Extraction, Separation, and Production of High Purity Rare Earth Elements and Critical Minerals from Coal-Based and Related Resources

DE-FE0032122

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U.S. Department of Energy

National Energy Technology Laboratory

Resource Sustainability Project Review Meeting

October 25 - 27, 2022

Project Overview (Part I)

- Funding (DOE \$200,000 and Cost Share \$50,000)
- Overall Project Performance Dates (1/16/22-4/16/23)
- Project Participants
  - University of Utah (UofU)
  - Virginia Tech (VT)
  - Other original partners (noncontract partners)

    Blacksand Technology, LLC

    Grimstone Mining, LLC

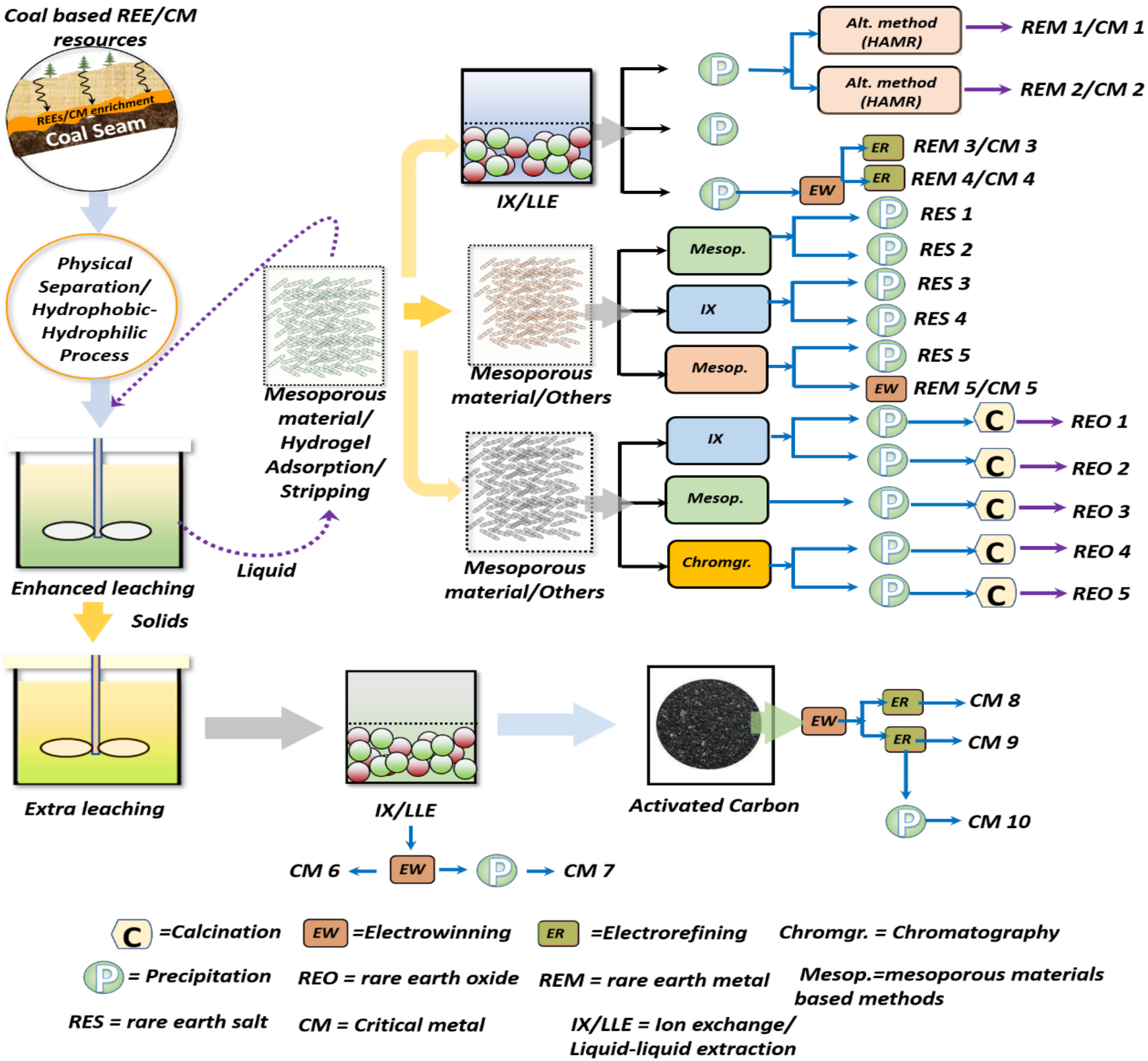
    Minerals Refining Company

    Energy Fuels Resources Inc.

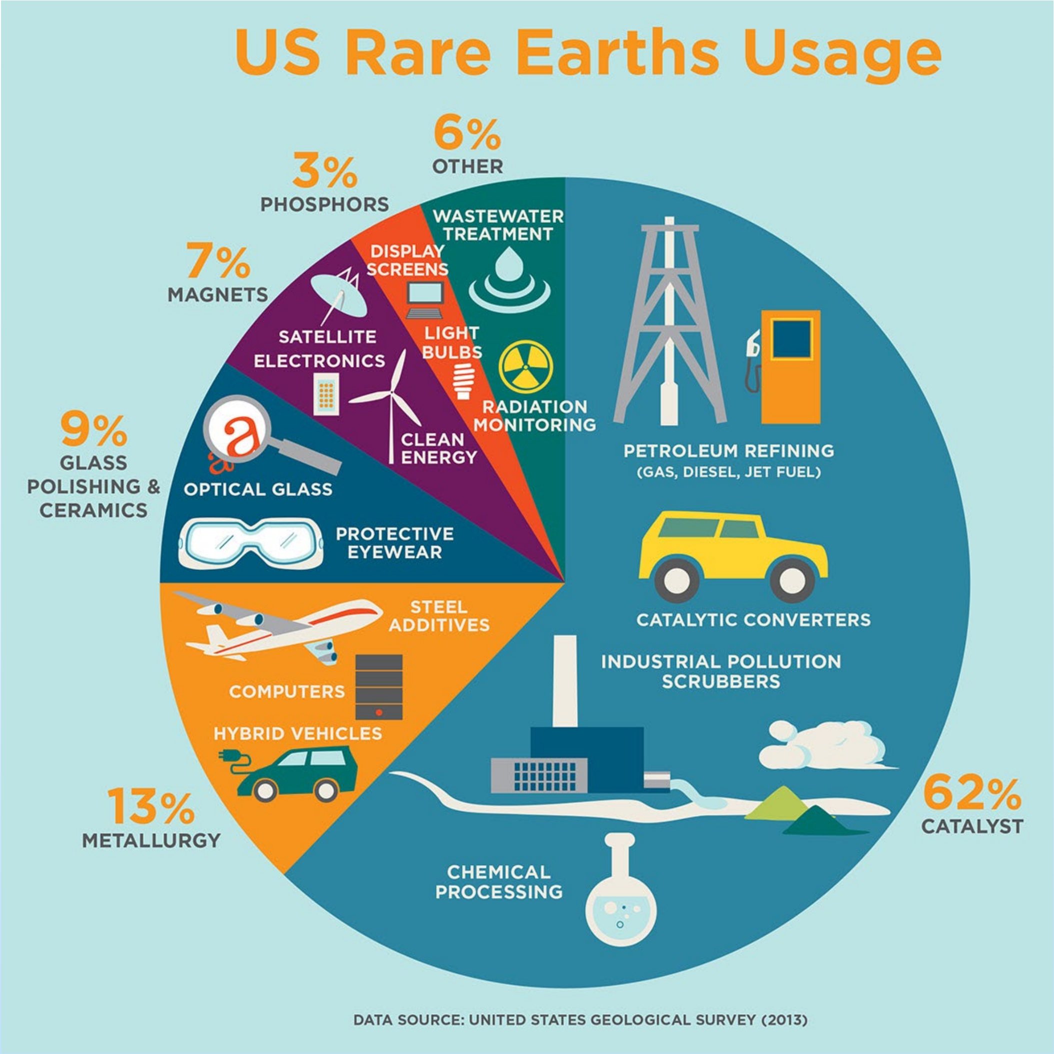
Project Overview (Part II)

Overall Project Objectives:

The general objectives of this project are to develop concepts for rare earth metal and critical mineral production from coal-based and related (minerals associated with coal) resources and incorporate them into a Technical Research Plan with an associated overall flow sheet and develop appropriate industry partnerships.



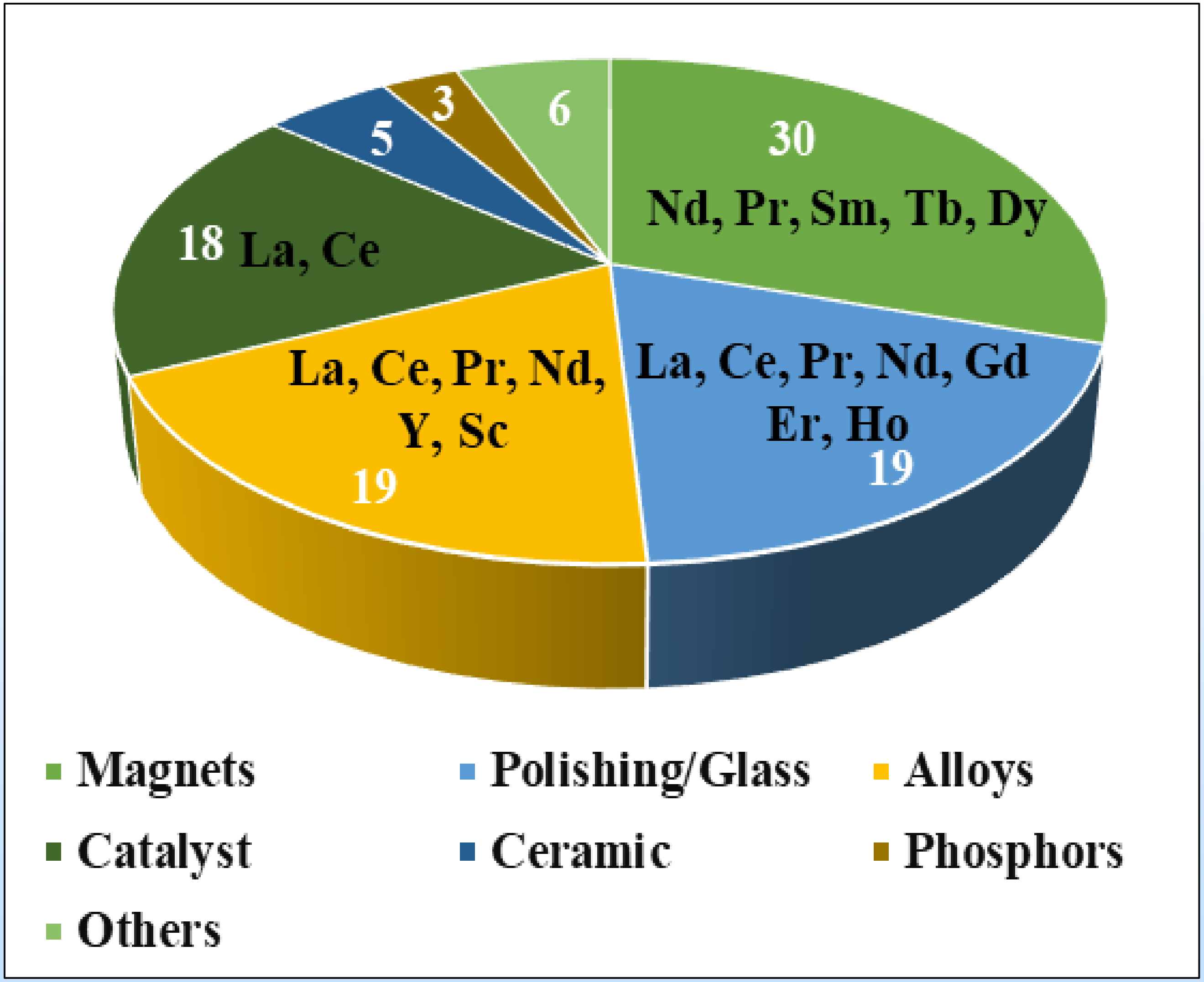
Schematic diagram to illustrate an example of what a process flow sheet could look like for REE/CM extraction and purification system into the required types of high purity products for AOI 1a for 20 elements.



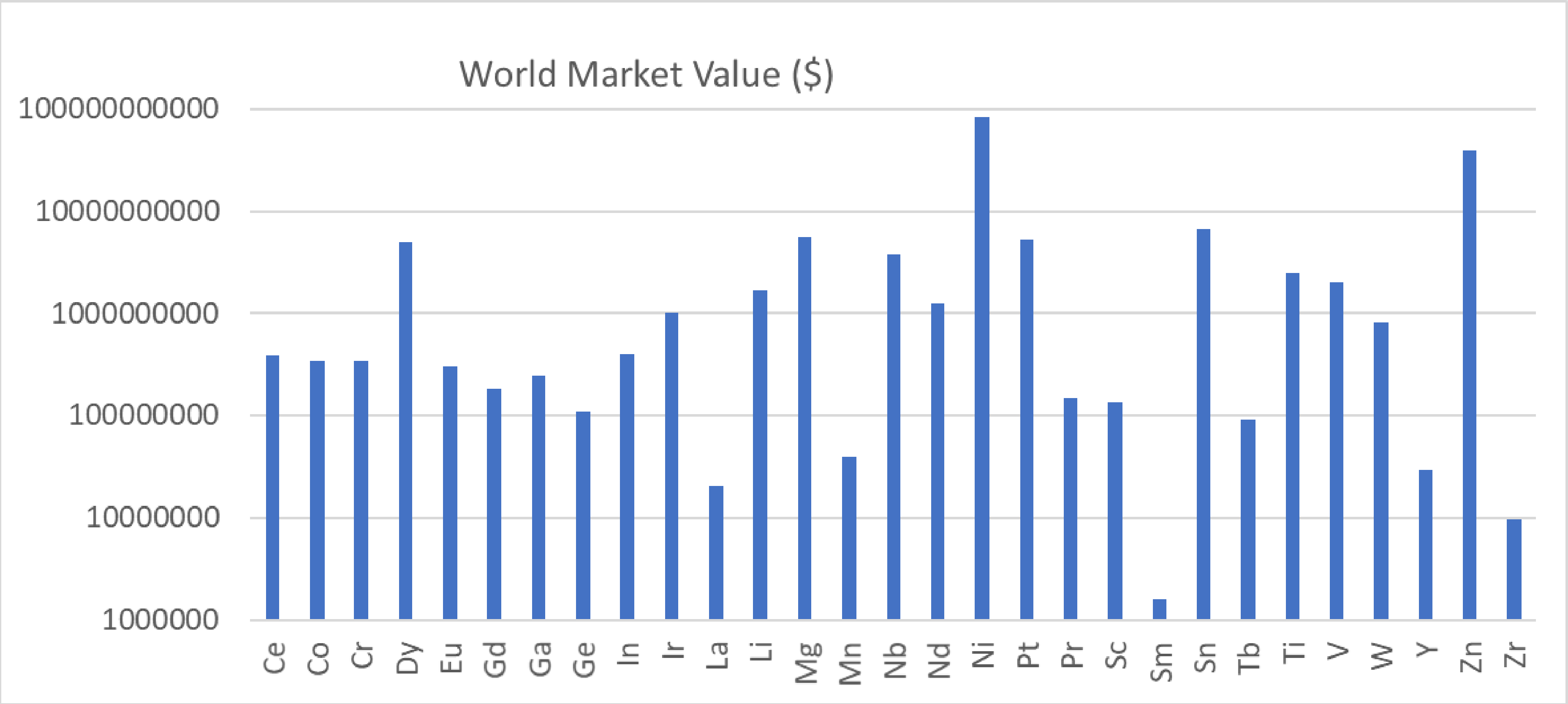
Why are some elements so critical?

