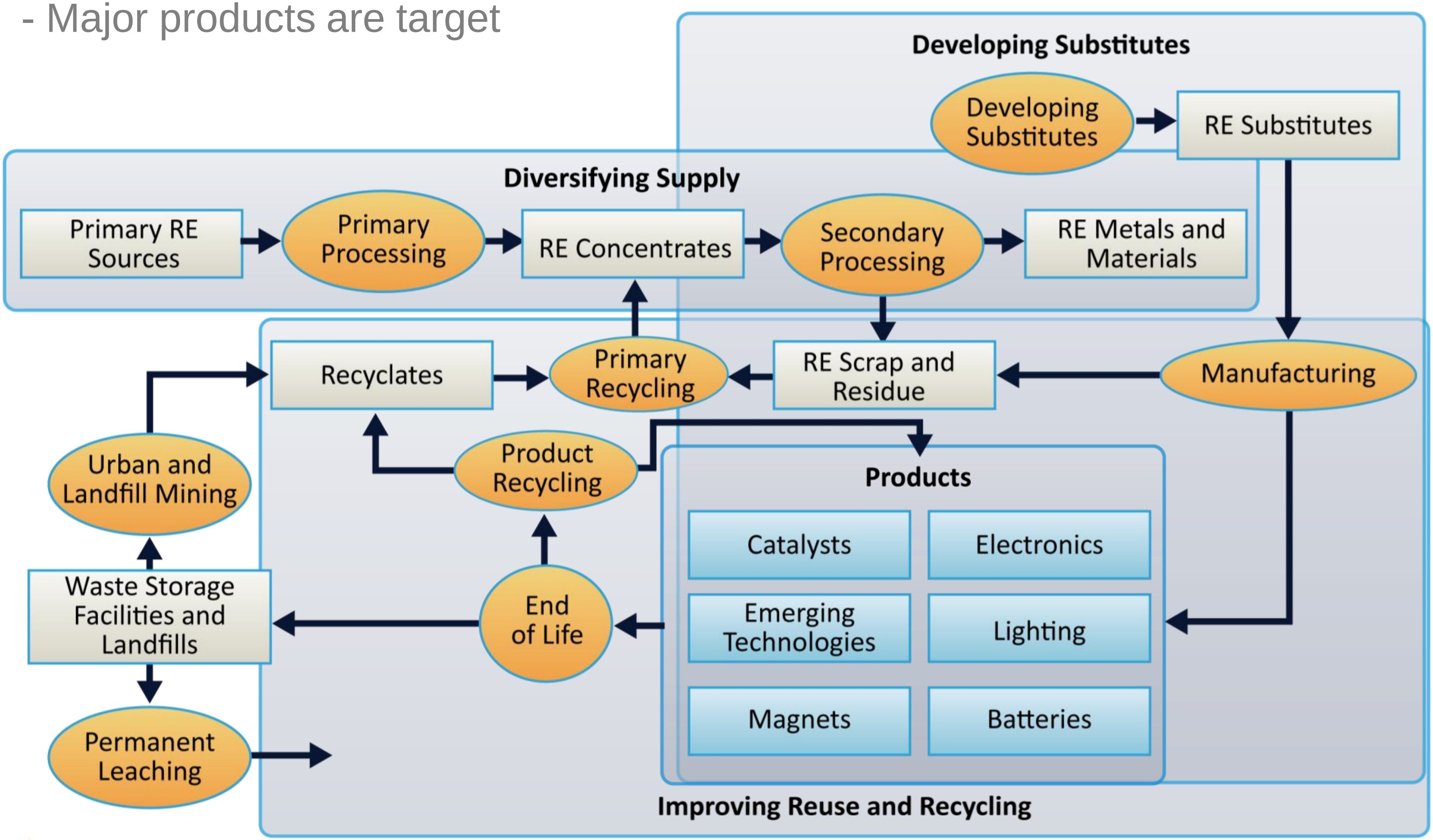
The Supply Chain and Economic Analysis

-Inherently connected
- Major products are target



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Improving Reuse and Recycling Research
2 Objectives/Thrusts, 3 Product Area Focus

Recovery from commercial product focus:
- Magnets
- Phosphors
- Electronics

Objective/Thrust 1: Enhance source preparation methods to maximize recovery of elements

- Topics:
  - Understanding Collection methodologies (Cross Cutting Component) ←
  - Phosphor recovery and processing ←
  - Large and small magnet identification, recovery, reuse, recycling ←
  - Electronics recovery and recycling

Objective/Thrust 2: Enhanced elemental extraction methods to maximize recovery.

- Topics:
  - Supercritical fluid recovery and extraction methods for phosphors ←
  - Membrane mediated solvent extraction methods ←
  - Electro- and pyro-chemical extraction, separation and purification methods ←
  - Biologically-based extraction and separation methods
  - Stabilized Filtration Methods (Cross Cutting Component) ←

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Some Sobering Statistics

INL/MIS-13-29862

Total Waste number in USA

- **~250.9 million tons of municipal solid waste was land-filled in 2012.**

Phosphors:

- **~30 - 38% of "industrial" CFLs at "end of life" are recycled.***
  - **~1 – 5% of "consumer" CFLs are recycled.**
  - **Market share of "industrial" vs. "consumer" is unknown.**

Sources: *www.lamprecycle.org ** www.kab.org. Association of Lighting and Mercury Recyclers

Electronics:

- **~15 - 25% of all consumer electronics at "end of life" are recycled.****
  - **~17 - 40% of all computers are recycled.**
  - **~17% TVs are recycled.**
  - **~8 - 11% cell phones are recycled.**

Magnets

- **Numbers are elusive**

- **Despite current recycling/recovery efforts *less than 1% of the REEs available in "end of life" consumer goods is currently being recovered* (Meyer and Bras, 2011; Tanaka et al., 2013; Anderson et al., 2012).**

- **Consumer electronics recycle/recovery legislation is currently stalled in the US Congress.**

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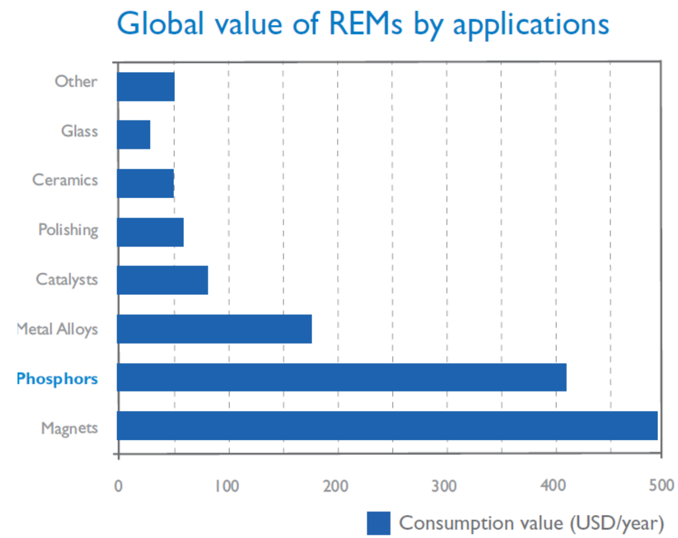
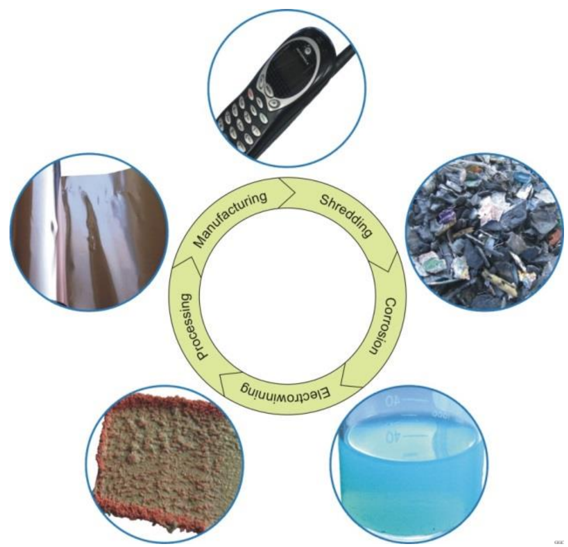
REE Reuse and Recycling Challenges

