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VG13-060

A Low-cost Rare Earth Elements Recovery Technology

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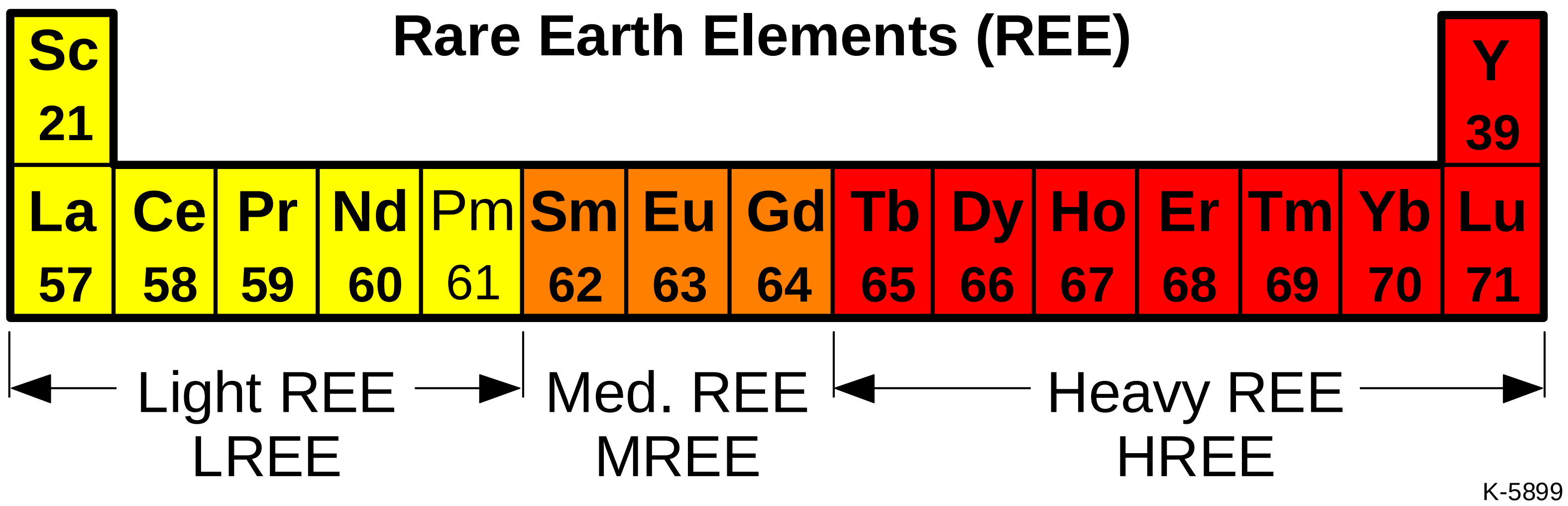
Purpose

- **Describe rationale for economical recovery of Rare Earth Elements (REE) using fly ash from U.S. coal-fired power plants**

Rare Earth Elements Nomenclature

- **Group 3 Elements: Scandium, Yttrium, and lanthanides**
- **Classified into light, medium, and heavy**