They are needed for many common products, but their supply is small or unstable.

Distribution of specific rare earth element uses in different applications



How large is the world market?



Salient Statistics

	Cobalt	Nickel	Lithium	Magnesium Metal	Refined Zinc	RE Metals and Compounds
Apparent Domestic Consumption (mt/yr.)	6,700 to 12,500	190,000 to 273,000	2,000 to 3,000	50,000 to 65,000	829,000 to 939,000	5,400 to 11,200 (REO equivalent)
Net U.S. Import Reliance	64% to 78%	48% to 52%	>25% to >50%	<25% to <50%	76% to 88%	>90% to 100%
Price	$9.26 to $72.47 / kg (LME Cash)	$10.38 to $18.26 / kg (LME Cash)	$8 to $17 / kg (battery grade)	$4.73 to $8.58 / kg (US Spot)	$2.26 to $2.99 / lb. (LME Cash)	Varies by element
% Produced Within a Single Country	54%, Congo	30%, Indonesia	46%, Australia	87%, China	33%, China	83%, China
High Importance in Clean Energy Tech[1]	EVs, battery and storage	Geothermal; EVs and battery storage; hydrogen	EVs and battery storage	N/A	Wind	Wind; EVs and battery storage
Largest U.S. Import Source	17%, Norway	43%, Canada	54%, Argentina	20%, Canada	63%, Canada	78%, China

1: As defined in IEA, 2021

Rare Earth Elements

US Consumption by End-Use (USGS)

End Use Application	Content (metric tons REO equiv.)	% of Total
Rare Earths		
Catalysts (La and Ce)	5,005	55.0%
Ceramics and Glass (Y, La, Ce, Pr, Nd, Eu, Gd, Dy, Lu)	1,365	15.0%
Metallurgical Applications and Alloys (Y, La, Ce, Pr, Nd)	910	10.0%
Polishing (La, Ce, Nd, Pr, Nd, Gd, Ho, Er)	455	5.0%
Other uses	1,365	15.0%
Total	**9,100**	**100.0%**

US Imports by Form (USGS)

Compound/Metal	Metal Content Imported (metric tons REO equiv.)	Value (thousands)	Value (% of total)
Rare Earth Compounds			
Cerium Oxides	679	$16,600	12.9%
Other Cerium Compounds	1,710	$9,350	7.3%
Lanthanum Carbonate	450	$2,270	1.8%
RE Carbonate Mixtures	3.23	$316	0.2%
Scandium or Yttrium Chloride Mixtures	0.02	$22	0.0%
Unspecified Mixtures of Oxides or Chlorides	269	$2,640	2.1%
Lanthanum Oxides	2,220	$6,580	5.1%
Scandium or Yttrium Oxides	43.9	$1,740	1.4%
Other Oxides	39.9	$1,740	1.4%
Unspecified Compounds or Mixtures	5,540	$84,700	66.0%
Yttrium Materials 19% to 85% Y_2O_3	41.3	$2,420	1.9%
Total	**10,996**	**$128,378**	**100.0%**
Rare Earth Metals and Alloys			
Ferrocerium and Other Pyrophoric Alloys	309	$4,340	44.9%
Rare Earth Metals and Alloys	84	$581	6.0%
Lanthanum, unalloyed	115	$891	9.2%
Neodymium, unalloyed	3.94	$146	1.5%
Other RE Metals, unalloyed	47.9	$1,720	17.8%
Other RE Metals, alloys	273	$1,980	20.5%
Total	**833**	**$9,658**	**100.0%**

Cobalt and Nickel

US Consumption by End-Use (USGS)

End Use Application	Metal Content (metric tons)	% of Total
Cobalt		
Steels and Other Alloys	1,420	15.4%
Superalloys	4,240	45.9%
Cemented Carbides	753	8.1%
Chemical and Ceramic Uses	2,830	30.6%
Total	**9,243**	**100.0%**
Nickel		
Chemicals	1,550	1.5%
Electroplating	7,350	7.3%
Other Nickel and Nickel Alloys	13,600	13.4%
Stainless and Heat Resistant Alloys	39,900	39.4%
Alloys, excluding Stainless	6,810	6.7%
Superalloys	26,000	25.7%
Other[2]	6,090	6.0%
Total	**101,300**	**100.0%**

US Imports by Form (USGS)

Compound/Metal	Metal Content Imported (metric tons contained metal)	Value (thousands)	Value (% of total)
Cobalt			
Co Metal	9,530	$465,000	80.8%
Co Oxides and Hydroxides	1,520	$76,600	13.3%
Co Acetates	47	$2,210	0.4%
Co Carbonates	330	$17,300	3.0%
Co Chlorides	9	$412	0.1%
Co Sulfates	471	$14,300	2.5%
Total Co	**11,907**	**$575,822**	**100.0%**
Nickel			
Ni cathodes[1]	118,000	$1,240,000	73.5%
Ferronickel	22,700	$243,000	14.4%
Ni Powder and Flakes	5,430	$92,100	5.5%
Metallurgical-Grade Ni Oxide	225	$5,900	0.3%
Ni Catalysts	1,590	$82,900	4.9%
Ni Salts[2]	1,660	$24,100	1.4%
Total Ni	**149,605**	**$1,688,000**	**100.0%**

Magnesium, Lithium and Zinc

US Consumption by End-Use (USGS)

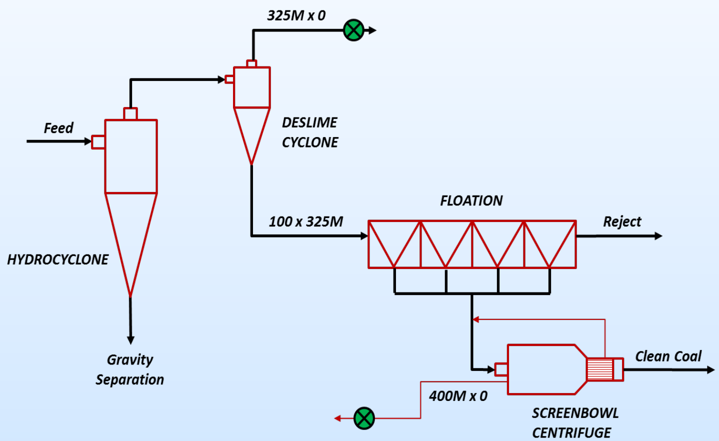
End Use Application	Metal Content (metric tons)	% of Total
Magnesium Metal		
Die Castings	26,700	49.8%
Permanent Mold Castings	302	0.6%
Sand Castings	1,370	2.6%
Other Castings	892	1.7%
Aluminum Alloys	15,300	28.6%
Iron and Steel Desulfurization	7,120	13.3%
Nodular Iron	439	0.8%
Reducing Agents[3]	300	0.6%
Other	1,150	2.1%
Total	**53,573**	**100.0%**
Lithium[1]		
Batteries	29,378	74.0%
Ceramics and Glass	5,558	14.0%
Lubricating Greases	1,191	3.0%
Continuous Casting Mold Flux Powders	794	2.0%
Polymer Production	794	2.0%
Air Treatment	397	1.0%
Other Uses	1,588	4.0%
Total	**39,700**	**100.0%**
Zinc		
Galvanizing	450,000	88.3%
Zinc-base Alloys	21,100	4.1%
Brass and Bronze	34,000	6.7%
Other	4,490	0.9%
Total	**509,590**	**100.0%**

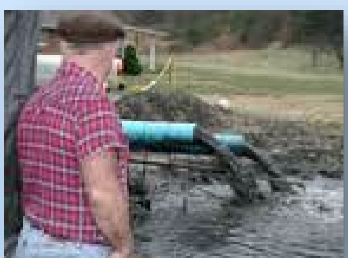
US Imports by Form (USGS)

Compound/Metal	Metal Content Imported (metric tons contained metal)	Value (thousands)	Value (% of total)
Magnesium Metal			
Mg Waste and Scrap	16,900	$32,900	23.9%
Mg Metal	16,500	$51,400	37.3%
Mg Alloys	5,290	$28,800	20.9%
Other Mg[3]	3,270	$24,600	17.9%
Total Mg	**41,960**	**$137,700**	**100.0%**
Lithium			
Li Carbonate	3,030	$79,000	73.9%
Li Hydroxide	302	$27,900	26.1%
Total Li	**3,332**	**$106,900**	**100.0%**
Zinc			
Chromates of zinc or lead	85	$664	0.2%
Lithopone	383	$1,860	0.5%
Zn Chloride	98	$1,770	0.5%
Zn Oxide	91,587	$294,000	75.7%
Zn Sulfate	36,887	$85,400	22.0%
Zn Sulfide	1,435	$4,680	1.2%
Total Zn	**130,475**	**$388,374**	**100.0%**

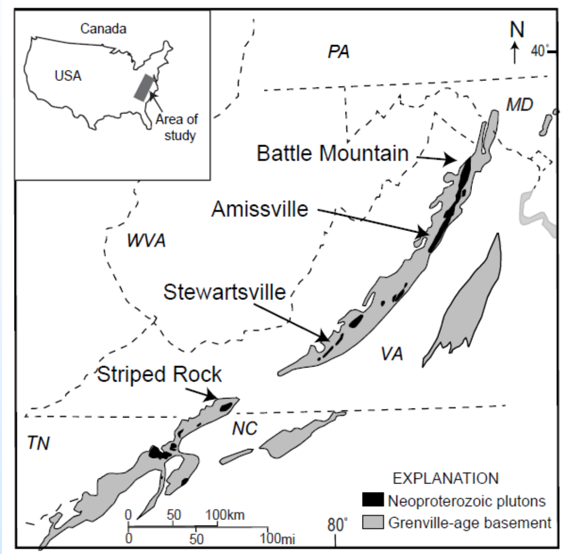
Ion-Adsorption Clay (IAC) in US

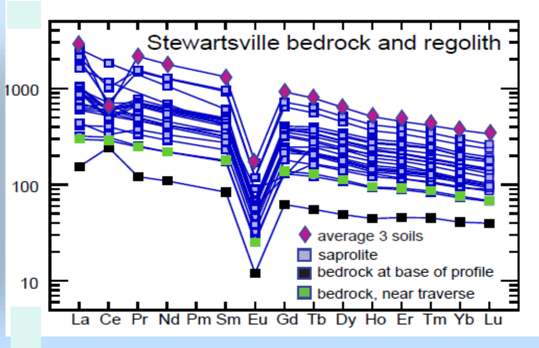
- U.S. coal industry has been discarding fine coal waste
  - ~4 billion tons
    - 40% carbon — feedstock for carbon-based materials
    - 60% kaolinite — feedstock for REE extraction

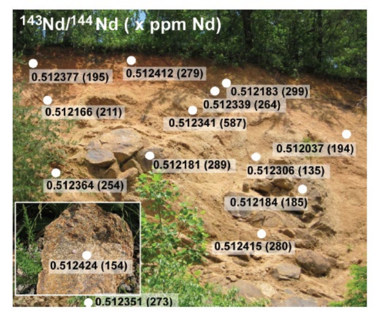




❑ USGS discovery (Foley, 2015)



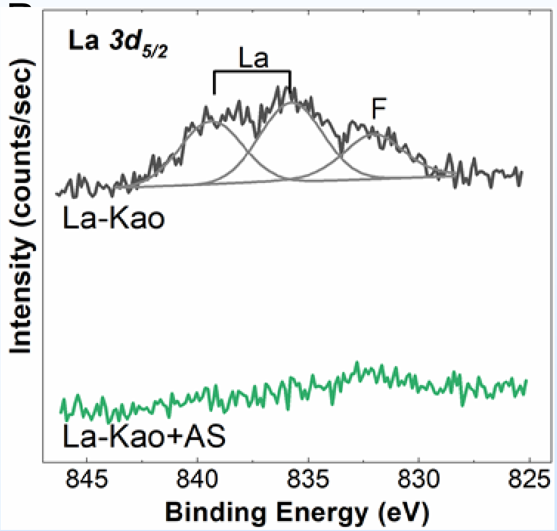


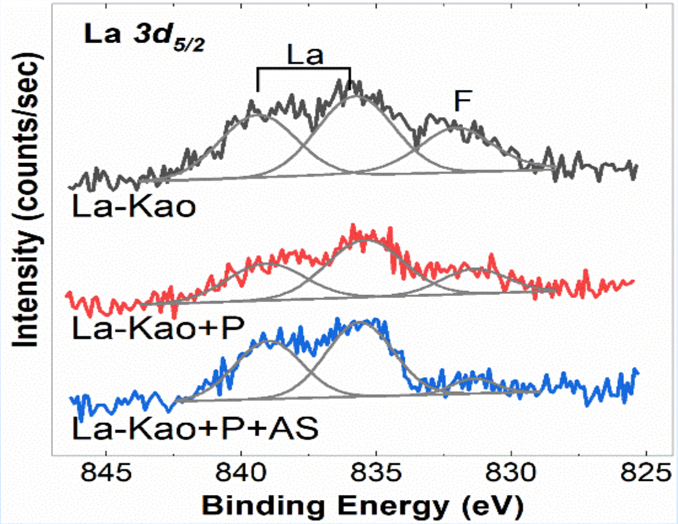


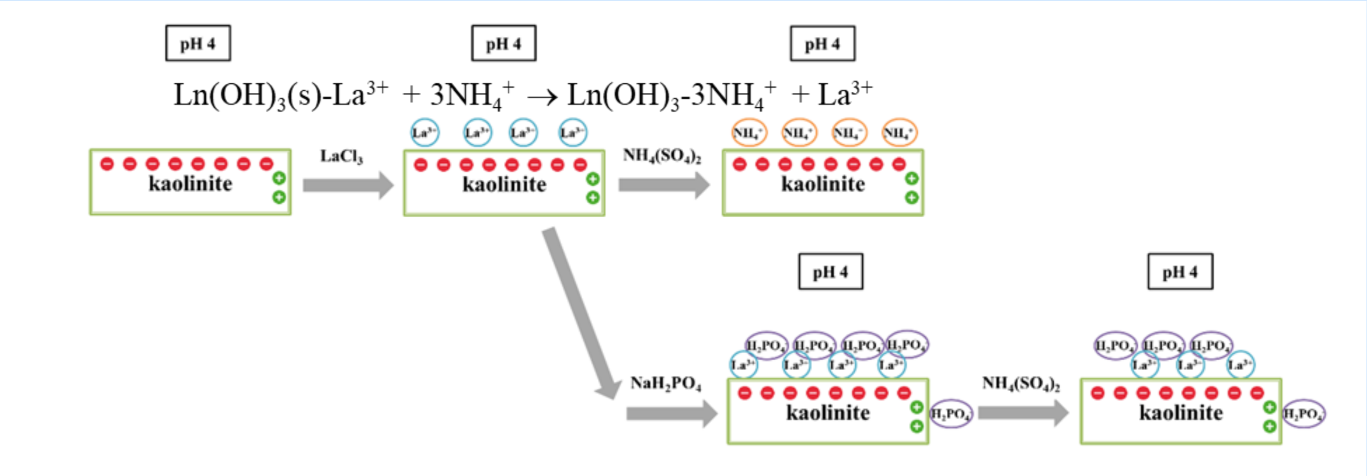
Ion-Exchange Leaching Tests

(Artificial IACs)