- Product diversity
- Collection of materials
- Processing of materials
  - Valuable/not valuable, or…..?
  - Environmental issues w/ byproducts/wastes
- Materials refining and purification





Mineralogy = None!

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Why is Efficient Use and Recycling Crucial?

- There will be a shortfall in heavy REEs supply within 10-15 years.

Here is why - - -

- No new sources of heavy rare earths have been brought on-line for over 20 years.
- Demand by 2017 of Heavy RE will be 3750 tonnes and the supply will be 1000 tonnes.
- **<u>One Example:</u>**
- 10 to 20 g of NdFeB magnets used in hard drives. Total hard drives made: 0.5 billion per year.

$$\left[\frac{5\times10^{8}\,drives}{year}\right]\left[\frac{10g}{drive}\right]\left[\frac{Nd}{3NdFeB}\right]\left[\frac{tonnes}{10^{6}\,g}\right]=1600tonnes/year$$

$$\left[\frac{19{,}000tonnesREO}{year}\right]\left[\frac{Nd_2O_3}{8REO}\right]\left[\frac{0.85Nd}{Nd_2O_3}\right]=2000tonnes/year$$

- Nd required: 1600 tonnes/year **<u>for hard drives only</u>**.
- Mountain Pass, CA can supply 2000 tonnes/year

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Why is efficient reuse and recycling crucial? - continued

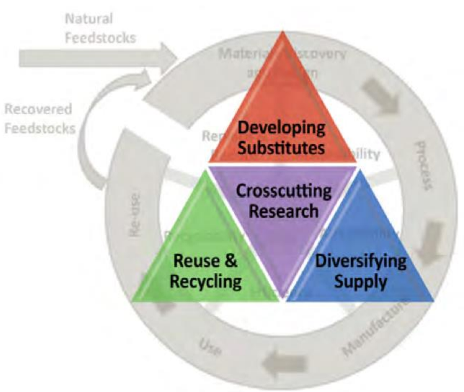
- No viable domestic source for Nd for all other applications like:
  - automobiles
  - windmills

We must recover and recycle!!!

- Y, Eu and Tb will continue to be in short supply with no domestic source for production.
- Y, Eu, and Tb REOs can be recovered from spent CFLs already demonstrated processing at Veolia-Global Tungsten & Solvay, **when the price is right.**
- Challenges:
  - generating the recycled REO from CFLs by improving the collection rate
  - recovery rate and purity
  - minimizing processing cost
  - Inventing lower energy demanding/cost refining approaches

CMI's Improving Reuse and Recycling

- To further diversify global supply chain of critical materials by:
  - understanding collection processes
  - enhancing recycling technologies
  - improving product design
  - understanding recycling techno-economics
  - using the thermodynamics of separations



- Why?
  - Low reuse and recycling is due primarily to poor economics and lack of methods that have high enough yield or low enough cost
  - Sources and matrices of recyclable materials are highly diverse
  - To prevent loss to garbage dumps and environment

Major Challenge for CMI's work:

Diversity of sources + policy to drive the technology adoption + process economics

Challenges for all efficient use and recycling projects

- Obtaining samples of materials
  - Radioactive ores at labs
  - Radioactive ores and shipping
  - Mercury/other metals (Pb, Sn, etc.) contamination in recycling material streams at the labs
    - Phosphors
    - Electronics powders
  - Sourcing of samples – treatability study? or purchase “products” – regulatory issues???
- Getting materials processed
  - Electronics conversions to powders
    - Hammer mill to powder
    - “Oxidation” (heating to nearly burning) followed by crushing to powders
- Dynamics of the industry
  - One partner was bought up
  - One partner went out of business then returned to working with us
  - Financing of businesses and their work
  - Super Storm Sandy and partners in New Jersey

Feedstock Formulation and Logistic Design Model from CMI's Crosscutting Science Focus Area

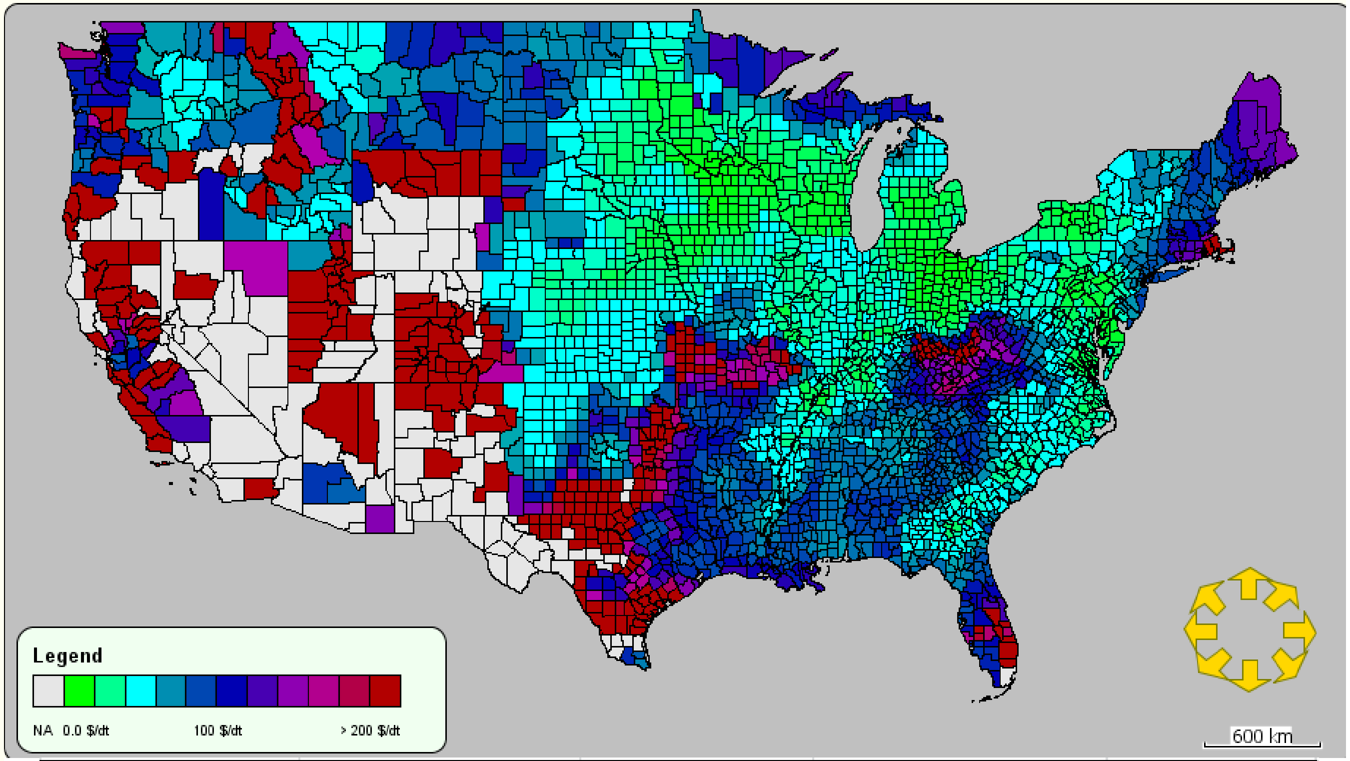
Corn Stover
Blend fraction: 0.64
Volume: 512 kt

