Rare Earth and Related Materials:

Value Chain Overview

Lake Superior, MI

CORE-CM Kickoff Meeting
January 18, 2022

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Overview/Outline

- Introduction to the Rare Earth Elements
- Rare Earth Properties and Applications
- Where do We Get REEs?
- The Supply Chain
- Summary
- Future Opportunities and Needs
- Questions

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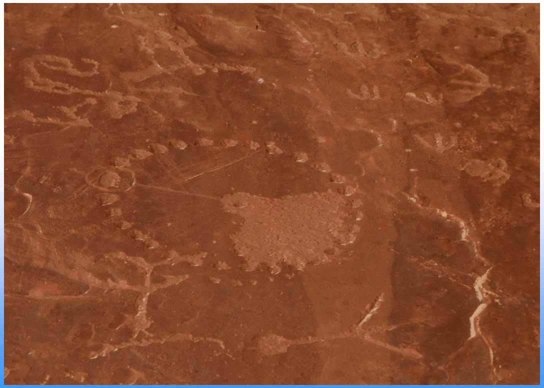
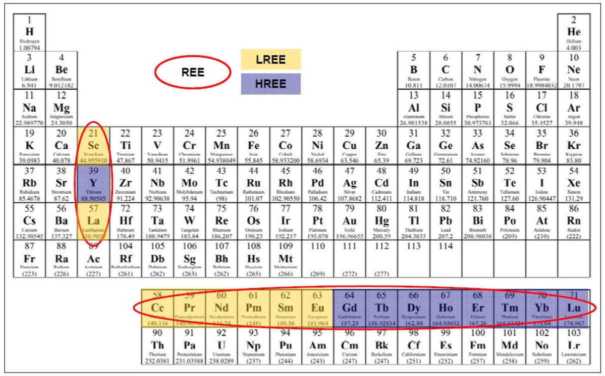


Hummingbird and Ancient Calendar,
2nd Pueblo Period (AD900-1150), Utah

Introduction to the Rare Earth Elements



Periodic table of the elements showing the division between LREEs and HREEs (Schuler et al., 2011).

A group of 17 elements in the periodic table

Referred to as "rare" because they are not found in commercially valuable quantities

"Earths" because they could not easily be dissolved in acids – from alchemy

Wikipedia photo = Assortment of lanthanoide group elements. Uploaded at 22:12,19 April 2006 by User:Tomihhndorf. Author User:Tomihahndorf. Permission=GFDL.

2 main subgroups:
- **Light REEs (LREEs)**
- **Heavy REEs (HREEs)**

REE ore bodies are normally rich in one or the other, but not both

Vital in Clean Energy and High Technology Applications

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REE Properties and Applications

Light REEs

(La) Lanthanum

(Ce) Cerium

(Pr) Praseodymium

(Nd) Neodymium

(Sm) Samarium

Heavy REEs

(Eu) Europium

(Gd) Gadolinium

(Tb) Terbium

(Dy) Dysprosium

(Ho) Holmium

(Er) Erbium

(Tm) Thulium

(Yb)Ytterbium

(Lu) Lutetium

(Y) Yttrium

Properties

-Silvery-white gray color

-High luster, quick to tarnish in air

-Most REE compounds are strongly paramagnetic

-Catalytic, chemical, electrical and optical properties

-High electrical conductivity

-May fluoresce under UV

-High melting and boiling points

-React with dilute acids to produce H_2 at RT

-React with H_2O to liberate H_2 slowly cold, quickly upon heating

Applications

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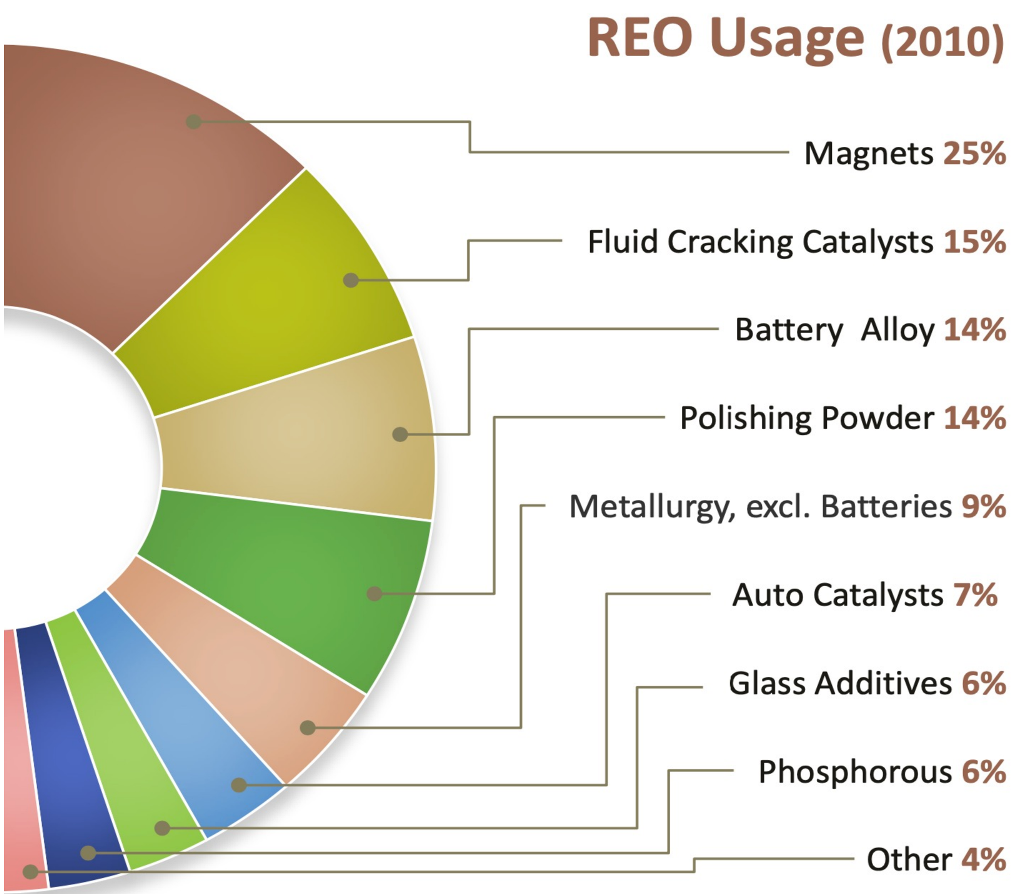
REEs are Integral to Many Growing Markets



Application	Estimated Compound Annual Growth Rate 2010-2015
Phosphors	30%
Rechargeable Batteries	18%
Permanent Magnets	16%
Polishing Powder	15%
Auto Catalysts	8%
Fluid Cracking Catalysts	6%
Glass Additives	4%