- Passivated by PO_4^- ions

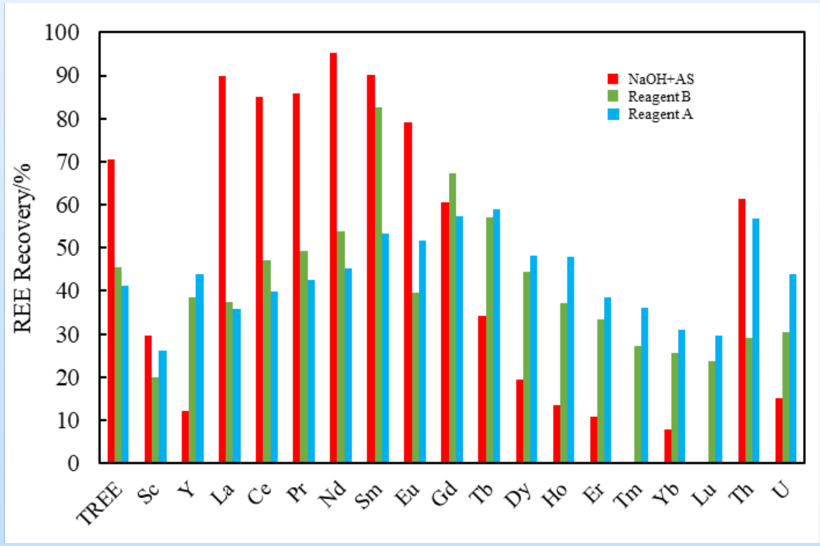




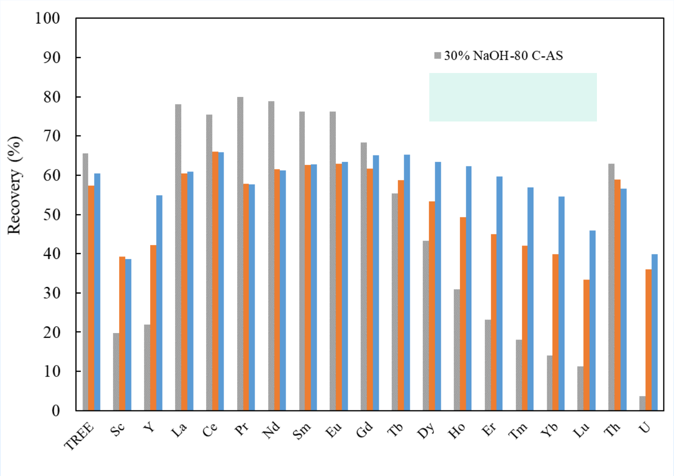


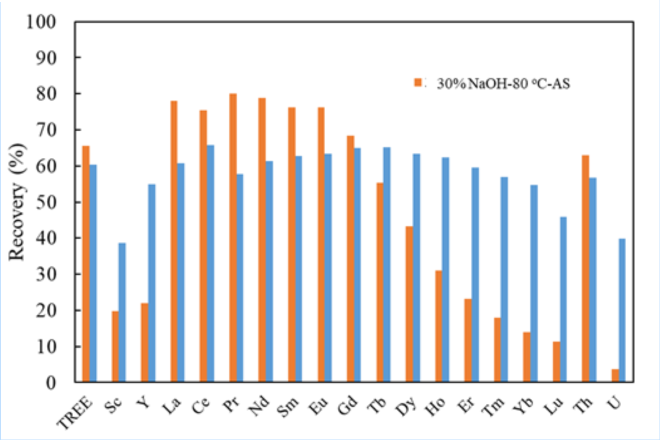
Activation Leaching of IACs

- Clay from the Upper Freeport coal, WV
  - Step 1: Activation
    - 10% NaOH, 0.1 M EDTA, 60°C, 24 h
  - Step 2: Ion-exchange leaching
    - 0.5 M AS, pH 3-4
    - 1 hr
    - Ambient temperature



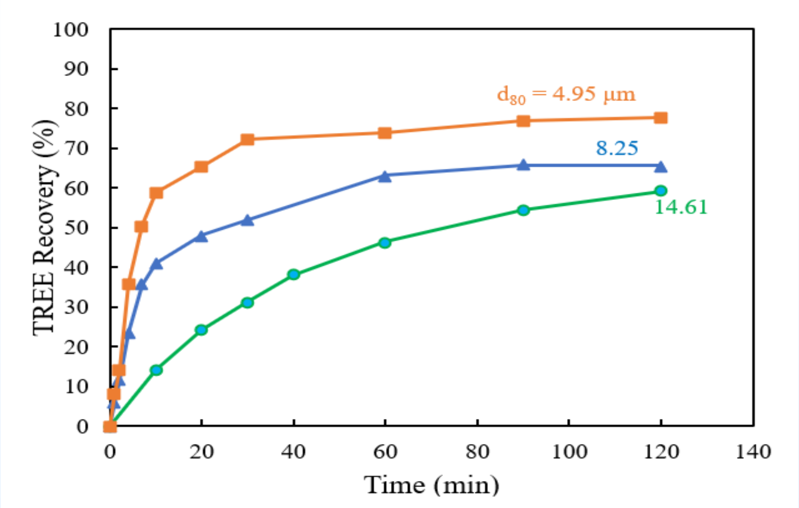
- Another clay source
  - 30% NaOH
    - 80°C, 1 h

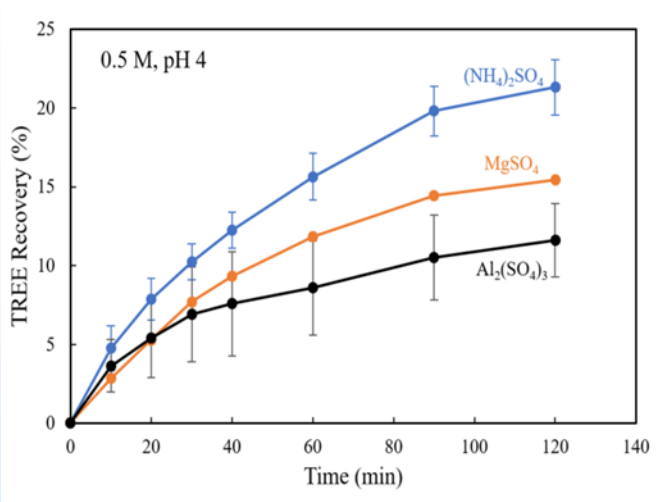


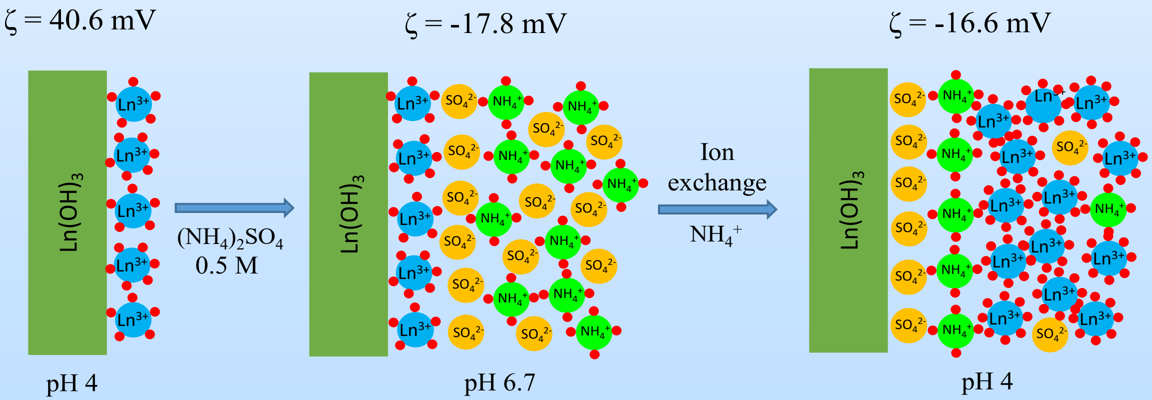


Ion-Exchange Leaching of Monazite at pH 4-5

(Liu *et al.*, Mineral Engineering 188 (2022) 107817





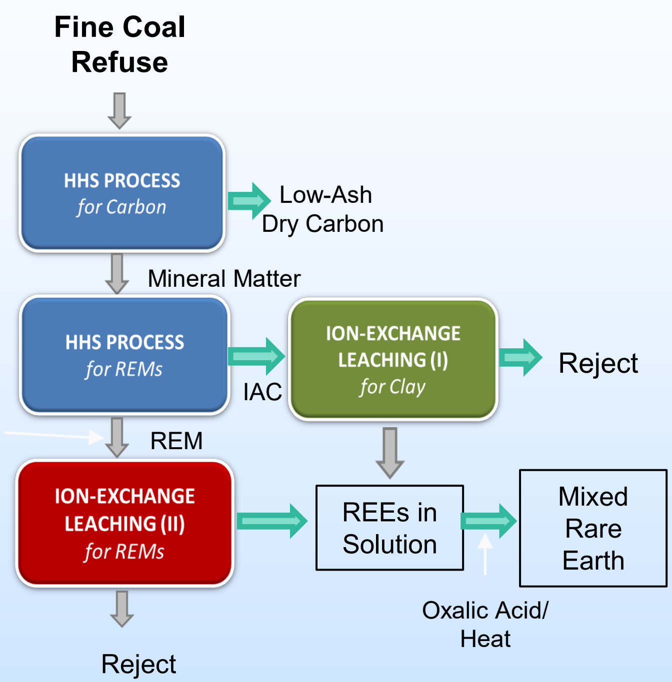


$LnPO_4(s) + 3NaOH \rightarrow Ln(OH)_3(s) + 3Na^{3+} + PO_4^{3-}$

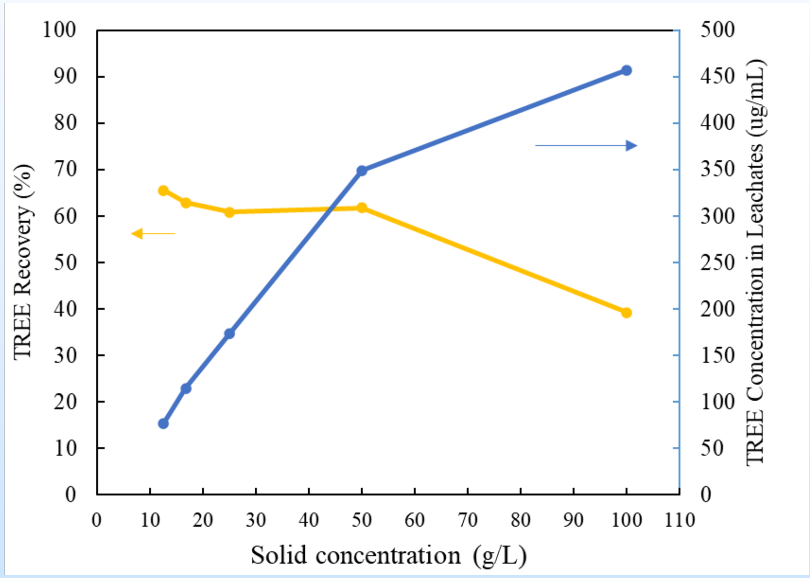
$Ln(OH)_3(s)\text{-}La^{3+} + 3NH_4^+ \rightarrow Ln(OH)_3\text{-}3NH_4^+ + La^{3+}$

Process

- Flowsheet

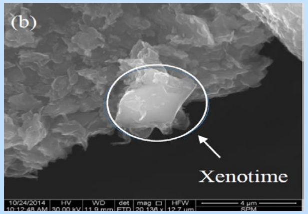


- PDU design
  - Effect of solids content
  - Necessary for the design of pilot plant



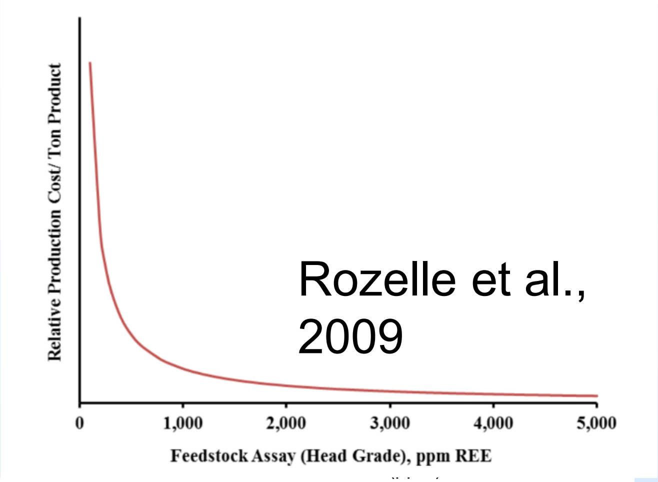
- Preconcentration

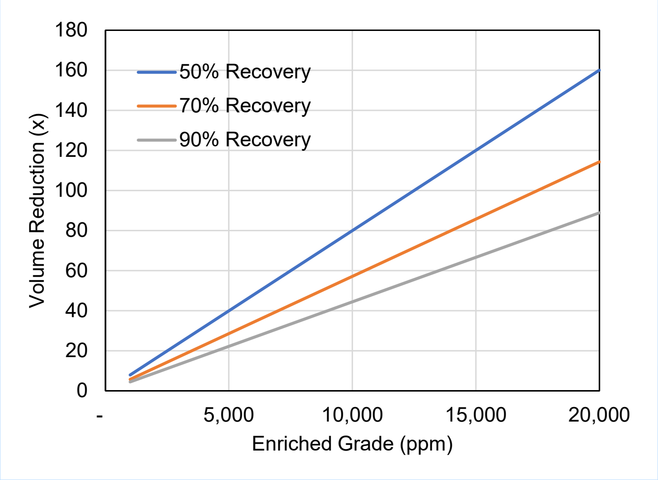
Test	Particle Size	Conc Grade, % (Total)	Conc Grade, % (Dry Ash Basis)	Overall Recovery, %
HHS 4	2.2	6.34%	56.14%	14.2%
HHS 8	3.0	3.73%	-	4.54%