Switchgrass
Blend fraction: 0.07
Volume: 56 kt

Wheatstraw
Blend fraction: 0.1
Volume: 80 kt

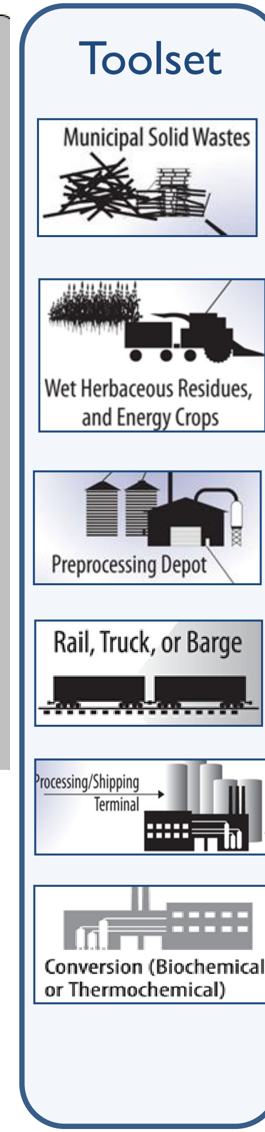
Woody Residue
Blend fraction: 0.12
Volume: 96 kt

Short Rotation Woody
Blend fraction: 0.07
Volume: 56 kt



	Ash (%)	Moisture (%)	Sizing	Lignin (%)
Woody Residues	15	30	0.25	30
Stover	10	15	0.25	15
Switchgrass	8	12	0.2	15
Wheatstraw	10	10	0.25	20
SRW	12	40	0.35	35
Formulation	**12**	**18**	**0.25**	**20**

	Ash (%)	Moisture (%)	Sizing	Lignin (%)
Formulation	12	18	0.25	20
Target	10	12	0.2	20
Difference	**-2**	**-6**	**-0.05**	**0**



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Phosphors: Efficient Recovery and Reuse

Objective: Develop technical pathways to recover and separate rare-earth metal oxides and other reusable products from phosphor dusts

Current hydrometallurgical processes applied recover 15 wt. pct. of rare-earth metals as oxides contained in phosphor dust

Processing:
Recovery of mixed rare-earth oxides are separated or returned to CFL manufacturing.
Selective digestion allows the separation of 80 wt. pct. of calcium phosphate and glass present in dust.

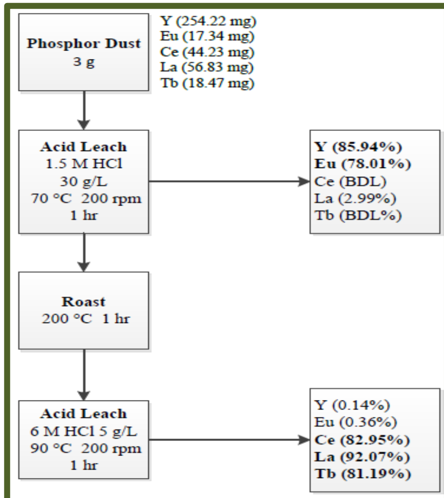
• Information collection and reporting on demand and supply, economics of recovery and current technological recovery options for rare-earth oxides from phosphor dust

• Cost-effective low energy flow-sheet for recovering mixed rare-earth oxides with over 85% recovery rates for five contained oxides developed

• Separation step for calcium phosphate dust recovery optimized

•Acid-recovery process to minimize hydrochloric acid cost developed

•**Industry Partners – Molycorp, Indium Corp of America, Veolia, GE**



Selective acid leaching/digestion gives 85% recovery of REE materials

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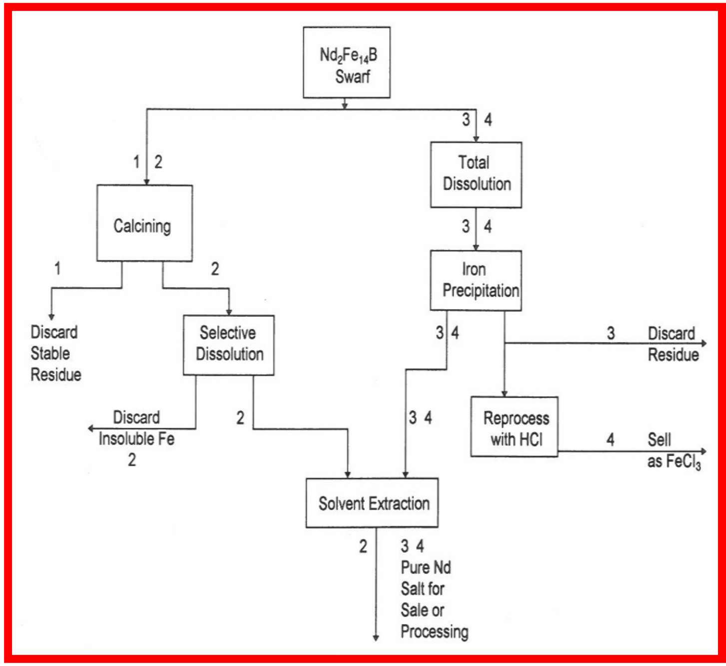
Magnets: Cost Effective Recycling

Objective: Develop cost effective approaches to recovery and recycle of REE magnets and their component materials

- Two major types of rare earth containing manufacturing waste:
  - broken magnets
  - large chunks left from cutting arcs, rectangular blocks and swarf
  - Focused on developing a two stage recycling scheme –
    1) physically processing swarf and magnets
    2) chemical processes
- Rare earth magnet swarf and bulk scrap samples obtained from two US manufacturers
- Disassembly for Chevy volt motor developed
- Removal of Al coating from RE magnets demonstrated
- Preliminary experiments performed on selective removal of Nickel and Cobalt being performed
- **Industry Partners: Molycorp, GE, etc.**

Roasting and Demagnetization



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Thrust #2: Create enhanced elemental extraction methods to maximize recovery.

- Topics:
  - Supercritical fluid recovery and extraction methods for phosphors
  - Membrane mediated solvent extraction methods
  - Electro- and pyro-metallurgical extraction and separation and purification methods
  - Biologically-based extraction and separation methods

Magnets, Phosphors and Electronics: Supercritical Fluid Beneficiation of Waste Streams

Objective: Develop supercritical fluid extraction processes for recovering lanthanide-based lighting phosphors from consumer electronics waste streams.