Source: CIBC World Markets, March, 2011

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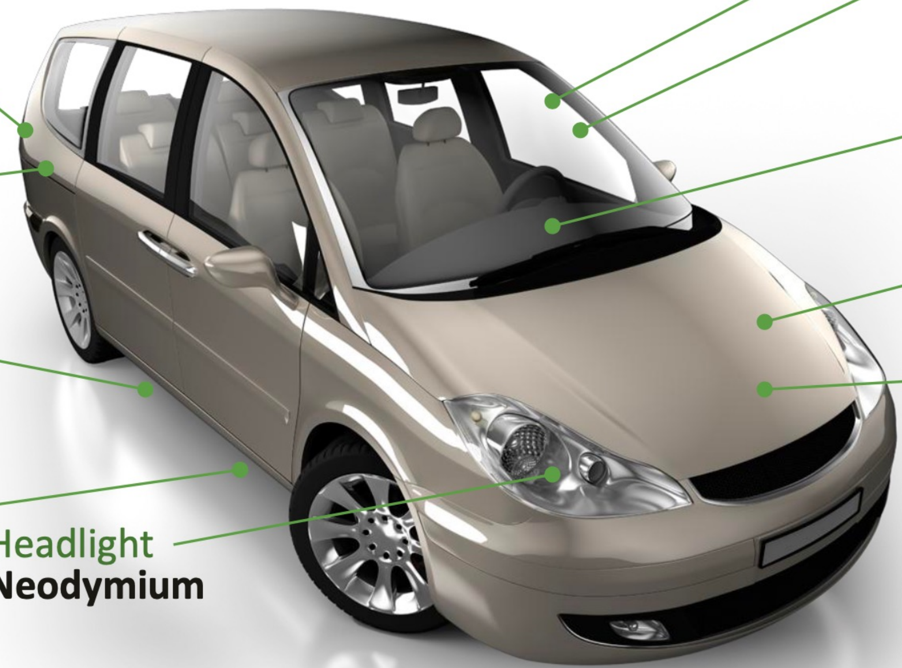
REEs Play a Key Role in Clean Energy Sector

Hybrid and electric cars can contain 20–25 pounds[1] of rare earths

(Twice the amount found in standard gasoline cars)



[1]Source: "The Race for Rare Metals", Globe and Mail, July 16, 2011

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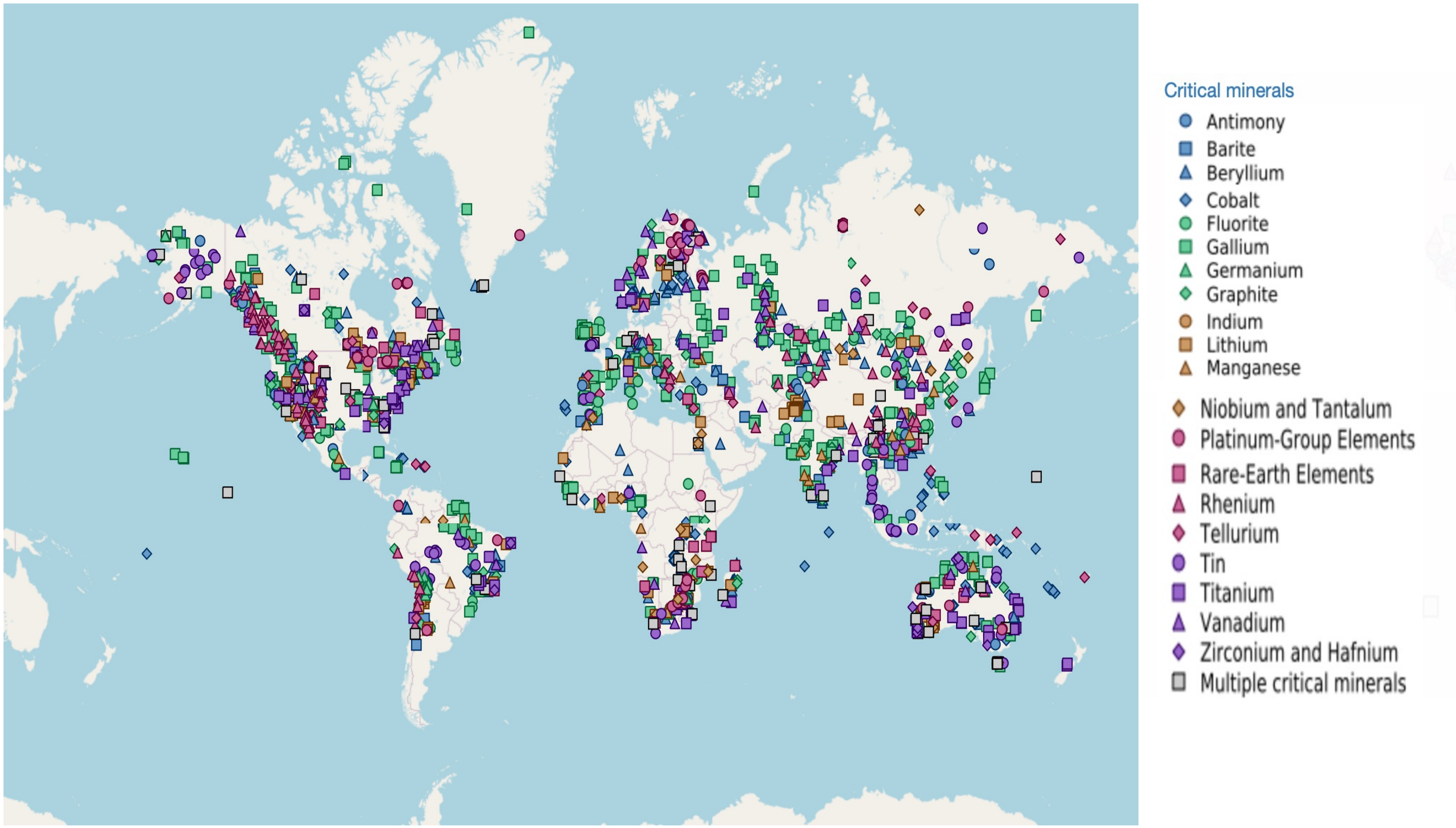
Where are CM deposits found globally?



Map showing occurrences of CMs, USGS, 2021.