Analytical Background
Role of Concentration

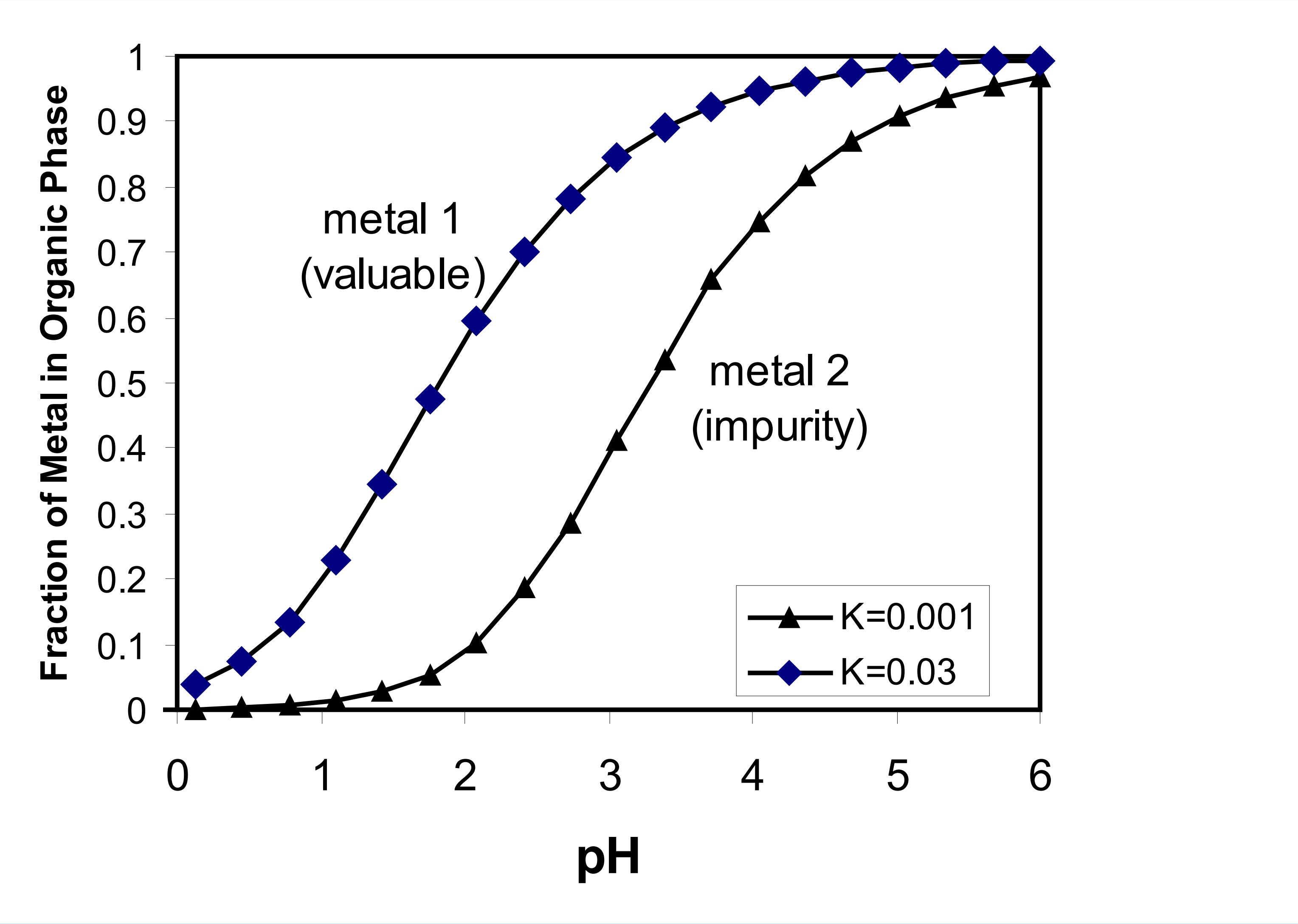
- One key feature of our process is the use of HHS to concentrate the feedstock prior to hydrometallurgical processing.
- This pre-concentration imparts notable cost reductions versus that of treating virgin material.
- Our current data suggest we can upgrade a 250 ppm REE material to 10,000 ppm at 50% to 70% recovery.
- This will in turn prompt a 60 to 80 fold reduction in volume for downstream processes.



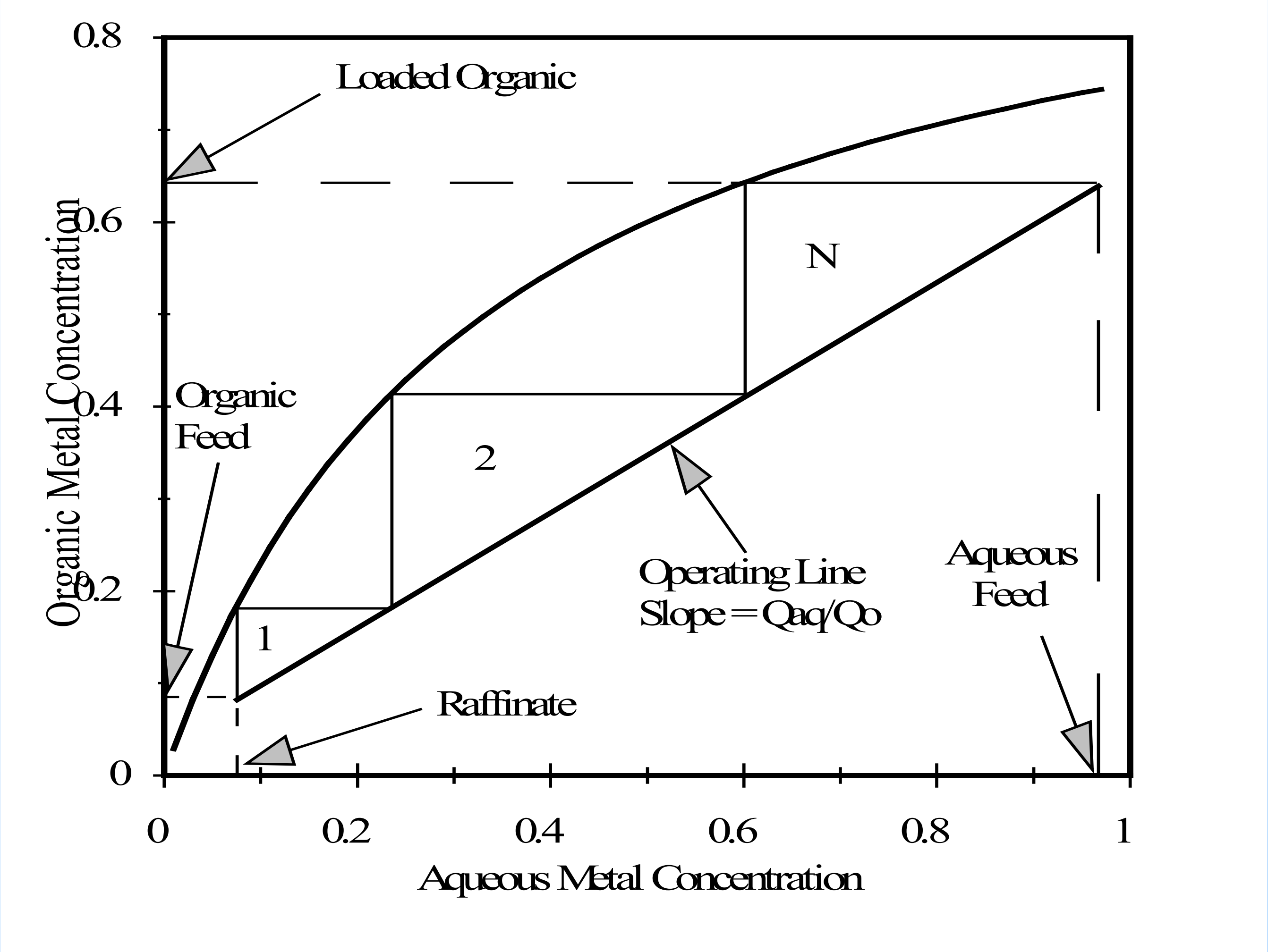


Assuming a 250 ppm feed grade

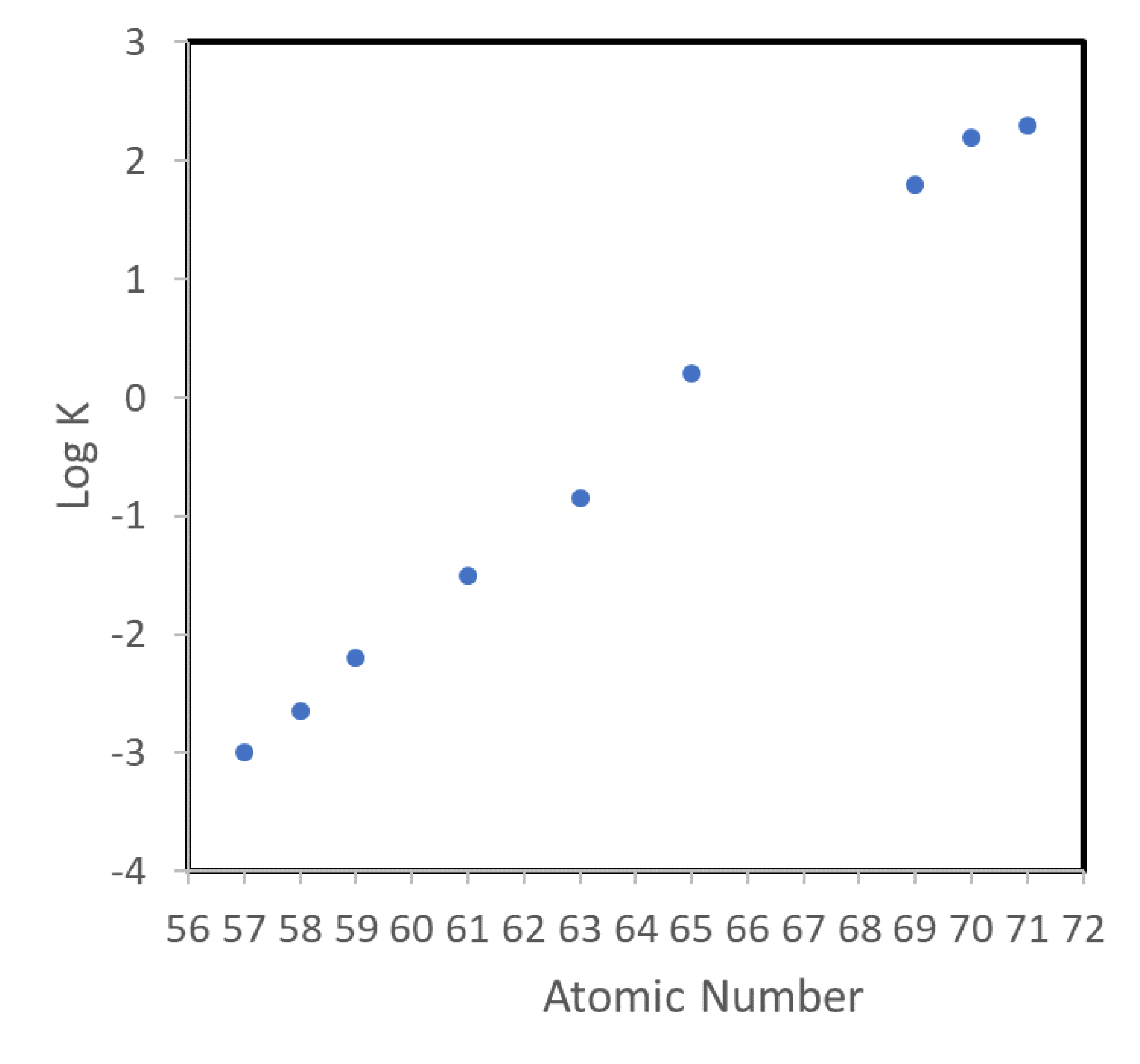
Chemical separations are feasible when the equilibrium data are significantly different



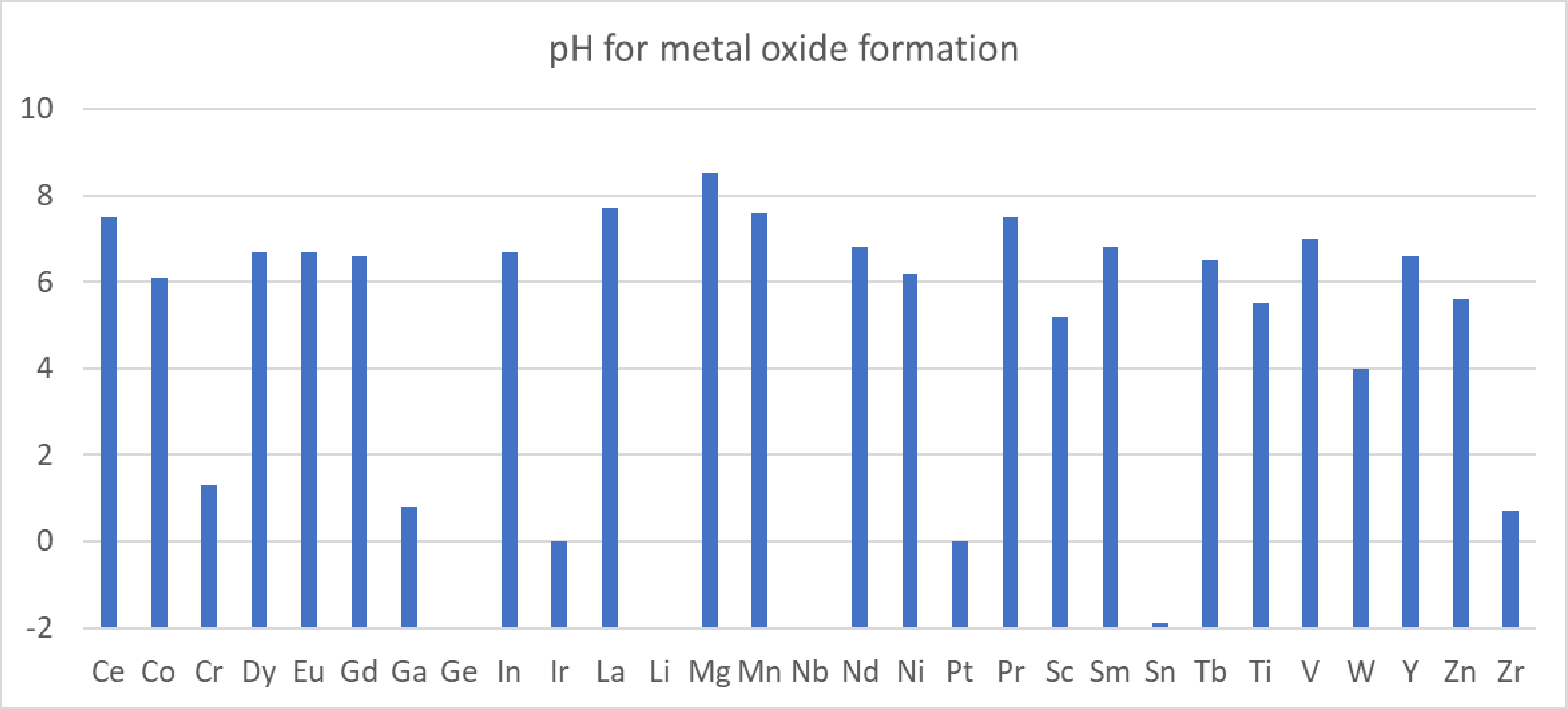
In practice, multiple stages are needed to realistically reach most of the chemical separation that is thermodynamically possible



Individual element separations are most challenging for elements with similar atomic numbers.