- Procured larger reaction vessel, pumps, and affiliated components.

- Made a hydrochloric acid (HCl) adduct by contacting tributylphosphate (TBP) with
- anhydrous HCl gas - did not yield a suitable HCl adduct.

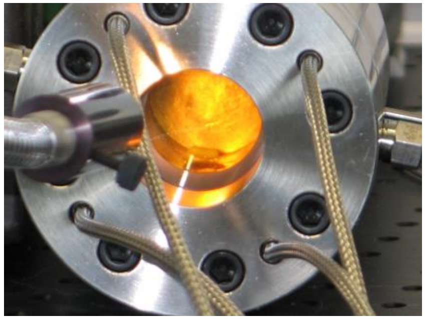
- Explored HCl adduct from:
  - tributyl phosphine oxide:HCl in SC CO_2 (TBPO:HCl)
  - tributyl phosphite:HCl (TBPI:HCl) in SC CO_2.
  - Both of those organophosphorus reagents make suitable HCl adducts.

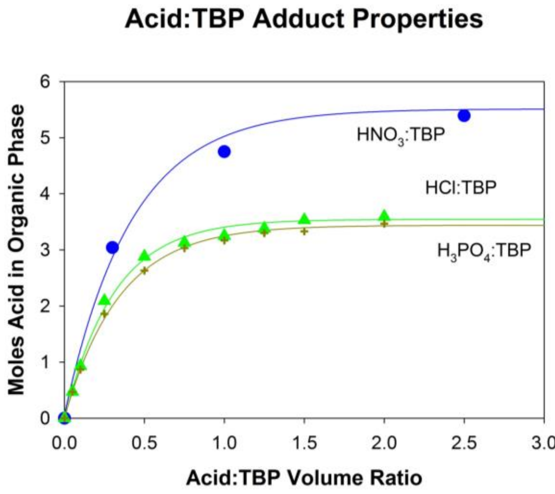
- Adducts currently show strong promise for dissolving fluorescent lamp phosphors.

- Initial data indicate the HCl adduct is highly suitable.

- Explored H_2SO_4, H_3PO_4, and HNO_3 adducts.

- Dissolution data give 90+% REE recovery





Industry Partners: Molycorp, GE, others

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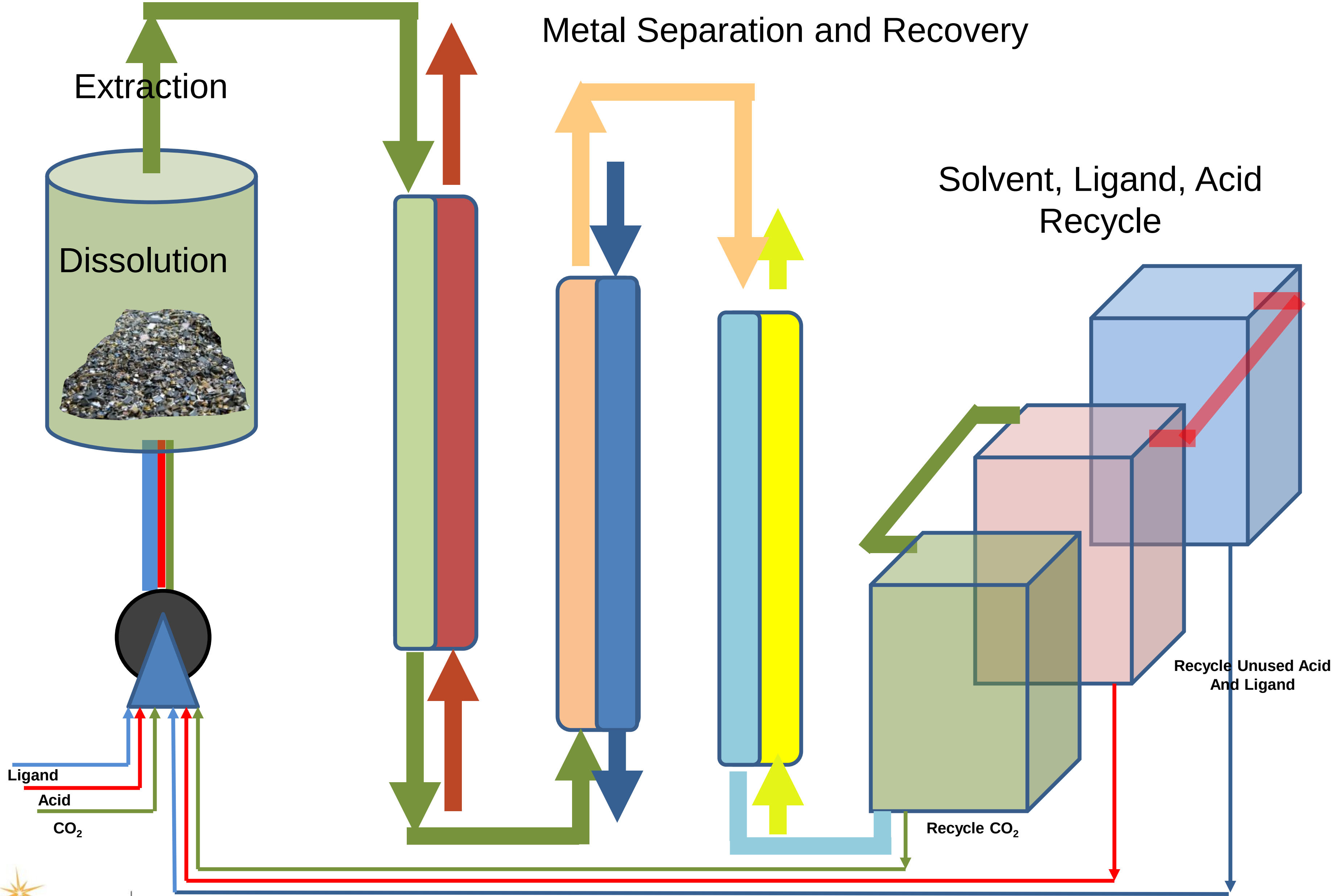

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INL/MIS-13-29862

INL/CON-14-32726

Trivalent lanthanide separations using TBDGA in molecular and ionic liquid diluents

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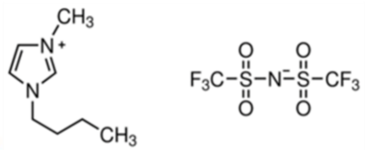
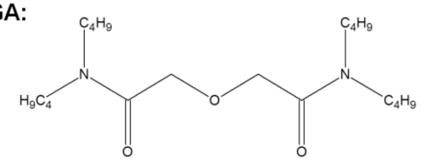
ABSTRACT: Intergroup lanthanide partitioning typically suffers from low separation factors due to their chemical similarity. Diglycolamides sometimes provide higher than typical separation factors, while extraction mechanisms vary between molecular diluents and ionic liquids, when using the same ligands. Here, tetrabutyldiglycolamide (TBDGA) was used to extract the lanthanides, (Y, La, Ce, Eu, Tb) found in lighting phosphors from nitric acid solution. The diluents were conventional molecular 1-octanol, and the ionic liquid 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)-imide, $[C_4MIM][Tf_2N]$. Although the work is preliminary, a series of extractions providing product streams containing separated lanthanides may be proposed.