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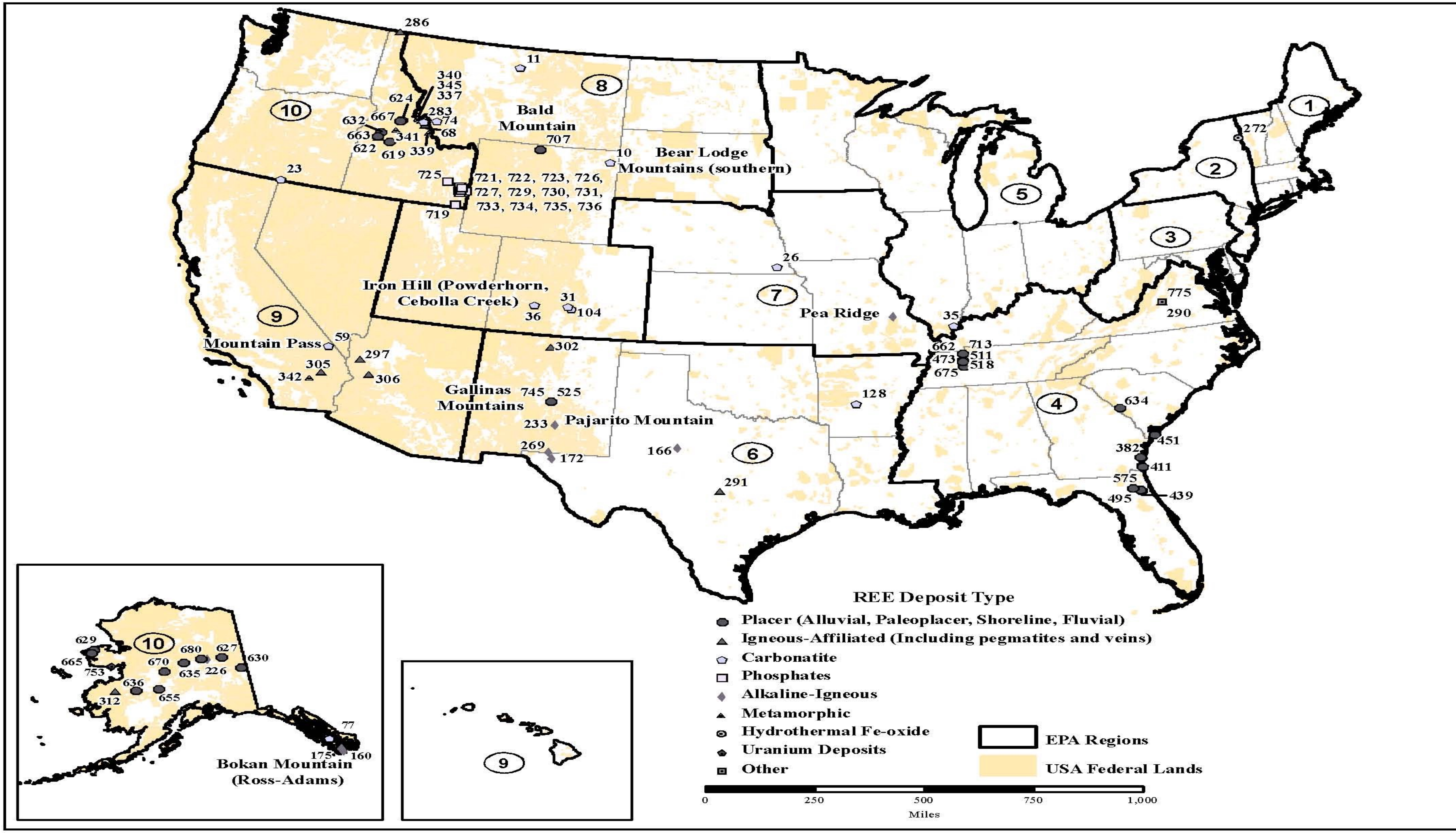
Where are REE deposits found in the US?



Map showing occurrences of REEs, by rock type (adapted from multiple sources, see *Appendix B of EPA ORD NRMRL ETSC REE document*)

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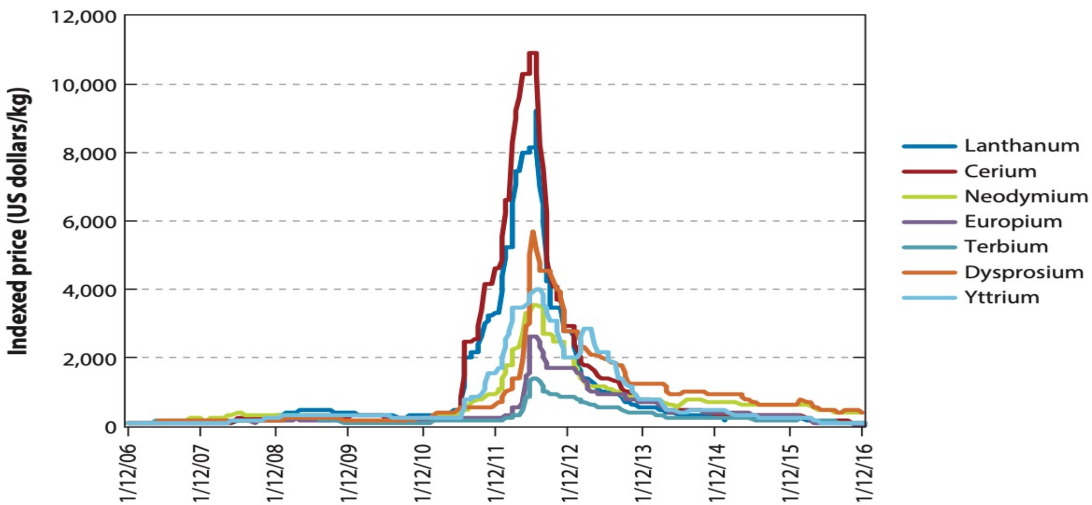
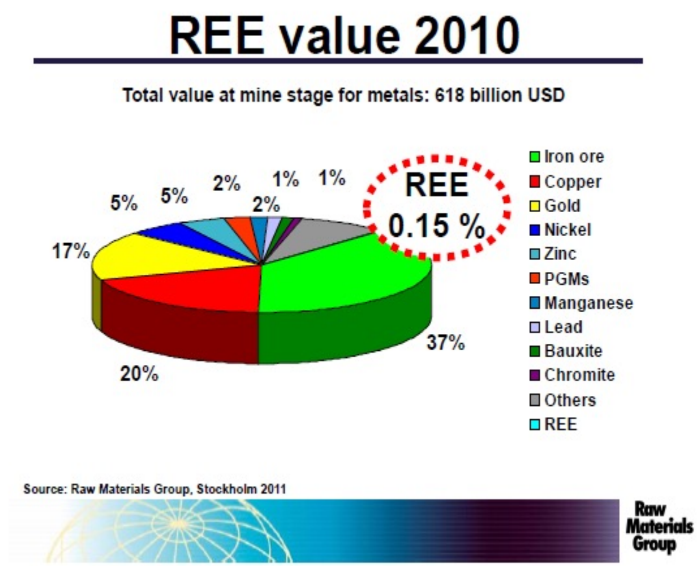
REE Pricing 2006 - 2016



(**https://direct.argusmedia.com**; used with permission).



Supply chain activities	Chinese percentage of world production at each stage in 2010[b]	Chinese percentage of world production at each stage in 2015
Mining and concentration	97%	80–85%
Separations	97%	80–85%
Metal refining	~100%	>95%
Alloying and magnet powders	90%	>95%
Manufacturing	75%	>80%
Components (motors, generators)	NA	NA
Recycling	NA	NA

[a]US Department of Energy (54).
[b]Abbreviation: NA, not available.

Eggert, et al; 2021

China and Japan have ongoing disagreement over ownership of Senkaku Islands and cut off supply of REEs to Japan – 2010 – restricting supplies to Japan - causing a price spike

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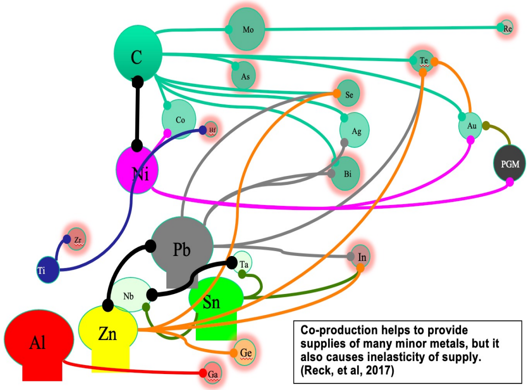
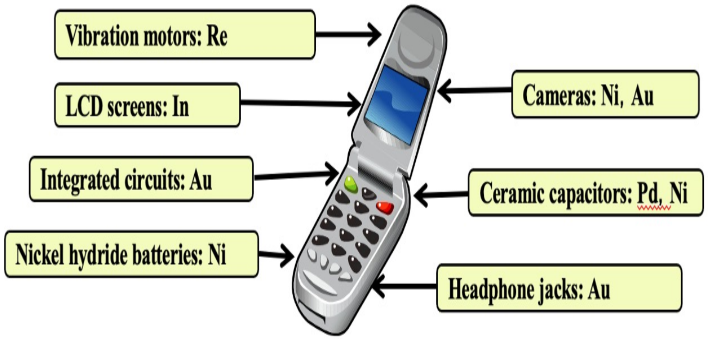
How do we get the REEs?