Data from Peppard, D.F., Driscoll, W.J., Sironen, R.J., McCarty, S., 1957b. Nonmonotonic ordering of lanthanides in tributyl phosphate-nitric acid extraction system. Journal of Inorganic & Nuclear Chemistry 4, 326–333.



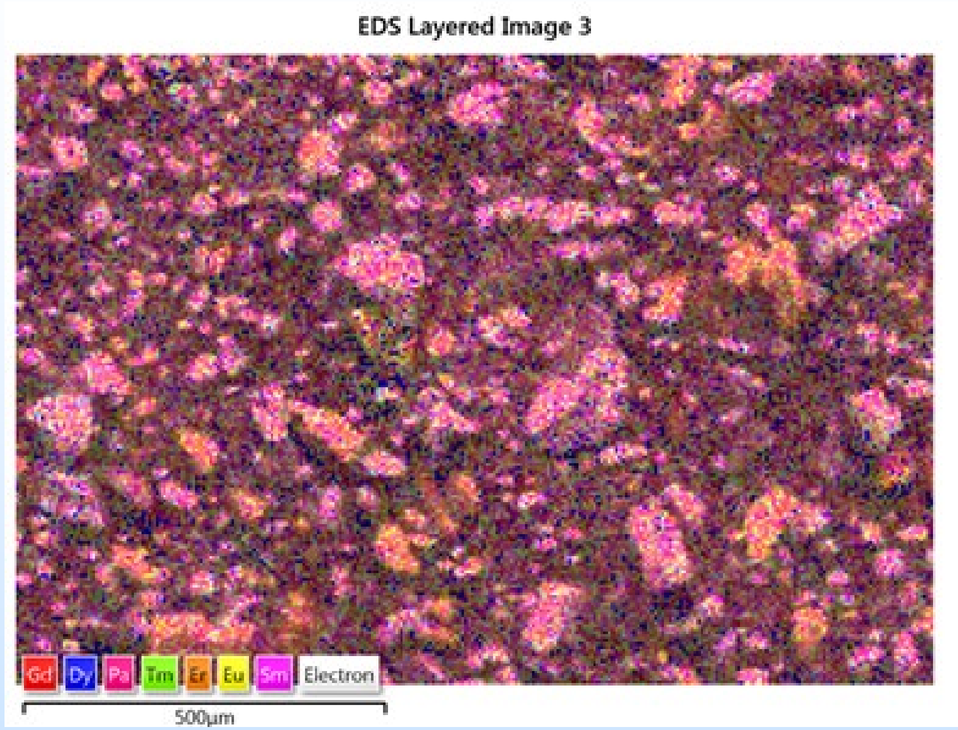
pH for metal oxide formation
10
8
6
4
2
0
-2
Ce Co Cr Dy Eu Gd Ga Ge In Ir La Li Mg Mn Nb Nd Ni Pt Pr Sc Sm Sn Tb Ti V W Y Zn Zr

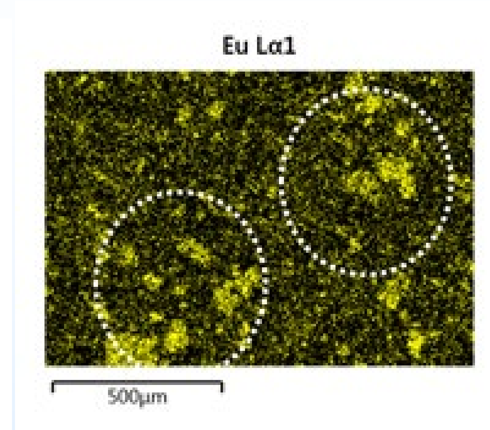
Selective Precipitation

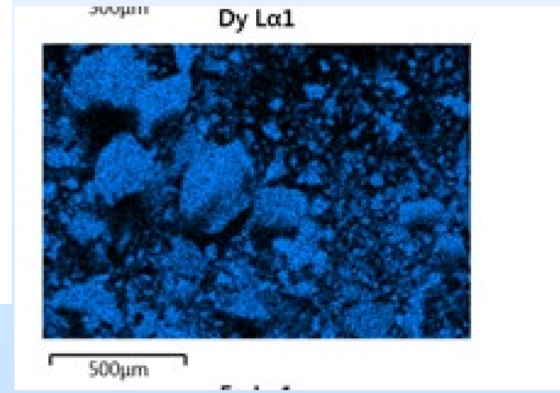
The most effective precipitating agent of the ones examined was Na_2SO_4. Utilizing sodium sulphate at a stoichiometric ratio of 2-3 times at 70 °C, the lanthanides can be precipitated. In this instance, the yttrium precipitation only reached roughly 40% by weight. Eight times the stoichiometric amount of sodium sulphate was needed to precipitate all of the yttrium, and 70 °C was the ideal temperature.

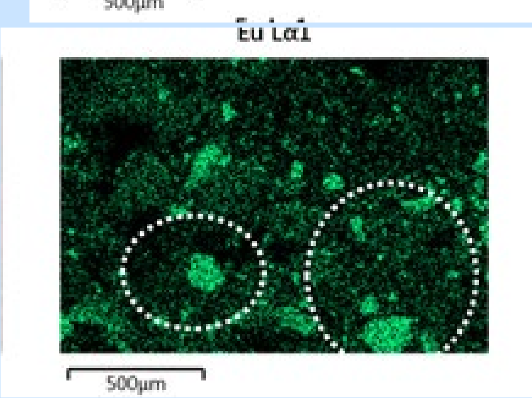
Precipitation

Initial precipitate after removing iron shows enriched rare earth elements.