Rare Earth Elements: Demand for the lanthanides for high tech applications is on the increase. One potential source to meet demand is recycle of lighting phosphors. However, methods for the recovery and separation of lanthanides from phosphors must be developed. The separations investigated here are envisioned as part of a process where lanthanides extracted into supercritical CO_2 will be stripped back to an aqueous phase.

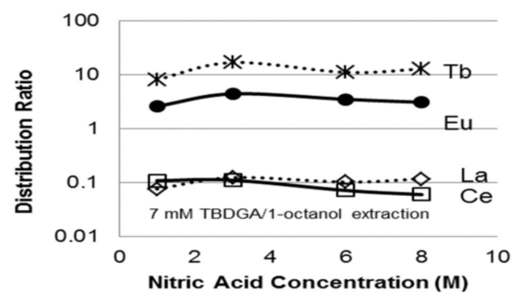
Ionic Liquids: ILs are salts that are molten at low temperatures. They have a unique set of properties that may offer new separations opportunities.



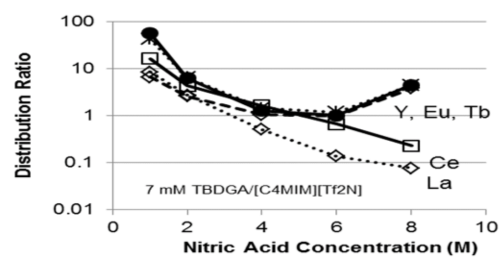
TBDGA:



Neutral Complex Versus Ionic Complex Extraction

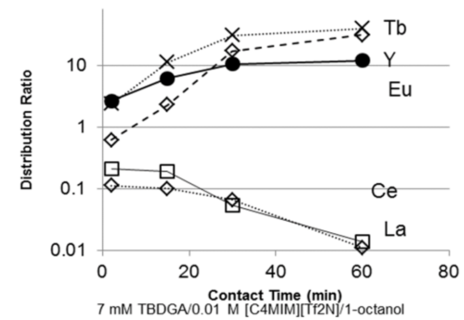


$Ln(NO_3)_3 \bullet (TBDGA)_3$



$[Ln(NO_3)_2 \bullet (TBDGA)_3]^+$

Kinetic Study



Conclusions:

- Y, Eu, Tb are readily separated from La, Ce in both diluents and by kinetics.
- Ce and La separated together. Redox chemistry may be necessary.
- Tb /Y may be extracted from octanol initially, with very low [TBDGA], separation factor from Eu ~ 4.
- No separation for Y,Tb.

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Idaho National Laboratory

University of Idaho
A LEGACY OF LEADING

Electronics: Electro-Recycling for Recovery of Rare Earth Elements

- **Objective: To develop electrolytic approaches to extraction of rare earth elements from materials contained in recycling streams with an initial emphasis on material from mobile electronics.**

- Electrorecycling - an approach to recovery of all value metals within the matrix.
  - 1) Generation/metal ion liberation (dissolving environment acid and oxidizing agents)) at anode
  - 2) Recovery of value metals (Cu, Ag, Au, Pd etc) at cathode – electowinning - OR - Membrane extraction (3.2.2) – OR - pH driven ppt of REE

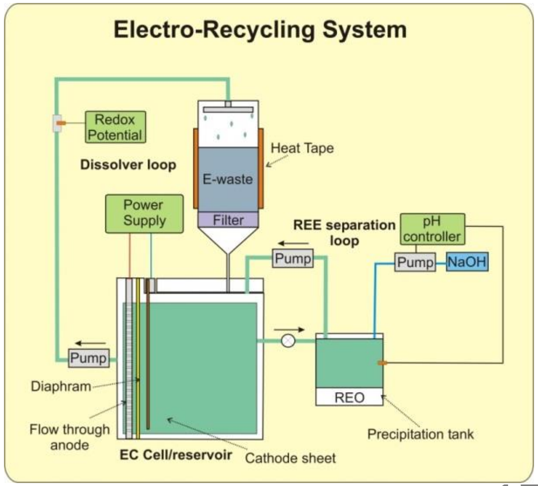
- Electrorecycling system developed and modified to perform two solution operation for enhanced efficiency

- OLI Systems calculated E vs pH and solubility thermodynamic diagrams for metals and oxidizers

- Dissolution rates for metals in oxidizer solutions performed under anticipated conditions

- Copper-tin redox chemistry experiments completed to understand potential interference and how to avoid metal passivation

- Industry Partners: Molycorp, OLI, Advanced Recovery



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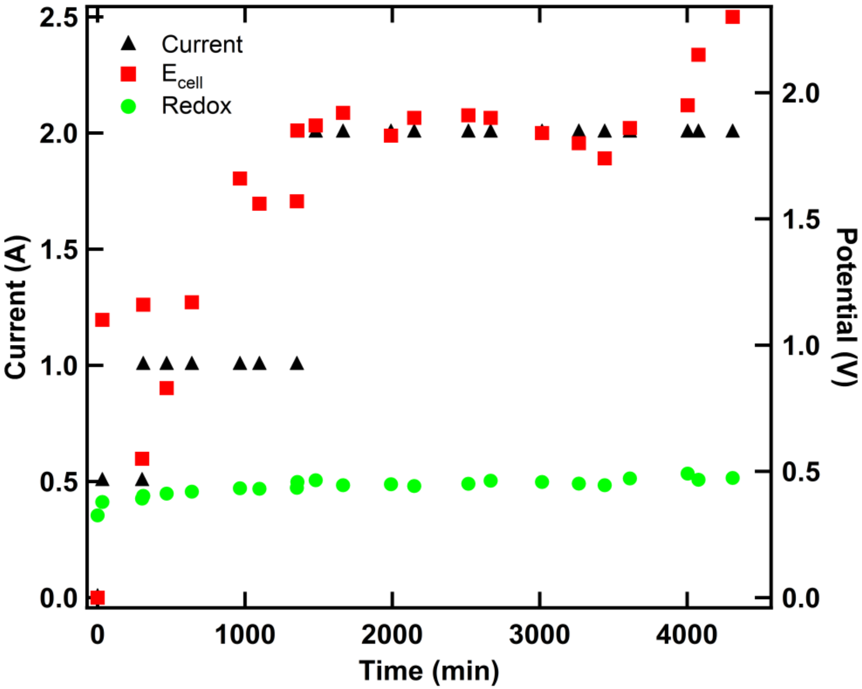
Electro-Recycling of Electronics

Feedstock:
80.003 g Cu shot
1.526 g Ag foil
0.0533 g Pd foil
0.1511 g Au foil
0.9503 g Nd-Fe-B 1/8" x 1/16" disks (Ni-Cu-Ni)

Operated 71 hrs

Recovery:
All Cu and magnet material dissolved
Dissolved 85% Ag, no Au and Pd
79 g deposit, 53 g compact, 26 g sponge
Minimal Fe deposition



Dissolved metals remaining (in g)

Pr	Nd	Gd	Dy	Ag	Cu	Fe	Ni
0.0516	0.1776	0.0080	0.0037	0.0269	0.7647	9.1762	0.0332

Cathode composition (wt%)

	Ag	Fe	Ni	Cu
Compact	0.56	0.02	0.0001	99.4
Sponge	3.77	0.14	0.0003	96.1

Cathode deposit

Magnets: Value Recovery of REEs by Remanufacturing or REE Recovery: Logistics, Economics, and Material Repurposing/Recovery

Objective: Develop a tool to support recycling and remanufacturing key REE containing products to recover REEs

Apply Design for Disassembly (DFD) to products containing REEs

Improved disassembly process plans and product designs that make it easier to disassemble end-of-life products to allow for more economic recovery, reuse, remanufacture, and recycling

- Understand the current barriers to recycling/remanufacturing/reuse of REE components, and develop/test DFD software
- Developed a genetic optimization algorithm to improve disassembly process plan for a computer hard disk drive.
- This method can provide an optimal or near optimal solution within a reasonable time and substantially reduce disassembly time and cost.