- Mine them….
  - Explore
  - Discover
  - Mine



- Co-Produce them….
  - Production resulting from other metals production
- Recycle them….
  - Collect
  - Dismantle/Remanufacture/Reuse
  - Process to elements



All of these feed the REE Value Chain

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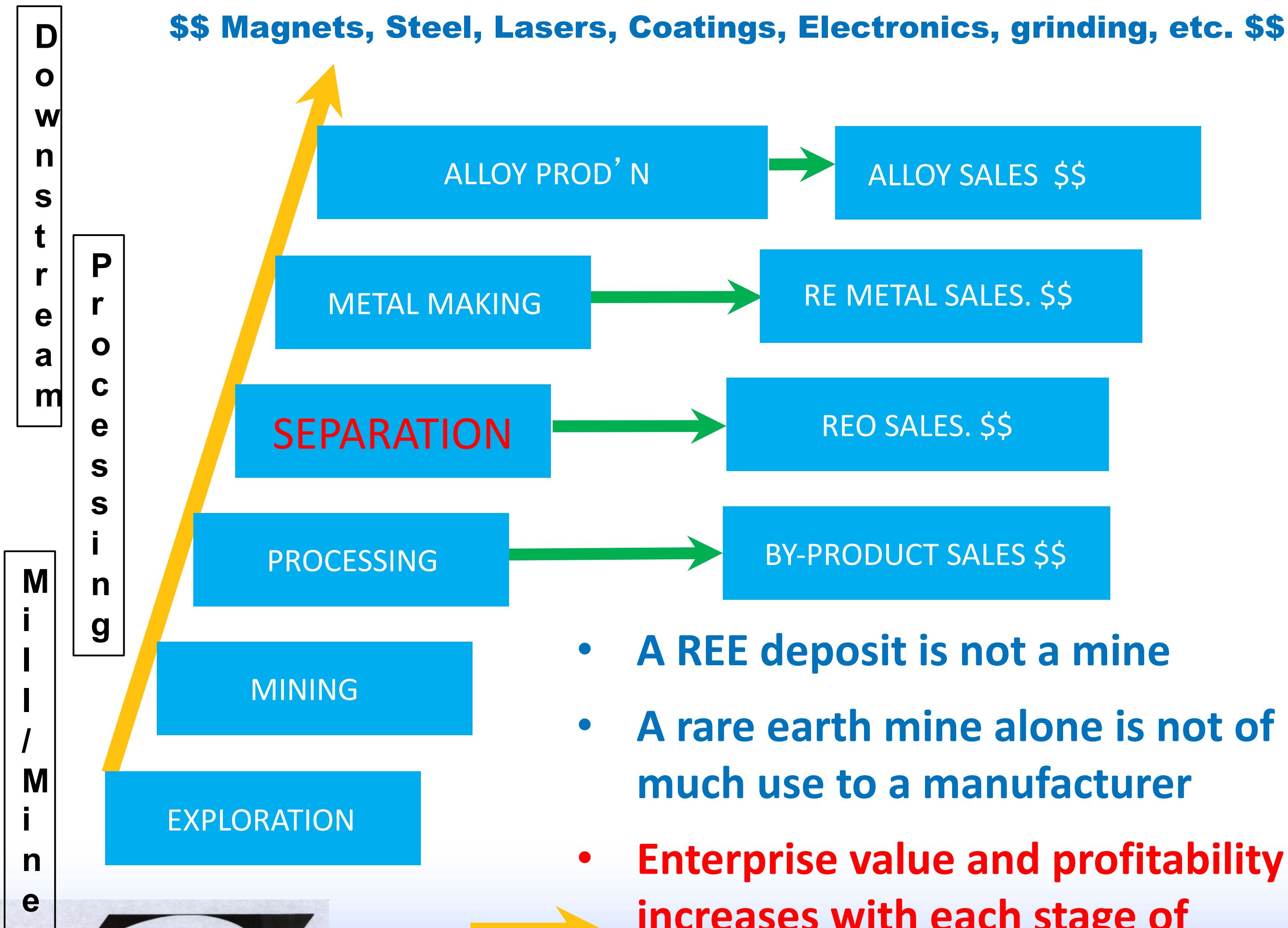
REE Value Chain



- A REE deposit is not a mine
- A rare earth mine alone is not of much use to a manufacturer
- Enterprise value and profitability increases with each stage of processing

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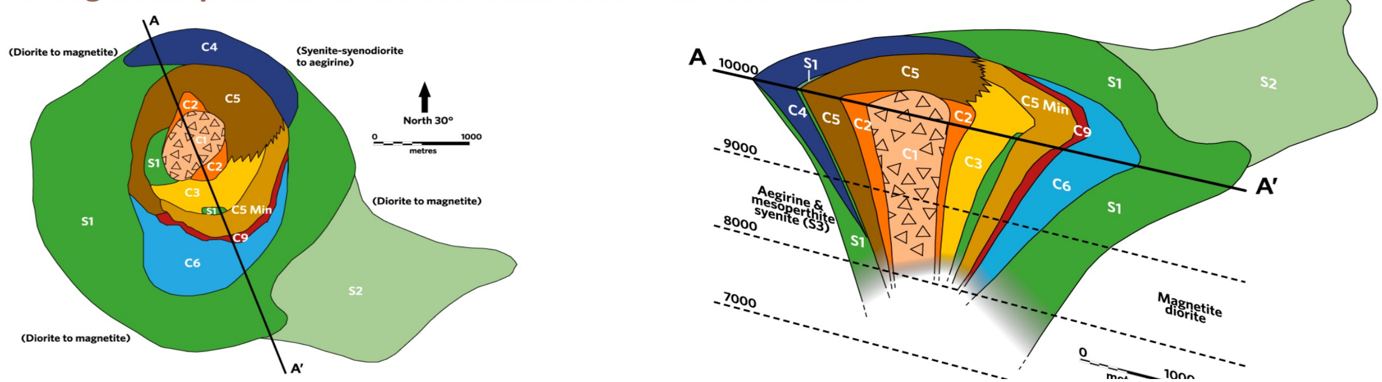
Graphic Courtesy of Great Western Minerals Group, Ltd, Jack Lifton Technology Metals Research, LLC

Exploration/Mining/Pre-processing

- Exploration and Discovery
  - Discover, evaluate the characteristics of deposit.
  - Transitions from geology to engineering
- Economic analysis to determine if minable mineral deposit exists.