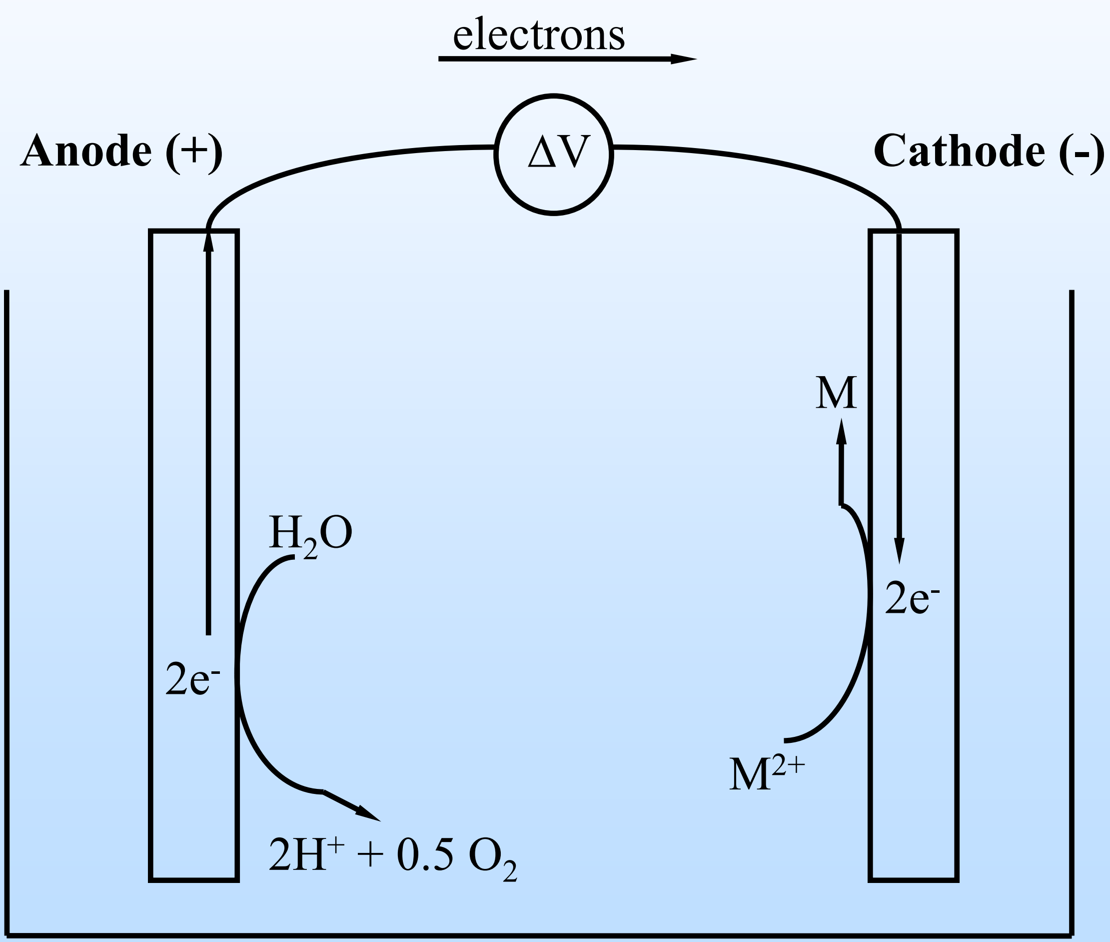




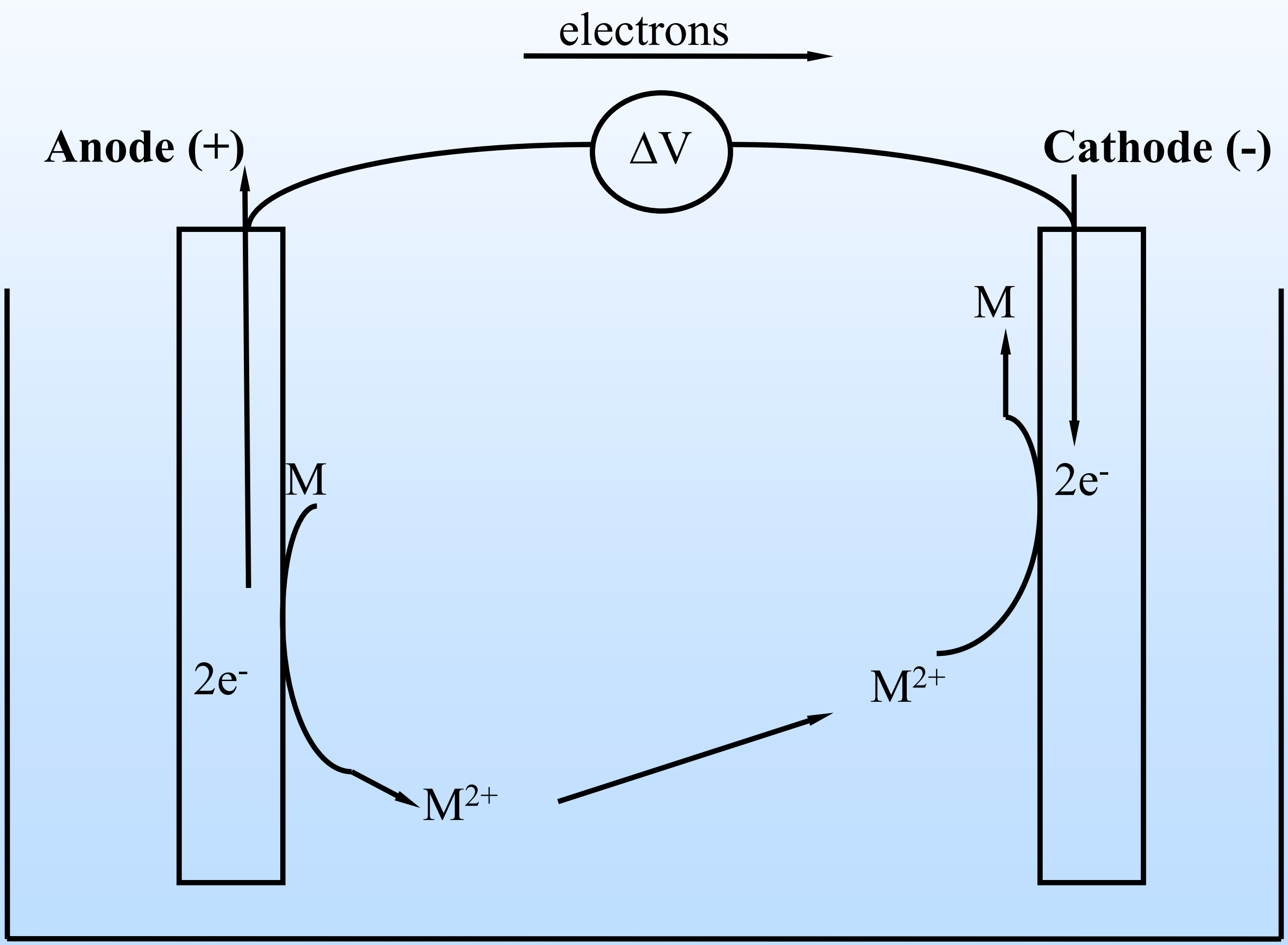




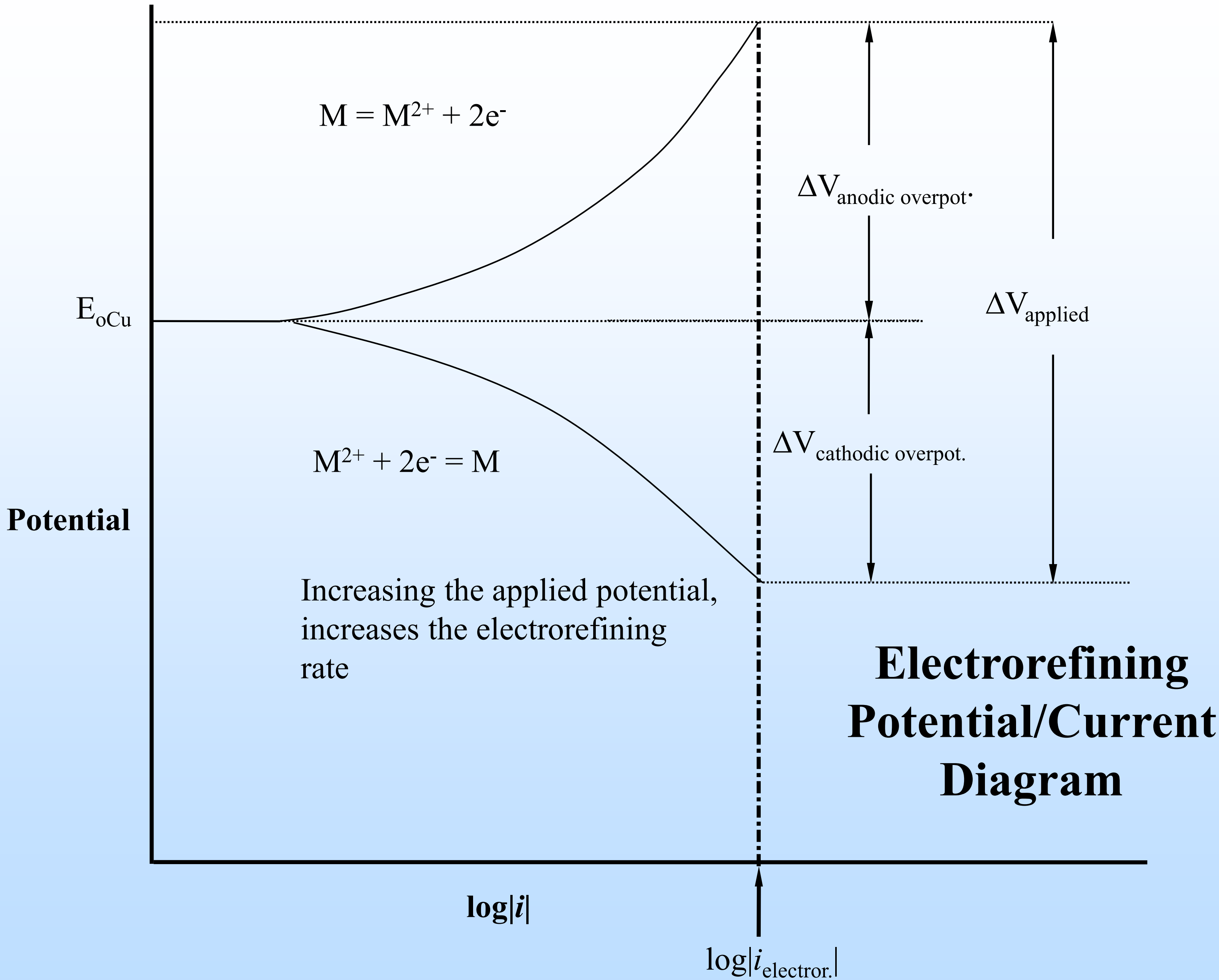
Electrowinning is the process of reducing metal by applying a negative potential to an electrode (cathode) on which the metal deposits by means of a power supply and a counter electrode and the associated reaction(s).



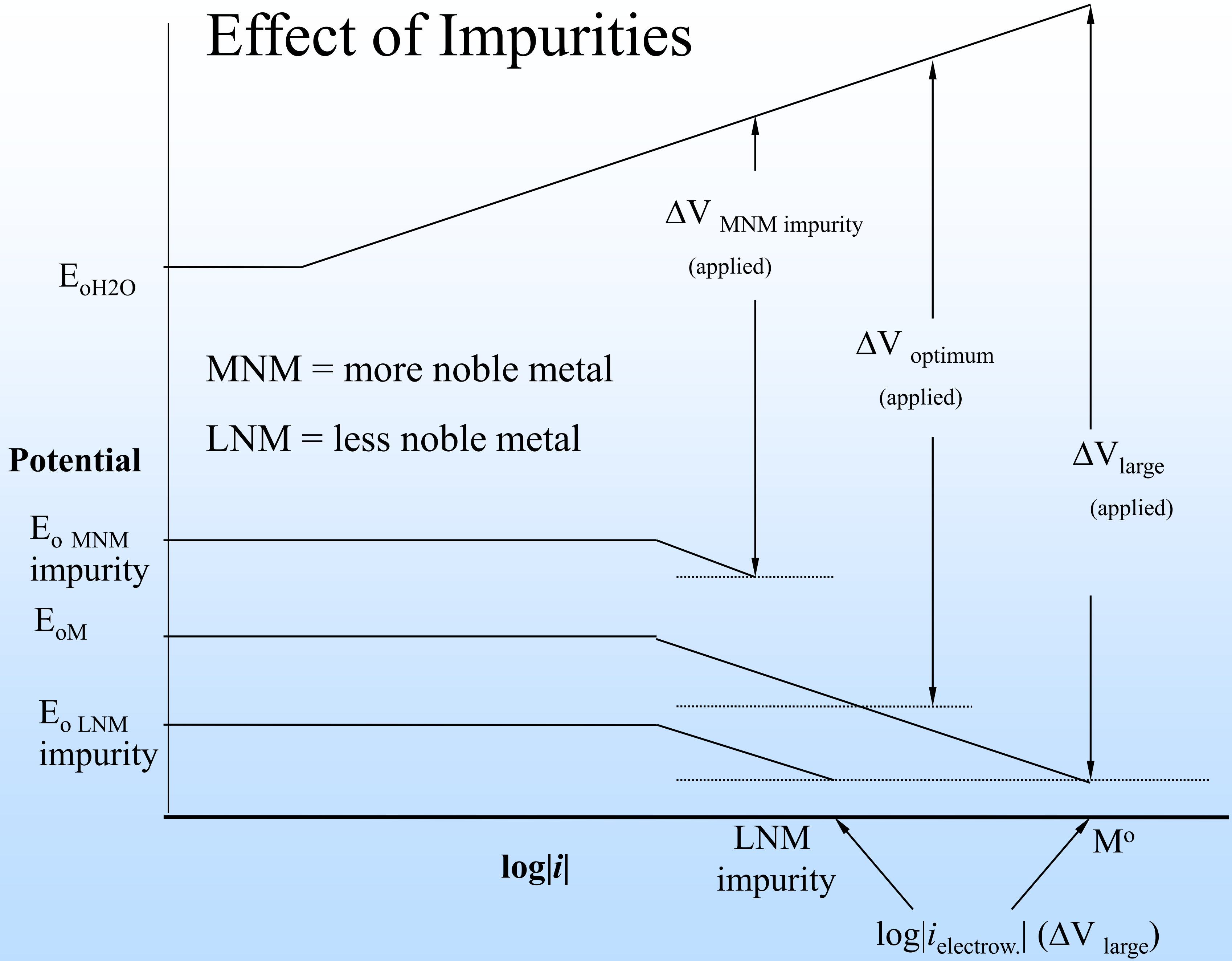
Electrorefining is the process of electrolytically dissolving a metal with impurities and redepositing the dissolved metal in a purified form at a cathode surface by applying an appropriate potential between the electrodes as shown.



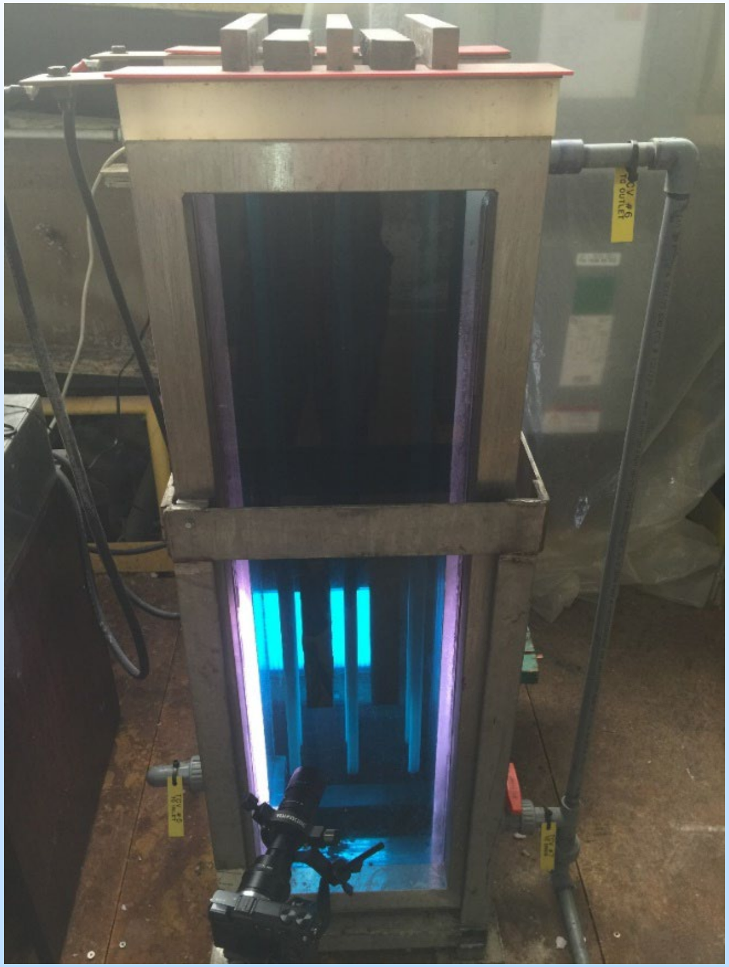
Electrorefining consumes a lot less energy than electrowinning



Effect of Impurities



Electrolytic Processing



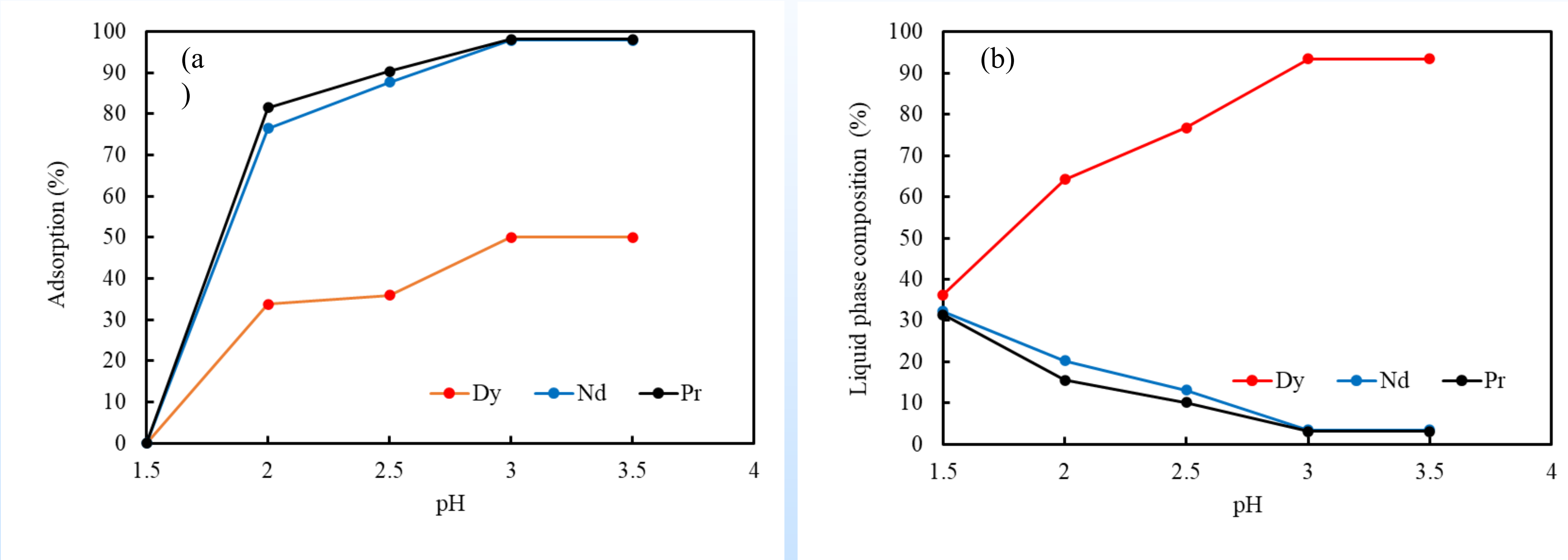
Through controlled conditions, metals can be recovered and purified through electrolysis.

Mesoporous Materials

- Nanoporous material
- Use of high surface area
- Use of organic materials
- Treated to create functional group

Name of Mesoporous material	Specific Selectivity for
Dy^{3+}-imprinted SBA-15-type mesoporous silica modified with acetyl acetone	Dy^{3+}
0IIP-HQP/SiO_2	Pr^{3+}
EDTA and DTPA functionalized chitosan	Nd^{3+}
Maleic anhydride functionalized OMS	Sm^{3+}, Eu^{3+}, and Gd^{3+}
KIT-6-1,3-PA	Ce^{3+}, Pr^{3+}, Nd^{3+}, and Sm^{3+}
KIT-6-1,2-PA	Lu^{3+}
CMK-8-DGO	Light lanthanides
Sc (III) ion-imprinted polymers	Sc^{3+}
ion-imprinted mesoporous carbon with vinylsilane	Gd^{3+}
(PAN) doped hybrid silica	Tb^{3+}

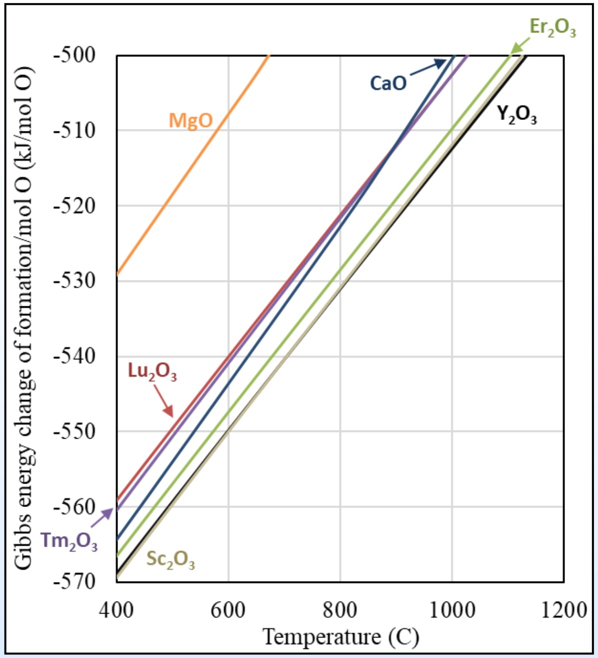
At pH 3: 50% dysprosium is separated and enriched into 93.4% composition

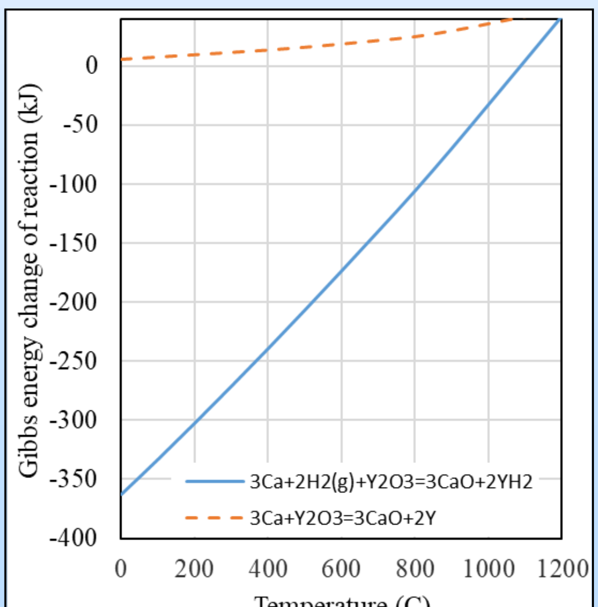


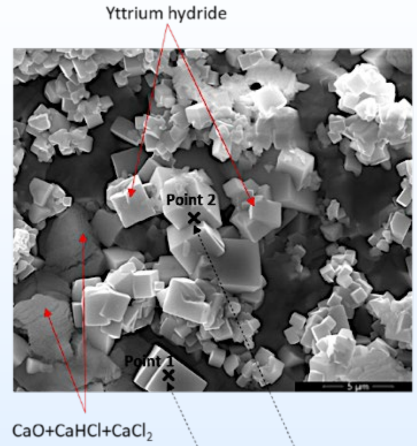
Effect of pH on (a) adsorption (%), (b) composition in the liquid phase (%).
At 23°C room temperature and 0.00625 mol/L per REEs salt.