Apply REE material flow analysis to close REE material loops

Improved understanding of material disposition routes at end of life; identification of recovery and reintroduction opportunities. Work with other CMI projects to characterize economic and environmental benefits of recovery/recycling routes.

- Developed a web based industry survey; pursuing IRB approval
- Survey link: https://purdue.qualtrics.com/SE/?SID=SV_9sDnuV2fsgfsspD
- Industrial Partners: Siemens, ABB, BBB, Ford, Bosch, GE

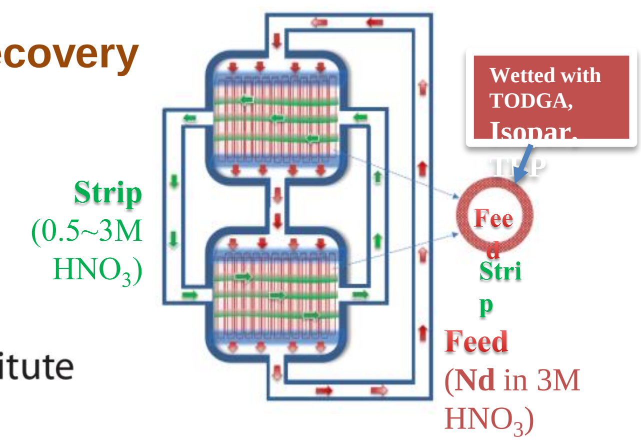
Objective: To demonstrate the potential of dispersion-free supported liquid membrane solvent extraction (MSX) for the separation, concentration and recovery of rare earth (REE) from REO scrap and wastewater (0.1 to 2 wt%).

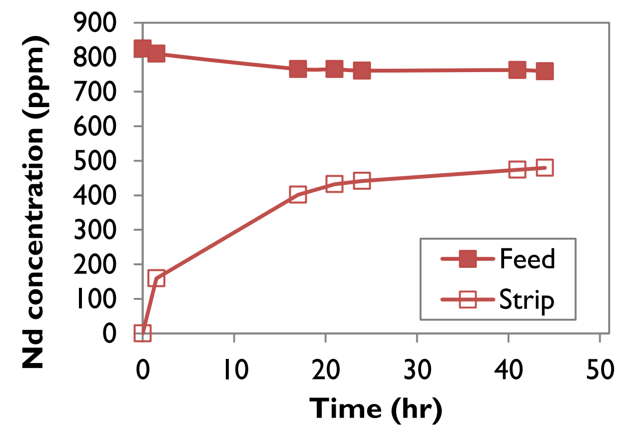
- Selected highly selective extractants for Nd/Dy and established process parameters to maximize REE recovery with MSX using polymeric hollow fiber modules.
    - Tetra octyl diglycol amide (TODGA) and alkyl phosphine oxide (Cyanex 923) extractants showed the best REE extraction efficiency. TODGA showed the lowest co-extraction of other constituents (Fe, B, and transition elements Al, Ni, Cu, etc.).

- Developed system configuration (modules in series) to increase REE recovery

- Demonstrated stable system operation for over 100 hours, with 99% Dy and Pr recovery, 0.5 L/min

- **Industry Partners: GE, Molycorp, Advanced Recovery**





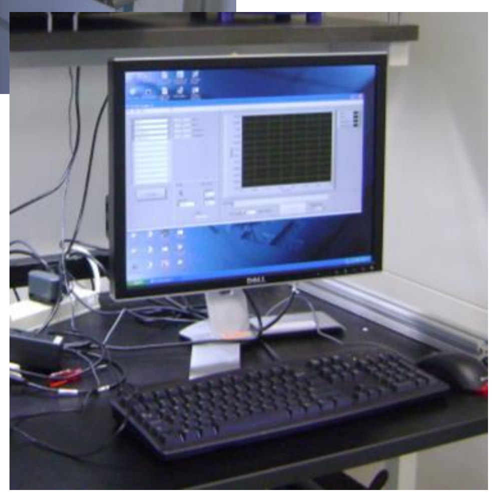
Current Nd Recovery:~ 99%

Efficient Water Recovery Using Microfiltration Membranes

Objective: Development of filtration devices for recovery and/or re-use of processed water streams in mining, agricultural or other recovery activities

Automated Benchtop Filtration System at INL

Computer Data Acquisition

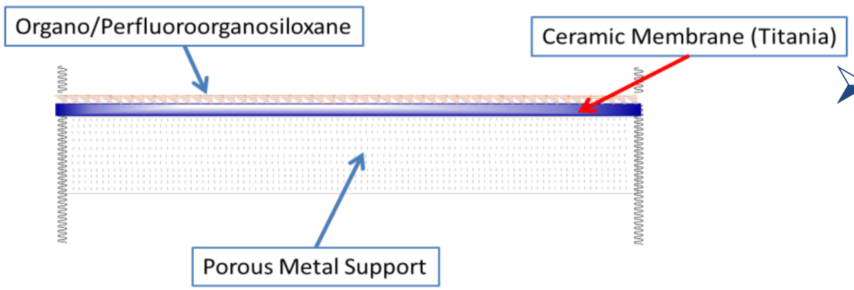


Feed container with flow meters

Efficient Water Recovery Using Microfiltration Membranes

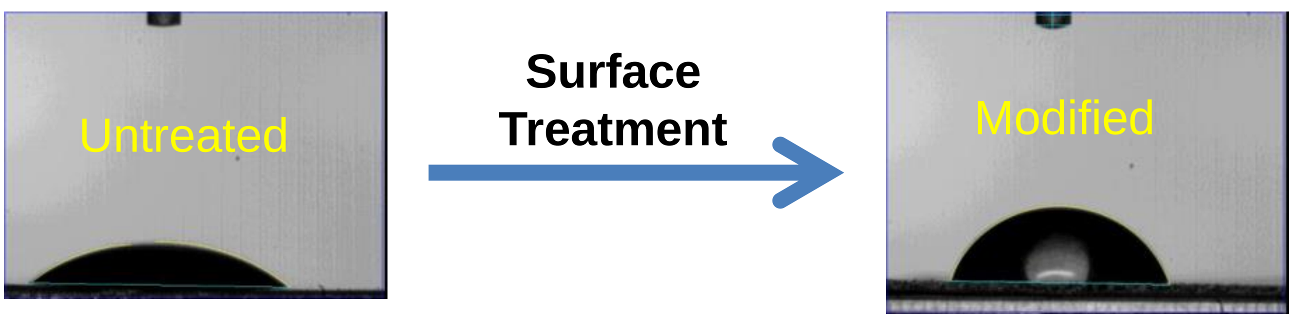
Fouling Reduction by Surface Modification

- **A project goal is surface modification of metal oxide (ceramic) membranes with organosilanes and fluorinated organosilanes**



- Minimize fouling by creating a hydrophobic surface on the ceramic membrane.