Geological Map and Cross Section of the St. Honoré Carbonatite



- Mining
  - Mine development,
  - Deposit is prepared for mining through investment:
    - Equipment,
    - Infrastructure,
    - Production facilities and activities
    - Environmental issues

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Pre-processing/Concentration

Mining is either open pit or underground, <1% - 15% REE/ton ore

- **Overburden/Non-ore rock**
- **Impoundments/waste handling**

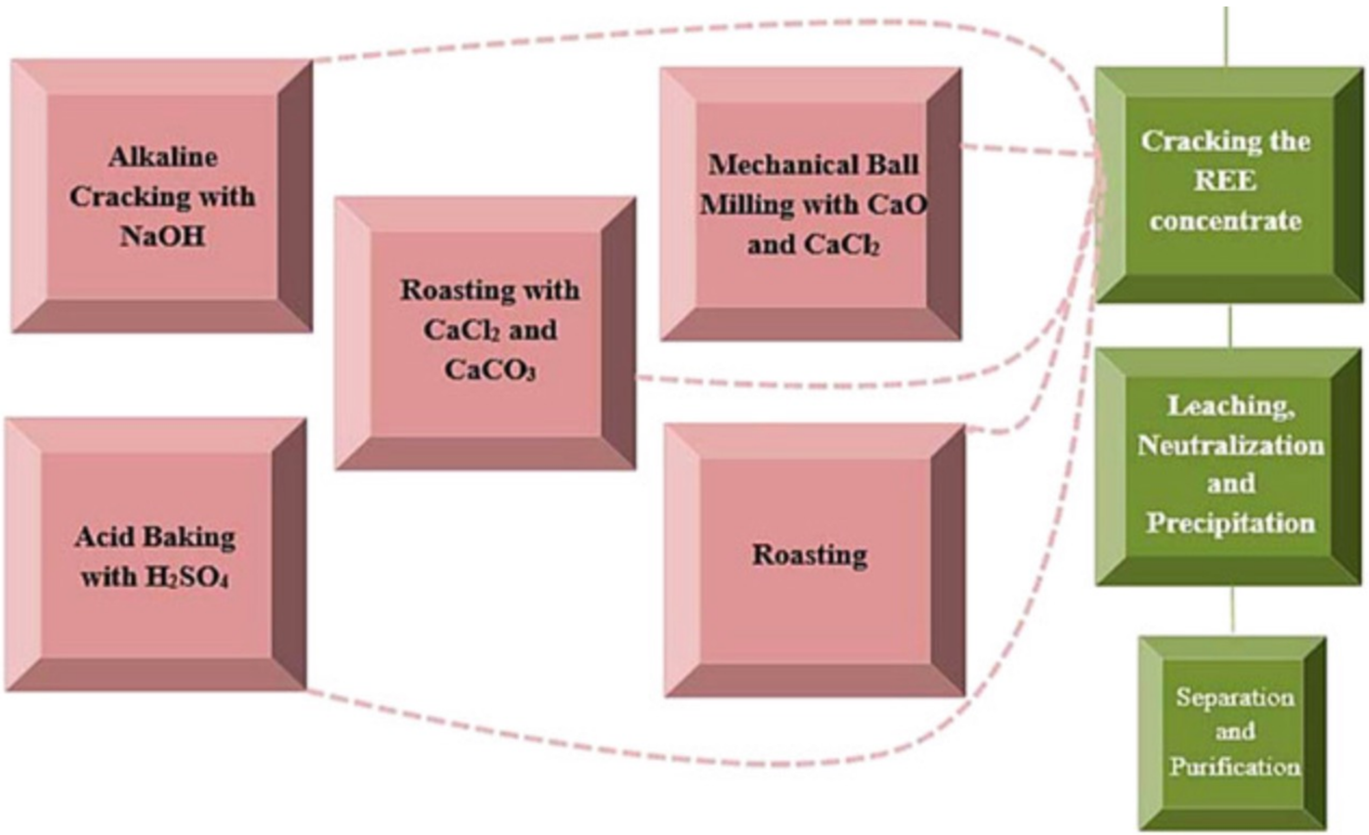
Efficient Processing

- **Beneficiation – Grinding and sizing the ore**
- **Concentration – typically at mine site**
  - **Magnetic,**
  - **Gravimetric**
  - **Flotation**

<u>Result</u>: REE material upgraded to 50–70% rare-earth content by weight for bastnaesite (a fluorcarbonate mineral) and monazite (a phosphate mineral), 90% or higher for the Chinese ion-adsorption clays.

Concentrate is smelted/"cracked" and dissolved into acids…

Cracking the Concentrated REE Mineral Phases – Liberating the Metal Ions!!!!



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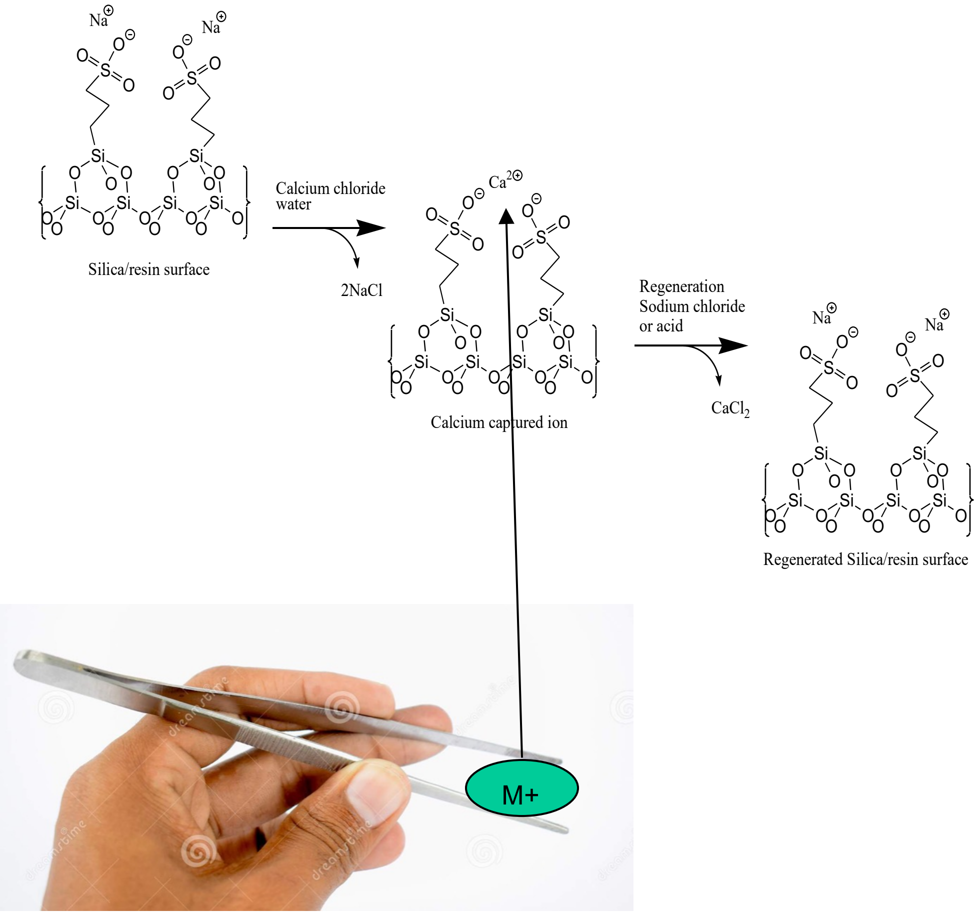
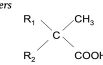
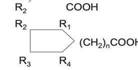
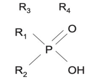
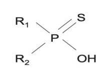
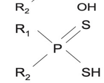
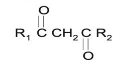
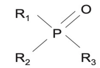
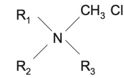
Separations
"Atomic Tweezers" Provide Metal Ion Selectivity