The results show that light REEs (Nd & Pr) can be separated from heavy REEs (Dy) using mesoporous materials

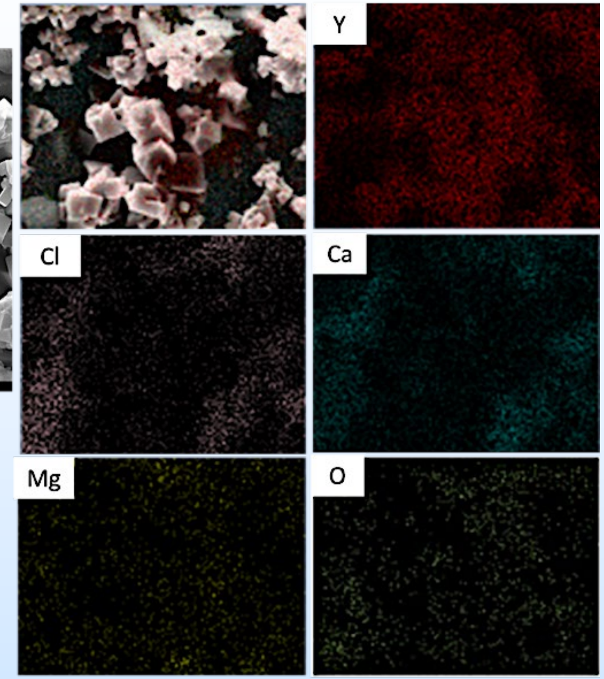
HAMR of Y_2O_3 to form Y

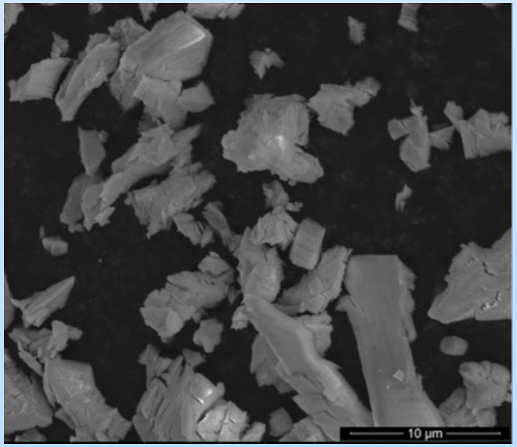






Element	Point 1 Wt.%	Point 2 Wt.%
Y	76.4	85.6
Ca	9.7	6.5
Cl	5.1	1.9
O	7.6	4.8
Mg	1.2	1.2





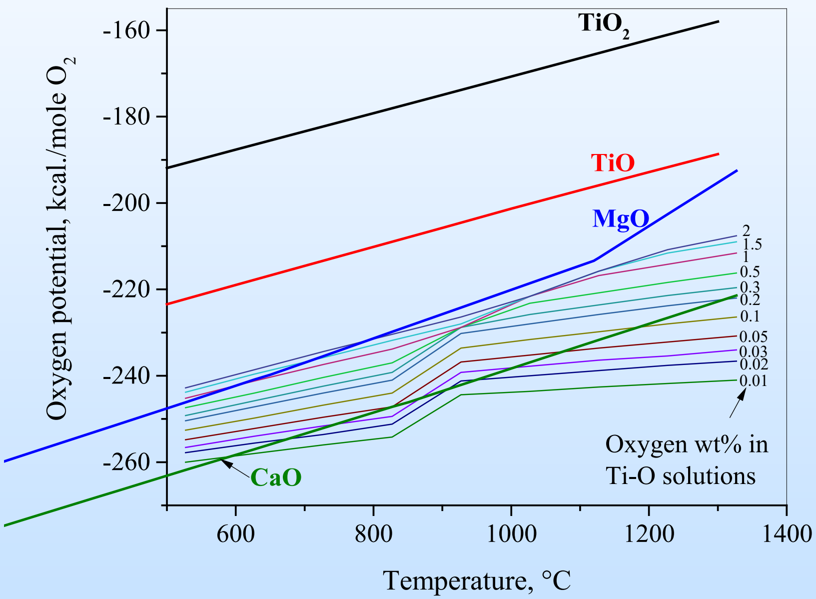
Background-HAMR of TiO_2

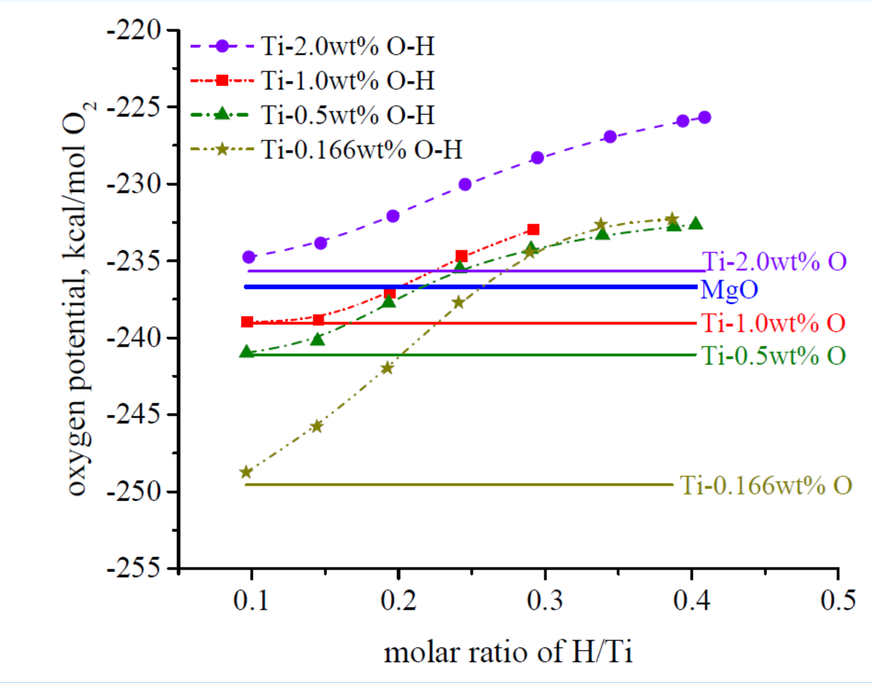
Challenges

- Mg reduction of TiO_2 is a straightforward idea and is thermodynamically feasible, however, Ti metal can contain up to 14%wt of oxygen
- Ti-O with 2%O is more stable than MgO, rendering Mg incapable of producing low oxygen Ti. Industry requires O% in Ti to be less than 0.2%

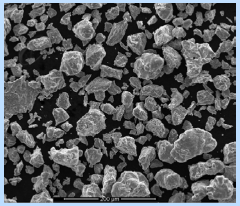
Solution: Hydrogen

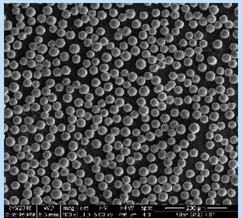
- Ti-O can absorb hydrogen and becomes Ti-O-H
- O potential of Ti-O-H is higher than that of Ti-O
- In effect, Ti-O is destabilized by H
- Enabling Mg to extract O from Ti-O until O is very low



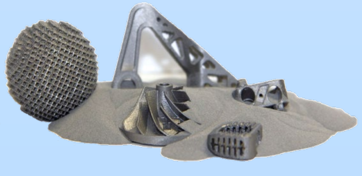


Ref.: Y. Zhang, et al. Thermodynamic Destabilization of Ti-O Solid Solution by H_2 and Deoxygenation of Ti Using Mg, ***JACS****, 2016, 138: 6916-6919.*