- Surface modified titania ceramic membrane using organosilanes.



Develop techniques to provide good surface coverage with high surface tensions for water

Membrane Development (Embedded Membranes)

- Porous metal filtration systems use surface coated using ceramics, such as titania.

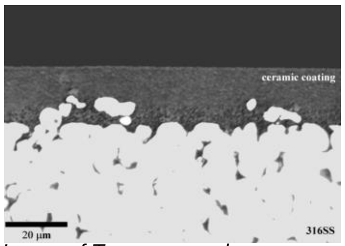
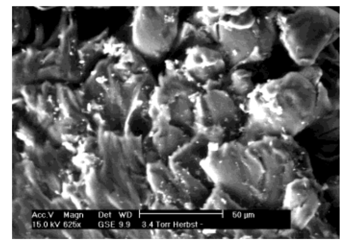


Image of Trumem membrane

Filtration with coarse particles

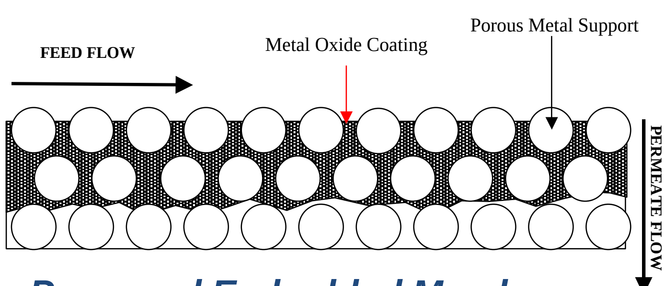


Abraded Membrane

Issue - Eroded by concentrated slurry feed solutions

Answer – Embedded Membranes

- **A project goal is to fabricate a metal oxide (ceramic) embedded membranes into a porous metal support**



Proposed Embedded Membrane

- Very difficult to erode due to the protection of the porous stainless steel support

Efficient Water Recovery Using Microfiltration Membranes

Accomplishments to date:

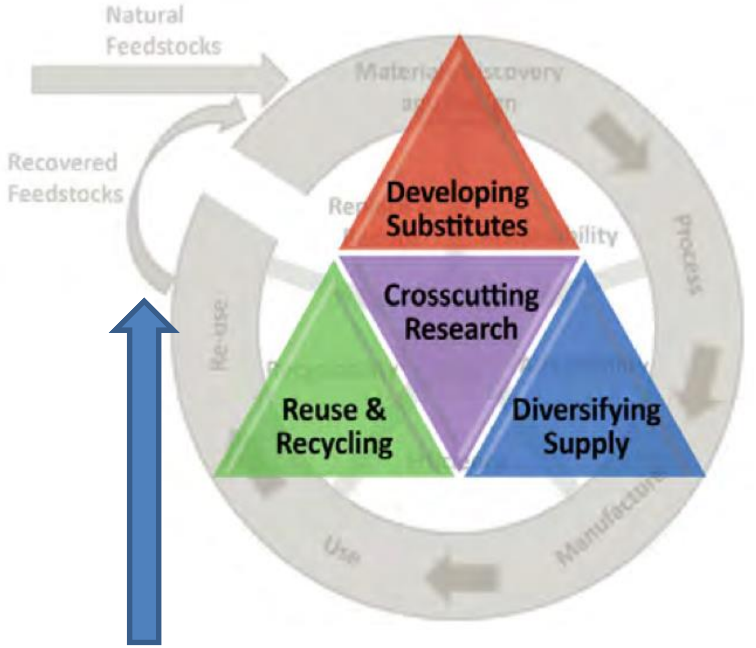
- Partners with Graver Technologies
- Upgraded to an automated benchtop filtration system for small scale analysis and tests on flat sheet or tubular cells
- Graver Technology tubular modules acquired and tubular housing assembled for future tests

Tubular Cell and Graver Filter Tubes

Automated Benchtop Filtration System

Summary

- CMI is enhancing efficient reuse and recycling of a highly diverse set of materials to further diversify global supply chain of critical materials by:
    - enhancing recycling technologies,
    - improving product design,
    - understanding recycling techno-economics
    - using the thermodynamics of separations.



We are closing the materials/product life-cycle loop!!

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Thank You!

Thanks to:

Department of Energy

Advanced Manufacturing Office

Critical Materials Institute

Questions?

eric.peterson@inl.gov

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- Backup Slides

Magnets and Elecgtronics: Pyro-metallurgical Approaches to REE Recovery and Recycling

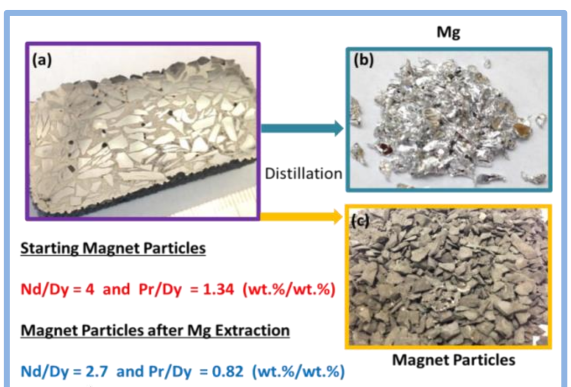
Objective: Develop pyrometallurgical approaches to reuse and/or extract REEs from materials such as magnet and battery alloys

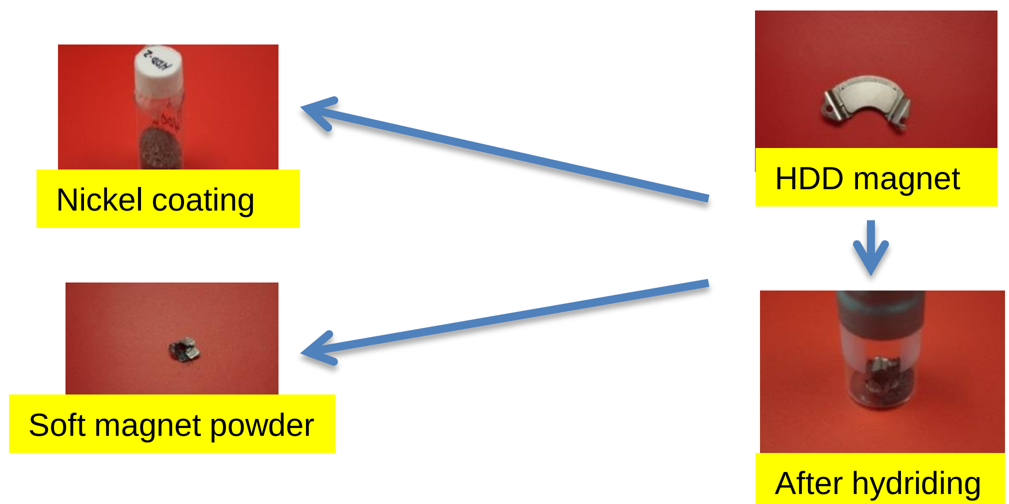
1) Hydriding-Dehydriding (HDDR) Process

- HDDR uses 88% less energy and is 98% more efficient in limiting toxicity
- Optimized experimental conditions to prepare fine alloy powders (soft magnet material)
- Examine re-fabrication of the magnet from the de-hydrided powders
- Evaluate magnetic properties of the re-fabricated magnets
- Examine the suitability of the de-hydrided powder for the recovery of Nd