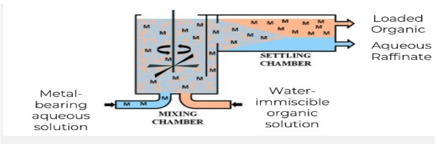
A Broad Selection of Tweezers

Reagents class	Structure	Extractants
1, Cation exchangers Carboxylic acids		Versatic acids: $R_1 + R_2 = C_7$, Versatic 10; $R_1 + R_2 = C_6–C_8$, Versatic 911
		Naphthenic acids: R_1-R_4: varied alkyl groups
Phosphorous acids		Phosphoric acids: $R_1 = R_2 = C_4H_9CH(C_2H_5)CH_2O–$, di-2-ethylhexylphosphoric acid (D2EHPA) Phosphonic acids: $R_1 = C_4H_9CH(C_2H_5)CH_2O–$, $R_2 = C_4H_9CH(C_2H_5)CH_2–$, 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (EHEHPA, HEHEHP, P507, PC88A) Phosphinic acids: $R_1 = R_2 = C_4H_9CH(C_2H_5)CH_2–$, di-2-ethylhexylphosphinic acid (P229) $R_1 = R_2 = CH_3(CH_2)_3CH_2CH(CH_3)CH_2–$, di-2,4,4-trimethylpentylphosphinic acid (Cyanex 272)
		Monothiophosphorous acids $R_1 = R_2 = CH_3(CH_2)_3CH_2CH(CH_3)CH_2–$, di-2,4,4-trimethylpentyl-monothiophosphinic acid (Cyanex 302)
		Dithiophosphorous acids $R_1 = R_2 = CH_3(CH_2)_3CH_2CH(CH_3)CH_2–$, di-2,4,4-trimethylpentyl-dithiophosphinic acid (Cyanex 301)
2, Chelating exchangers		β-diketones: $R_1 = R\text{-}C_6H_5$, $R_2 = CH_3(CH_2)_5–$, R: unknown side alkyl, (LIX 54)
3, Solvating extractants		Phosphorous ester: $R_1 = R_2 = R_3 = CH_2(CH_2)_2CH_2O–$, tri-n-butyl-phosphate (TBP) $R_1 = R_2 = CH_2(CH_2)_2CH_2O–$, $R_3 = CH_2(CH_2)_2CH_2–$, dibutylbutylphosphonate (DBBP) Phosphine oxides: $R_1 = R_2 = R_3 = CH_2(CH_2)_6CH_2–$, tri-n-octylphosphine oxide (TOPO, Cyanex 921)
4, Anion exchanger	RNH_2 RNH_2 	Primary amines $R = (CH_3)_3C(CH)_2C(CH_3)_2)_4$ (Primene JMT, N1923) Quaternary amines: $R_1 = R_2 = R_3 = C_8–C_{10}$ mixture (Aliquat 336, Adogen 464)

Separations

Solvent Extraction (SX) (current technology) Organic solvents – commercial

RapidSX – UCORE, Pilot stage

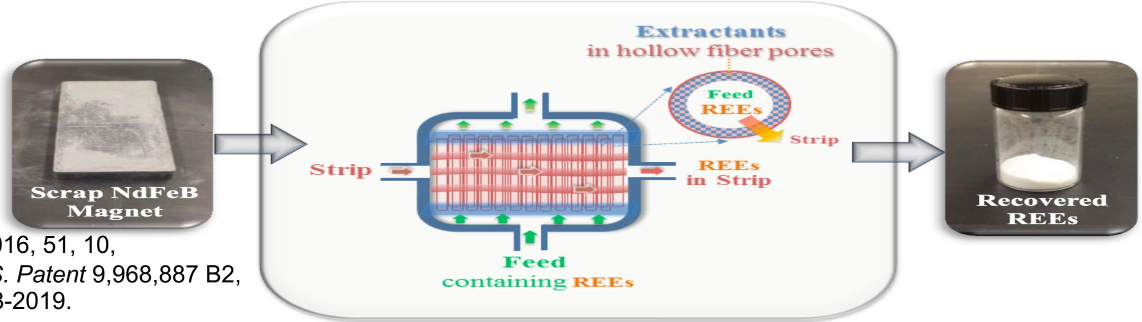


Schematic of a Single Mixer-Settler Extract Stage

UCORE Corporate Presentation, 2020

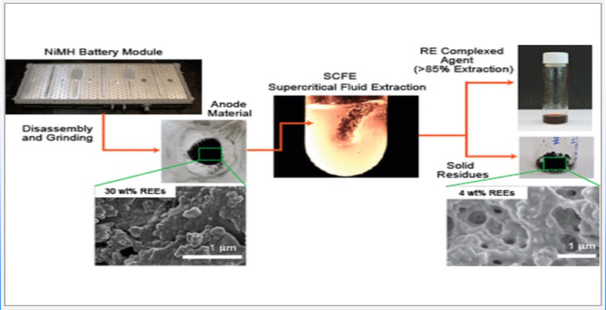
INL 30 Stage SX Demo Plant

Membrane Solvent extraction (MSE) – commercial



Separation Science and Technology, 2016, 51, 10, 1716–1726. Bhave, Kim, Peterson, *U.S. Patent* 9,968,887 B2, May 15, 2018. Y - BA-838, issued 06-18-2019. US10323300B1

Supercritical fluid extraction (SCFE) – R&D phase



ACS Sustainable Chem. Eng. 2018, 6, 1, 1417–1426
Publication Date: November 24, 2017
https://doi.org/10.1021/acssuschemeng.7b03803

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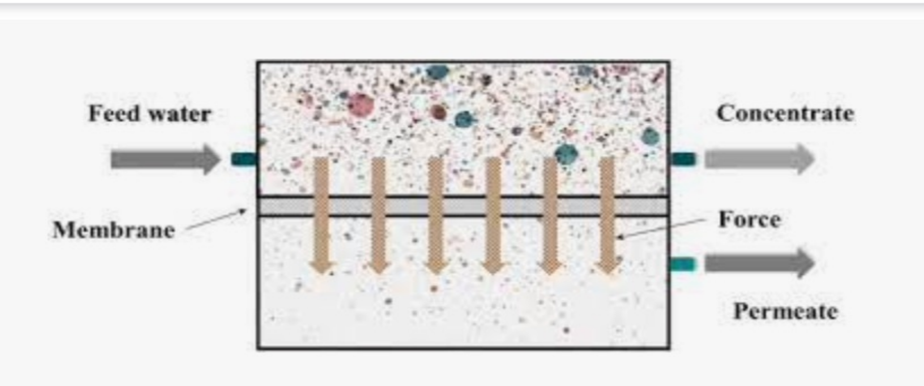
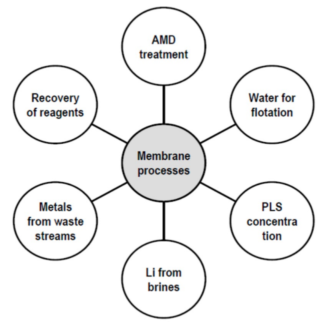
Separations