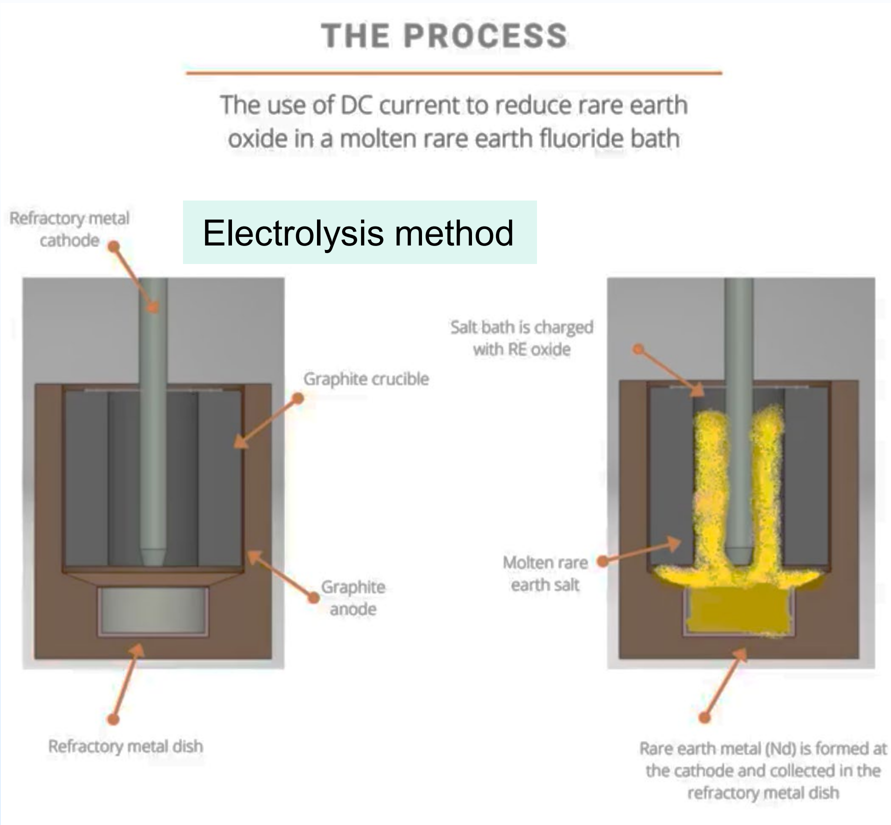




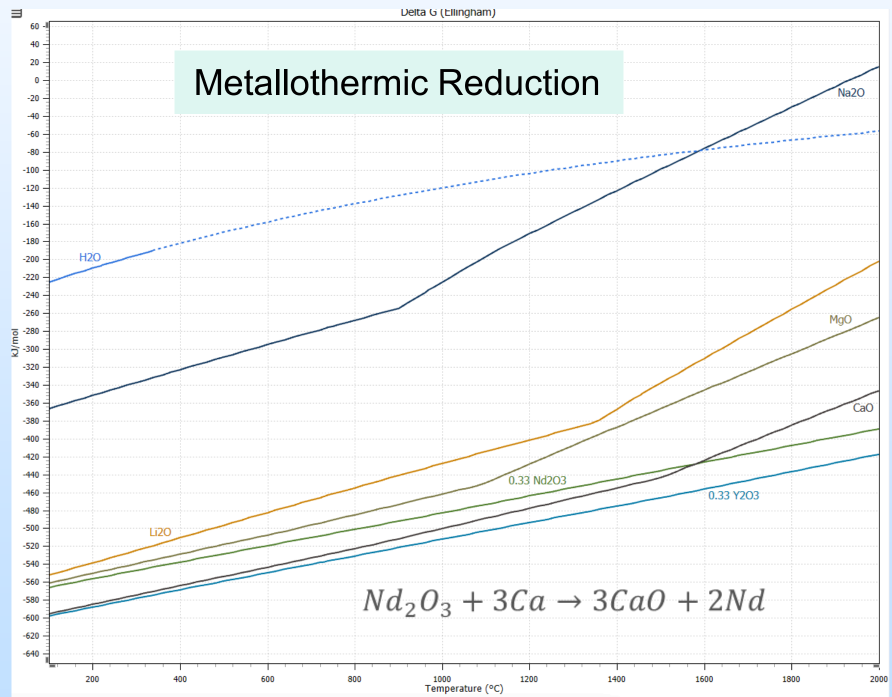
Outcomes

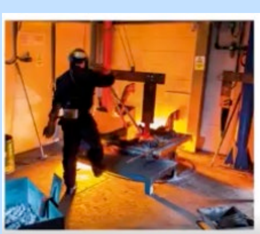


Production of Nd metal from oxide

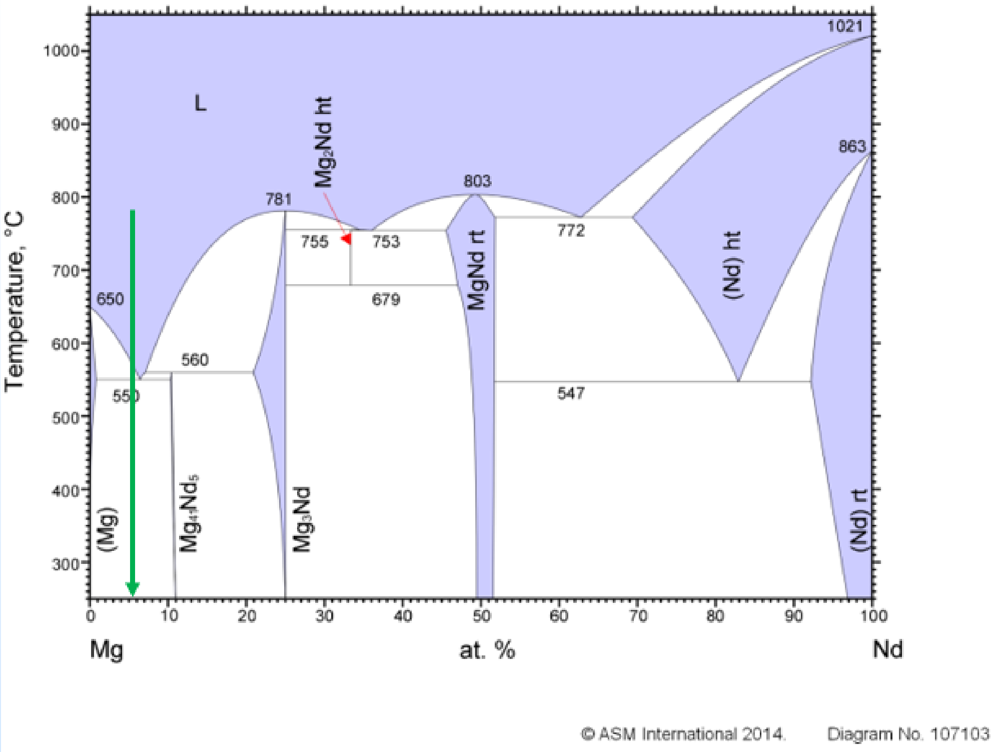


Ref.: https://www.lesscommonmetals.com/

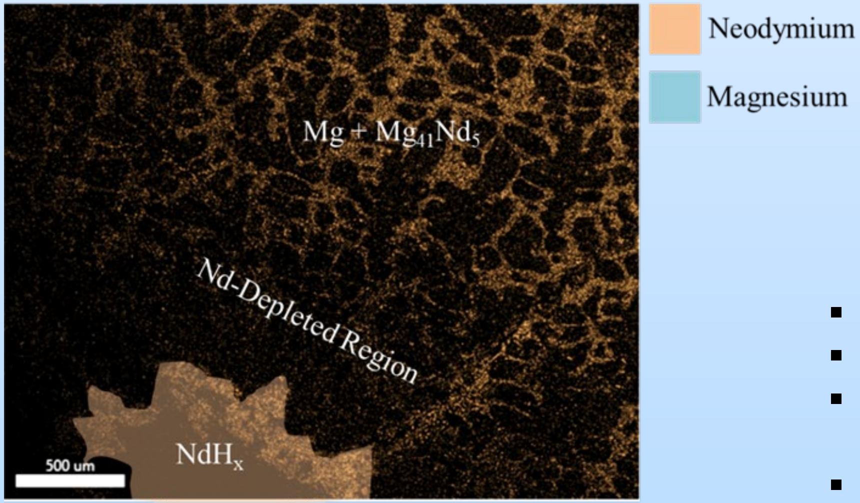




HAMR of Nd_2O_3

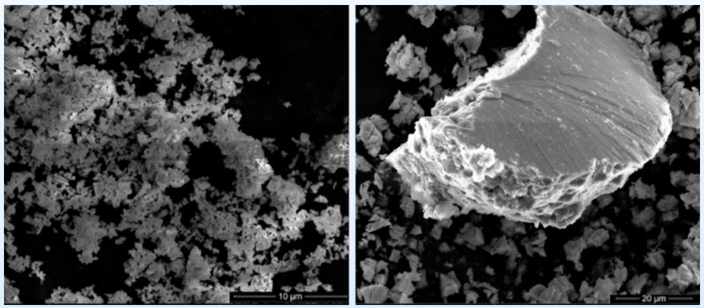


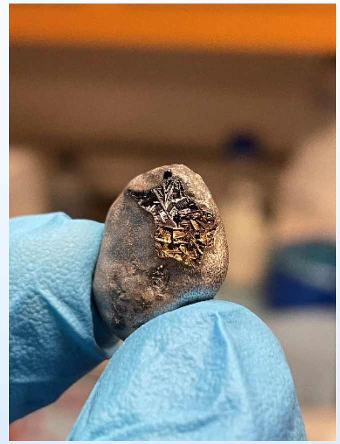
EDS element mapping of cross-section

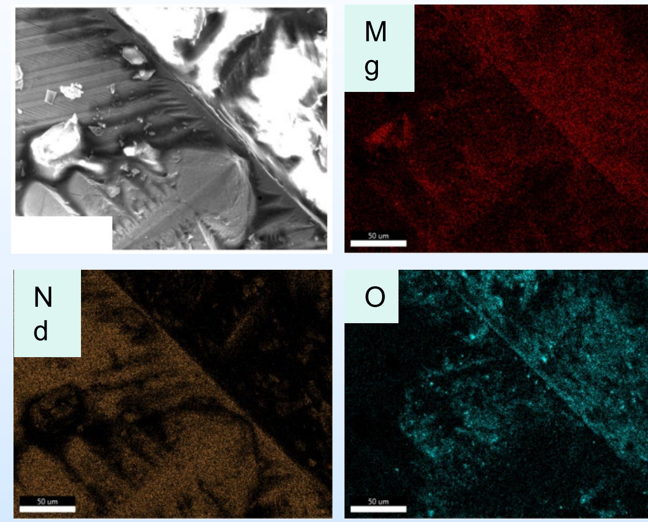


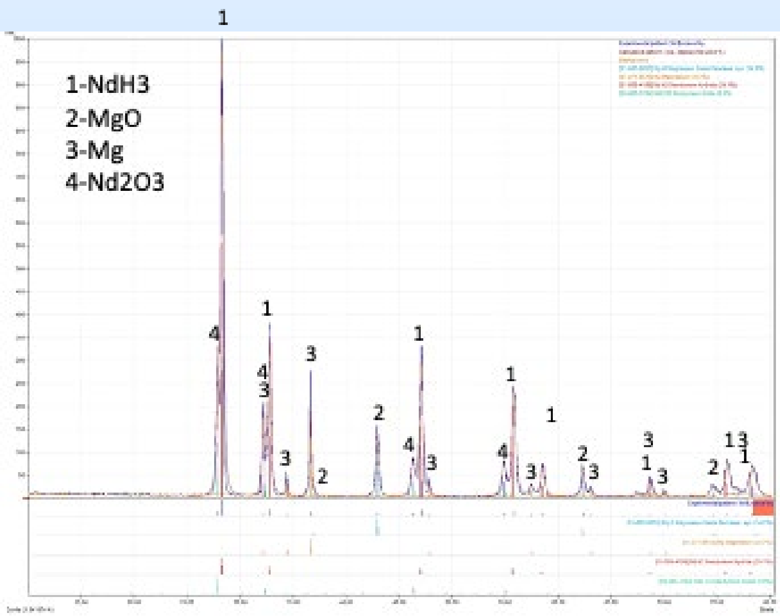
- Nd_2O_3 was reduced by Mg under hydrogen at 700-800 C
- Nd dissolved in molten Mg to form Mg-Nd alloy
- During cooling, Nd absorbed hydrogen to form Nd hydride on the top of the molten alloy
- Eutectic reaction happened at 550C

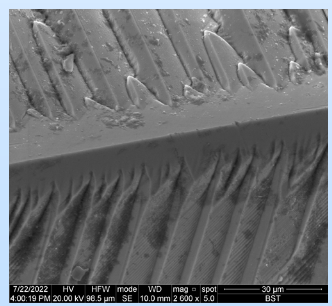
HAMR of Nd_2O_3 to form Nd











Element	Weight %	Atomic %	Net Int.	Error %
C K	5.7	36.2	187.3	7.3
O K	1.8	8.5	120.3	8.9
MgK	2.3	7.2	103.3	11.3
NdL	89.7	47.1	2497.5	1.6

Pilot Equipment

Ball Mill

Nominal Capacity: 250 lb/hr

Column Flotation Circuit

Nominal Capacity: 250 lb/hr

Pilot Equipment

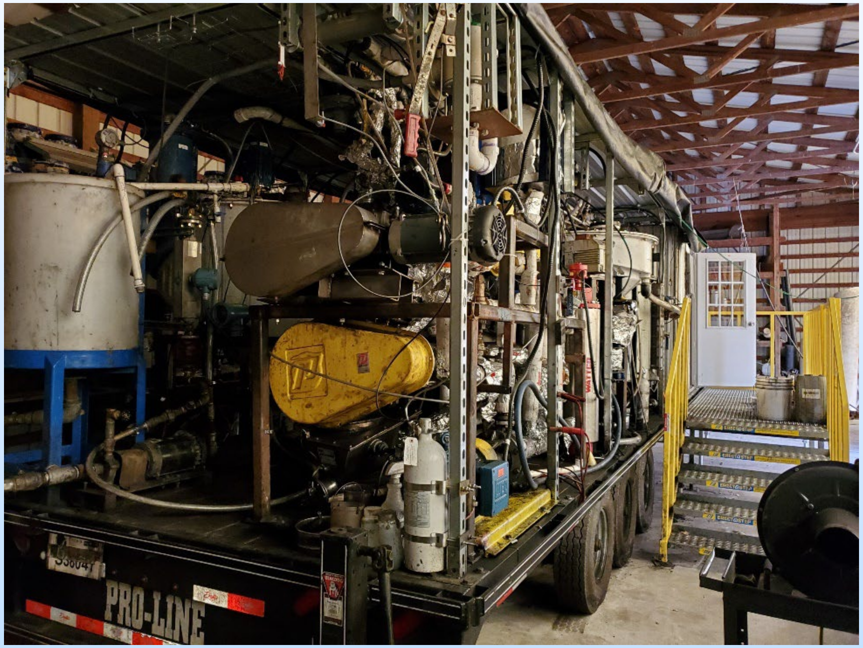
Stirred Attrition Mill

Nominal Capacity: 100 lb/hr

HHS Process

Nominal Capacity: 200 - 400 lb/hr

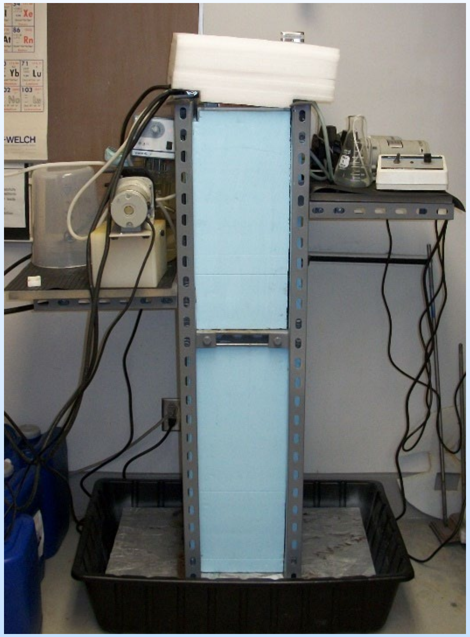
Pilot Scale Ore Concentrating (Virginia Tech)
Capable of processing 200-400 lb/hr of material



Pilot Scale Processing Units (University of Utah)

Columns (0.1-2 kg metal /hr)

HAMR Unit 0.1-2 kg metal /hr



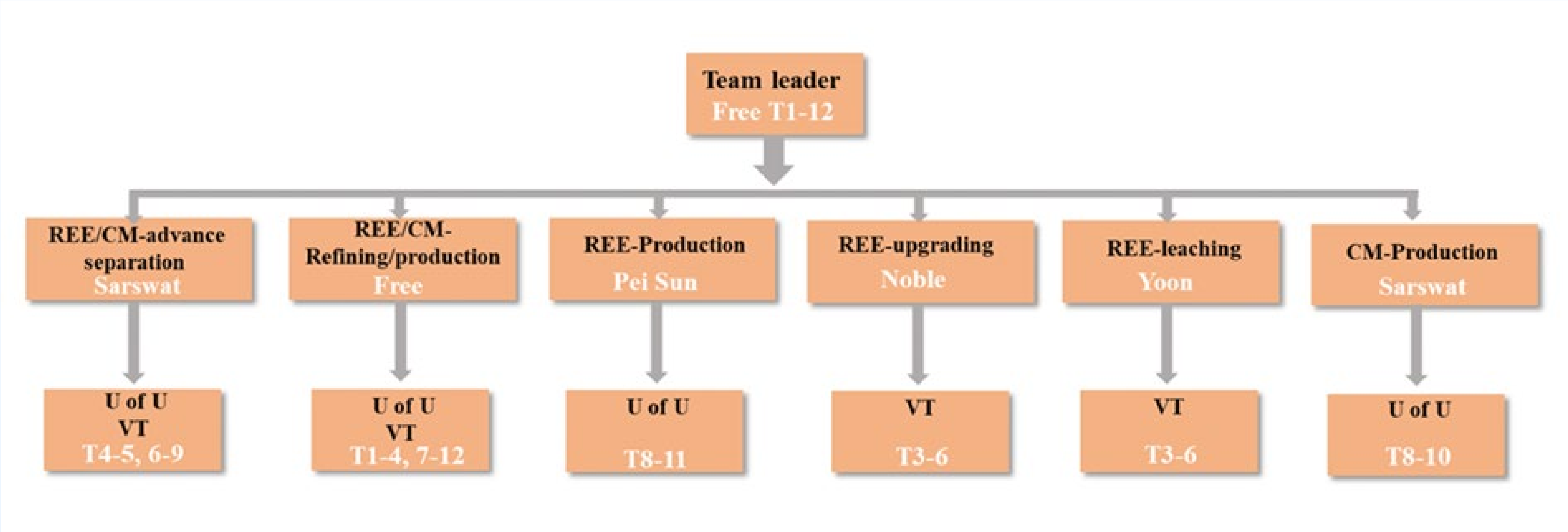
Electrowinning/refining (0.1 kg metal /hr)

Summary Slide

We have assembled a team of researchers and companies with feedstock and downstream processing capabilities at the pilot scale for rare earth element extraction, separation, and purification into appropriate product streams.

We have evaluated a variety of technologies and prepared a general concept for a flow sheet to produce 20 REE/CM products to meet DOE requirements.

Organization Chart



Task ID	Task description	Duration (month)														
		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
T1.0	*Project Management Plan*	■	■													
T1.1	*Project Management*	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
T2.0	*Development and Description of the technical and industrial partner team*	■	■	■	■	■	■	■	■	■	■	■	■	■	■	
T3.0	*Identification of project-focused REE and CM market(s)*			■	■	■	■	■								
T4.0	*Identification of critical materials used in markets/applications.*			■	■	■	■	■								
T5.0	*Evaluation and selection of coal-based resource feedstock materials*					■	■	■	■	■						
T6.0	*Assessment and Description of the extraction, separation and recovery processes*						■	■	■	■	■	■				
T6.1	*Assessment of first stage extraction processes (including literature review)*						■	■	■	■	■	■				
T6.2	*Assessment of advanced stage separation processes (including literature review)*						■	■	■	■	■	■	■	■		
T7.0	*Description of advanced concept/process ISHP REO, RES, CM production*								■	■	■	■	■	■	■	
T7.1	*Assessment of hydrogel /mesoporous materials-based separation processes*								■	■	■	■	■	■	■	
T8.0	*Description of advanced concept/process for production of REM from ISHP REO*								■	■	■	■	■	■	■	■
T9.0	*Technological Advances (description, performance capabilities, equipment etc.)*										■	■	■	■	■	■
T10.0	*Description of concept/process for production of CM*												■	■	■	■
T 11.0	*Development of a Technical Research Plan and Process Flow Diagram (PFD)*												■	■	■	■
T12.0	*Final report preparation and submission*														■	■

Gantt Chart