2) Liquid-Metal Extraction (LME) Process

- Develop process that can effectively extract RE elements end-of-life (EOL) scrap
- Develop process in which the RE element are separated from the liquid extractant in their metallic state
- Characterize the impurity (e.g., Fe) in the extracted RE metals
- Synthesize permanent magnet alloys from the recycled RE metals and characterize magnetic properties
- Extend this process to heavily oxidized swarf
- Extend process to recover rare earth metals from NiMH batteries
- Industry Partners: Molycorp, GE



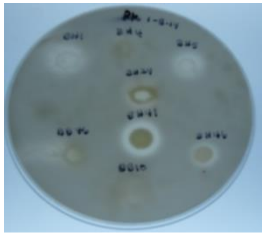


Phosphors, Electronics, and Magnets: Microbial Mediated Recovery of Rare Earth Elements

Objective: To develop and deploy a bioleaching and/or bioadsorption strategy for recovery of rare earth elements (REE) from recyclable materials

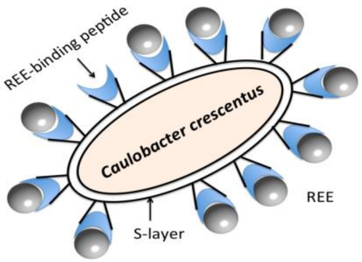
- **Enriched >100 microorganisms with ‘potential’ REE solubilizing characteristics from**
  - Acidic hot springs, Yellowstone National Park
  - REE ores, RER Bull Hill mine

- **Down-selected microbial isolates that have the ability to:**
  - Produce organic acids important for REE chelation
    - Utilized a calcium phosphate solubility assay for identifying microbes; these microbes may also solubilize REE-phosphates & REE-oxides
    - Produce >10 mM gluconic, citric, or succinic acid
    - 5 promising microbes plus several acidophilic microbial communities



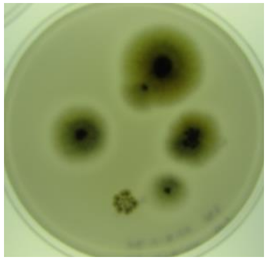
- **Obtain recyclable feedstocks and characterize by ICP:**
  - AERC retorted phosphor powders (Y, Eu, Tb, Ce, La)
  - Valero regenerated fluid cracking catalyst (Ce, La, & low Pr, Nd, Sm)

- **Genetically engineered *Caulobacter* with lanthanide binding sites:**
  - Ideal microbe-survives low-nutrient and heavy metal-rich environments, has well characterized genetic system
  - Lanthanide binding tags on cell S-layer protein (Figure
  - Optimizing for Tb binding

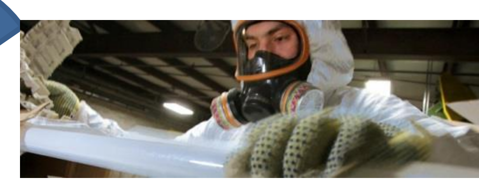


- **Industry Partners: Advanced Recovery, Molycorp, GE**

Potential Biological Process for REE Recovery



Strain isolation

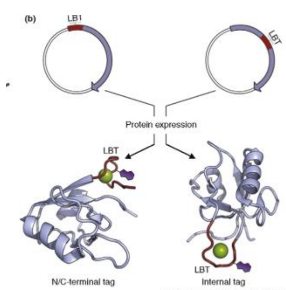


Recycled materials

Strain discovery

Biological Process

Phosphor powders



Strain engineering

REE Recovery

Critical Materials Institute
AN ENERGY INNOVATION HUB

Sources: RER Bull Hill; Allen 2010 Cur. Opin. Chem. Biol. 14:247; Veolia; Aliexpress

Filtration Test

- Two silicates of different particle sizes were mixed at 2.5 grams per 2 liters of DI water.
- 2-25µm silica and Carbo-Sil BC# Grade M5
- 2 Flat sheets (0.1 and 1µm) were analyzed.

Dead End Test

Sol 2 (**Carbo-Sil BC # Grade M5**)
0.1 um Trumem uncoated SS

(psi)	(l/m2hr)
120	6000
200	2700
325	1900

Re-pressure after 300 psi result

120	500

Low flow after re-pressure

No change with 2-25µm silica

Low Flow Test (Cross-Flow)

Sol 2 (Carbo-Sil BC # Grade M5)

0.1 um Trumem uncoated SS			1 um Trumem uncoated SS		
(psi)	(ml/min)	(l/m2hr)	(psi)	(ml/min)	(l/m2hr)
150	150	350	100	240	825
190	200	590	200	10	1250
300	250	280	300	15	1600

Minimal change in flow after re-pressure

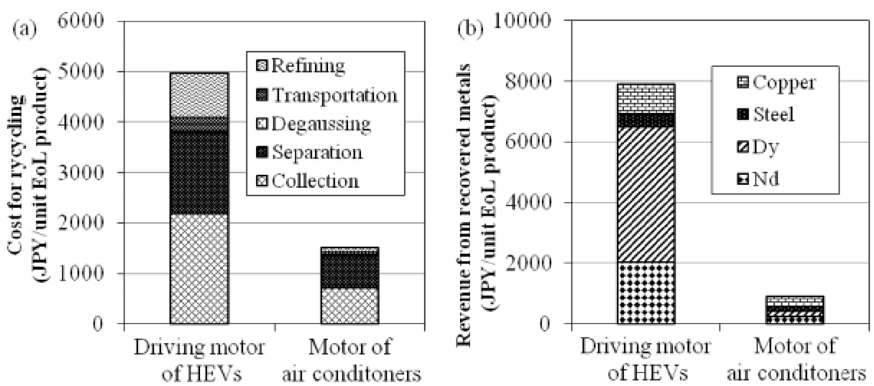
Face Velocity Study

Sol 2 (Carbo-Sil BC # Grade M5)
0.1 um Trumem uncoated SS

(psi)	(ml/min)	(cm/s)	(l/m2hr)
200	1000	18	1000
170	850	15	800
100	700	12	600

Improving Reuse and Recycling Overview - continued

- Examining materials streams:
  - **Developing economically viable and environmentally acceptable processing methods** that apply to more than one material stream and reduces challenge of processing diverse source materials.
  - **Reducing materials loss in manufacturing processes**:
    - End of life disposition for consumer and commercial products.
    - “Re-mine” and make available for utilization this secondary supply in economically feasible ways.
    - Recover critical materials plus other high value materials (such as precious metals) that provide opportunities for improved process economics and adoption/utilization.
  - Deliver technology in concert with industry



Costs and Revenues of Recycling Hybrid Electric Vehicles (HEVs) and Air Conditioner Motors in Japan

Sekine, N., Daigo, I., Matsuno, Y. & Goto, Y. (2013). Dynamic substance flow analysis of neodymium and dysprosium associated with neodymium magnets in Japan. *The 6th International Conference on Life Cycle Management in Gothenburg*.