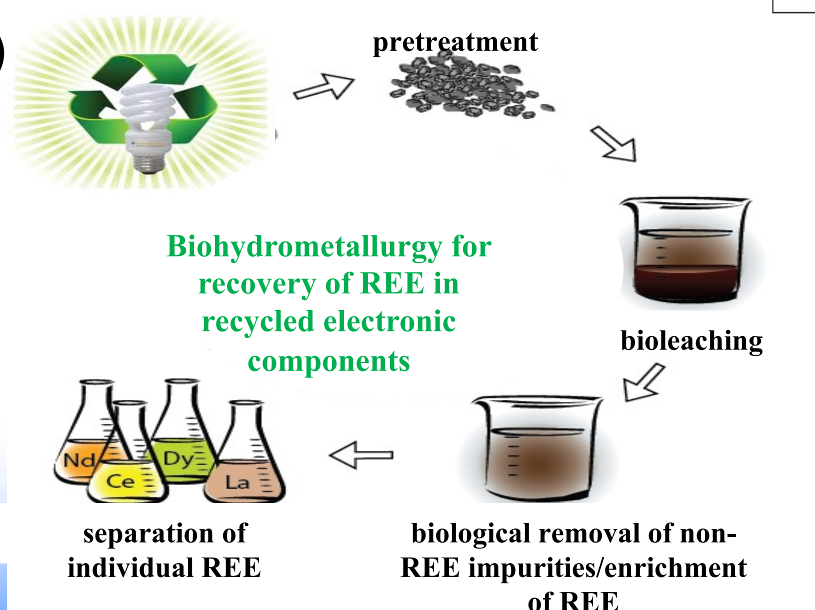
Membrane filtration – durability, selectivity and fouling issues – piloted/deployed





Driving force	Membrane process
Pressure difference	Microfiltration - MF, Ultrafiltration - UF, Nanofiltration - NF, Reverse osmosis - RO
Electric potential difference	Electrodialysis - ED, membrane electrolysis - ME, (membrane) electro-deionization -EDI, membrane electrophoresis
Chemical potential difference	Pervaporation, Per-traction, Dialysis , Vapour permeation, Liquid membranes - LM, Forward osmosis - FO
Temperature difference	Membrane distillation - MD

Biological processes – R&D phase (bio-hydromet)



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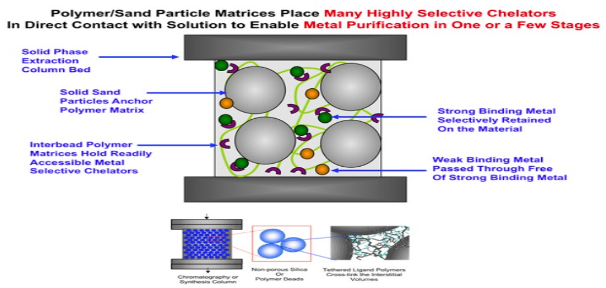
Separations

Ion Exchange/Solid phase extraction (SPE) – commercial

Solid Phase Extraction:
New Composite Matrices Enable High Throughput with Process Simplicity/Lower Cost

Polymer/Sand Particle Matrices Place Many Highly Selective Chelators In Direct Contact with Solution to Enable Metal Purification in One or a Few Stages



Relative REE Affinities for SPE columns

	Displaced Metal			
Displacing Metal	La	Pr	Nd	Er
Ce(+3)	2.55			
Pr	9.57			
Dd(Pr+Nd)	10.5			
Nd	10.6	2.18		
Sm	218		4.92	
Gd	282			
Er			6.73	
Dy			36.1	11.0

MetalsUS/Hammen, Missoula, MT
US Patent # 7220703
Peterson, et al US Patent # 6,576,335

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

Overlaid fractal theory on turbulent theory using CFD (INL)

$$\rho \frac{\partial U_i}{\partial t} + \rho U_j \frac{\partial U_i}{\partial x_j} = -\frac{\partial p}{\partial x_i} + \frac{\partial}{\partial x_j}(2\mu D_{ij} - \rho \overline{u}'_j \overline{u}')$$

where $-\rho \overline{u}'_j \overline{u}'_i = \tau_{ij}$

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

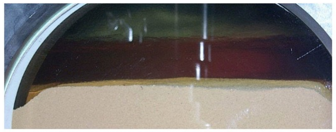
$$\frac{\partial \tau_{ij}}{\partial t} + V_k \frac{\partial \tau_{ij}}{\partial x_k} = -\tau_{ik} \frac{\partial V_j}{\partial x_k} - \tau_{jk} \frac{\partial V_i}{\partial x_k} + \varepsilon_{ij} - \Pi_{ij} + \frac{\partial}{\partial x_k}[\mu \frac{\partial \tau_{ij}}{\partial x_k} + c_{ijk}]$$

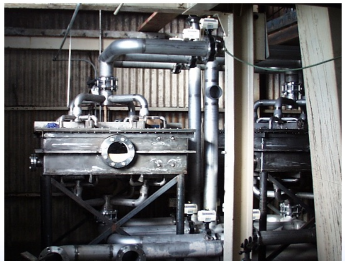
$$\Pi_{ij} = \frac{\overline{p'}}{\rho}(\overline{\frac{\partial v_i'}{\partial x_j}} + \overline{\frac{\partial v_j'}{\partial x_i}})$$

$$\varepsilon_{ij} = 2\mu \overline{\frac{\partial v_i'}{\partial x_k} \frac{\partial v_j'}{\partial x_k}}$$

$$\rho c_{ijk} = \rho \overline{v_i' v_j' v_k'} + \overline{p' v_i} \delta_{jk} + p' v_j' \delta_{ik}$$

From this to this

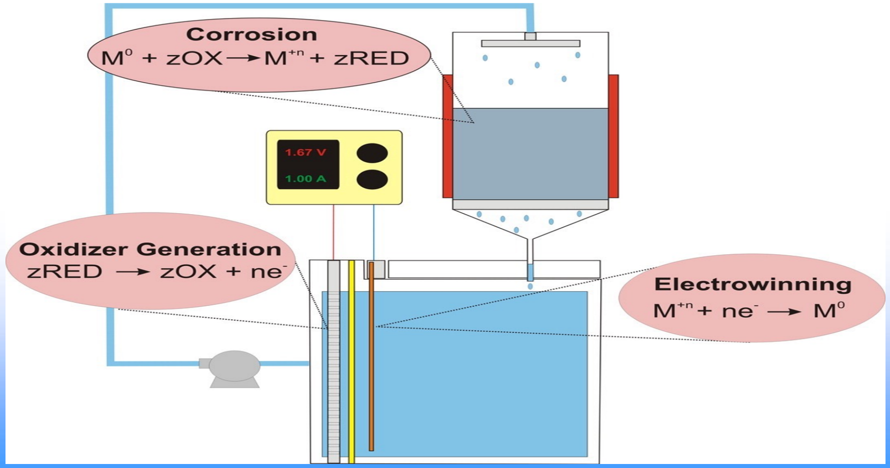




Amalgamated Research, Inc.; US Patent 8,741,146

Approx. Dimensions:
3' X 3' X 2' high, 700 gpm

E-RECOV Process (electrochemical) – R&D/Pilot Scale



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Reduction to Metal (Metal Making)

Metal Making/Reduction: high purity rare earth metals and alloys

Multiple methods to produce REMs:

- **Reduction of anhydrous chlorides or fluorides,**
- **Reduction of rare earth oxides,**
- **Fused salt electrolysis of rare earth chlorides or oxide-fluoride mixtures**
- **ERECOV – R&D 100 winner**
- **New/Research – Electroreduction in ionic liquids (R&D 100)**




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Ground to Market Process - Summary

Products

- Permanent magnets
- LED's
- Consumer Electronics

5 REFINING
to meet specific downstream technological applications

4 SEPARATION
separating and purifying the individual REE oxides

3 HYDRO-METALLURGY
cracking the REE minerals to produce mixed REE oxides concentrates

2 MILLING
grinding and beneficiation of REE minerals

1 MINING
From the ground to the crushed ore

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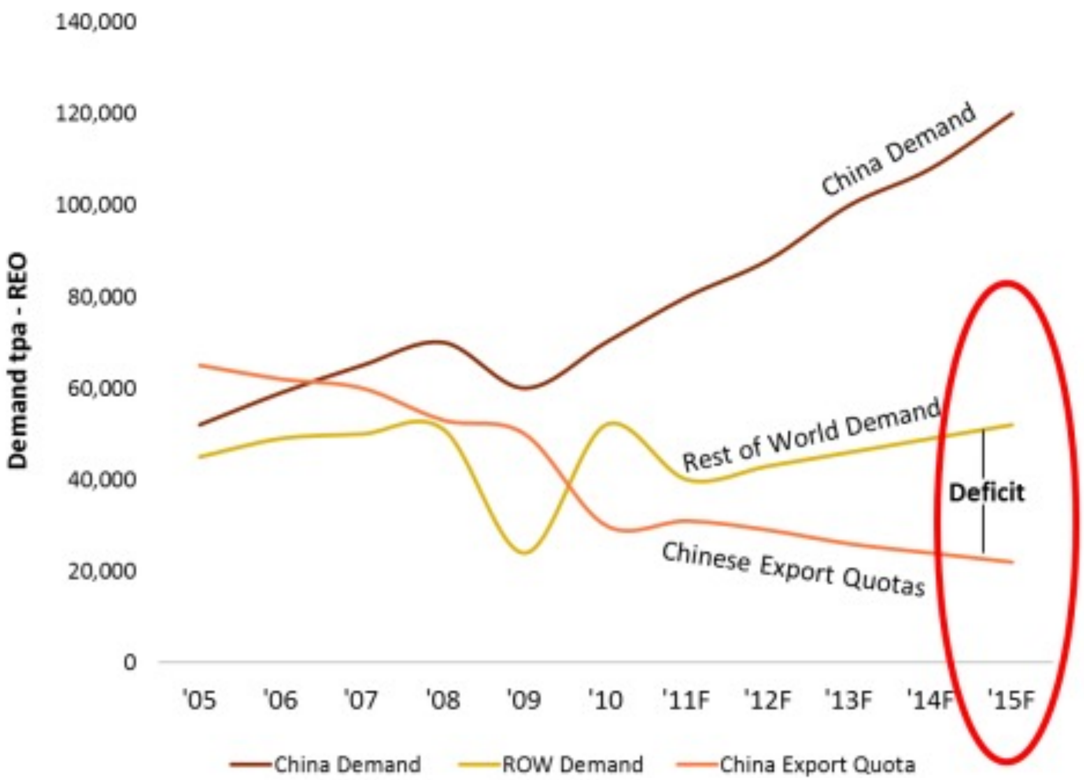
Future Outlook – Opportunities

Gap between Supply from China and Rest of World Demand is Growing

The following chart illustrates the widening gap between the supply from China and the demand from the rest of the world:



Source: D. Kingsworth IMCOA 2011

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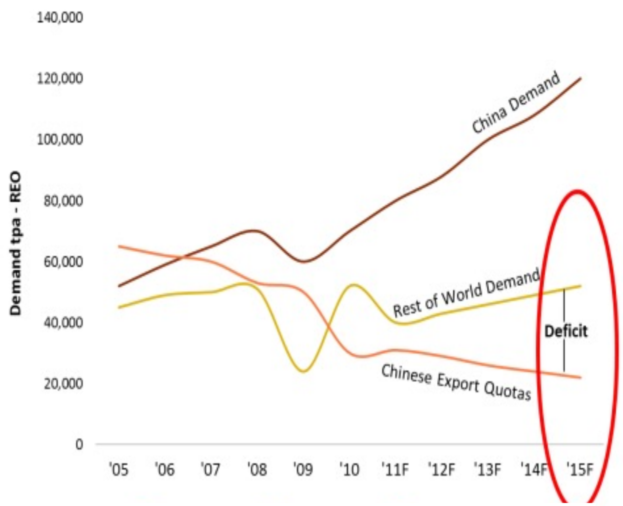
Future Outlook – Opportunities/Needs

Gap between Supply from China and Rest of World Demand is Growing

The following chart illustrates the widening gap between the supply from China and the demand from the rest of the world:



Source: D. Kingsworth IMCOA 2011

R&D Needs:

- Geologic discovery and sensing,
- Rapid in-field and in-plant analysis,
- Materials pre-processing/concentration,
- Efficient processing,
- Metals/alloys making
- New final products
- Education and workforce development

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Questions?

Auroras over Denali State Park, AK

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BACKUP SLIDES

Rare Earth Element Products and Applications

MAGNETICS

Computer Hard Drives
Disk Drive Motors
Anti-Lock Brakes
Automotive Parts
Frictionless Bearings
Magnetic Refrigeration
Microwave Power Tubes
Power Generation
Microphones & Speakers
Communication Systems
MRI

Nd Tb Dy Pr

DEFENSE

Satellite Communications
Guidance Systems
Aircarft Structures
Fly-by-Wire
Smart Missiles

Nd Eu Tb Dy Y Lu Sm Pr La

CERAMICS

Capacitors
Sensors
Colorants
Scintillators
Refractories

Nd Y Eu Dy Lu Gd La Ce Pr

CATALYSTS

Petroleum Refining
Catalytic Converter
Fuel Additives
Chemical Processing
Air Pollution Controls

Nd La Ce Pr

METAL ALLOYS

NiMH Batteries
Fuel Cells
Steel
Super Alloys
Aluminum/Magnesium

Nd Y La Ce Pr

GLASS & POLISHING

Polishing Compounds
Pigments & Coatings
UV Resistant Glass
Photo-Optical Glass
X-Ray Imaging

Nd Gd Er Ho La Ce Pr

PHOSPHORS

Display phosphors- CRT,LPD,LCD
Fluorescents
Medical Imaging
Lasers
Fiber Optics

Nd Eu Tb Y Er Gd Ce Pr

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