- **Similarities to actinide series; PUREX-like extraction**

Defense Applications of Rare Earth Elements

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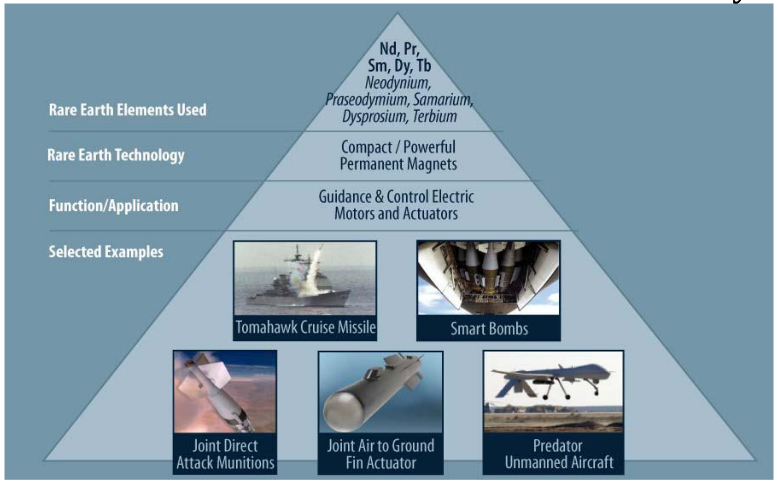
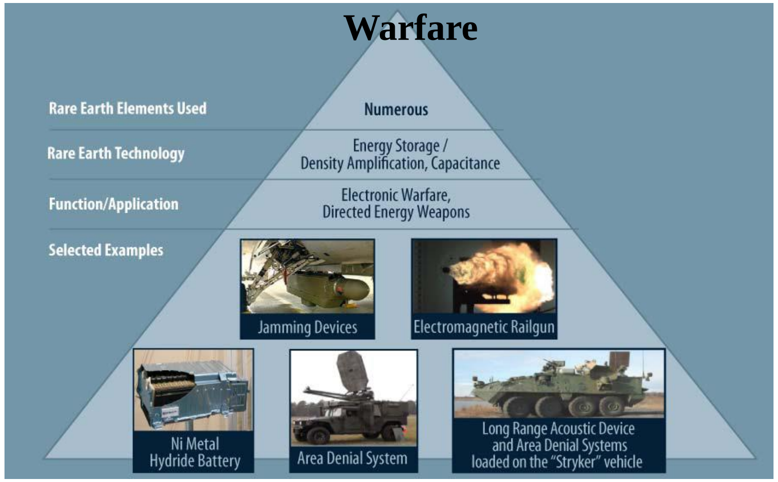
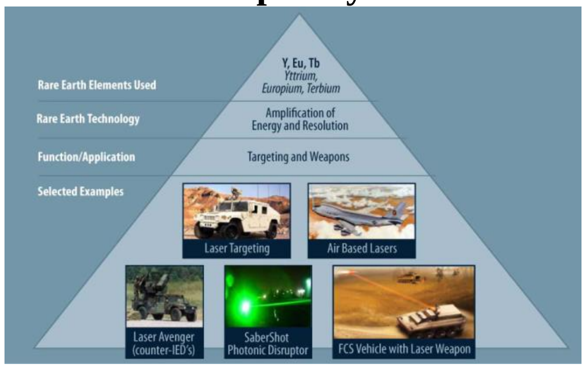
Rare Earth Elements in Guidance and Control Systems



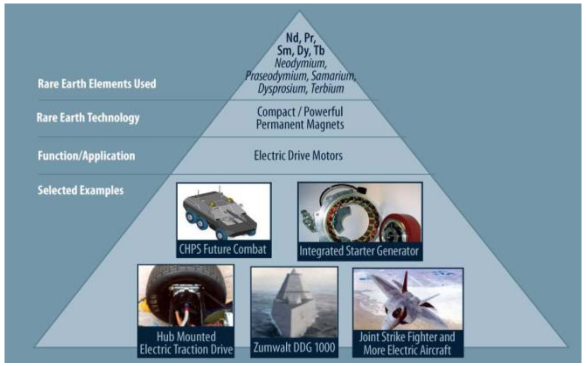
Rare Earth Elements in Defense Electronic Warfare



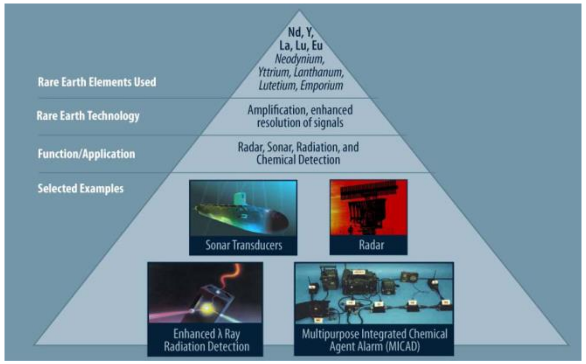
Rare Earth Elements in Targeting and Weapon Systems



Rare Earth Elements in Electric Motors



Rare Earth Elements and Communication



Source: "Rare Earth Elements in National Defense: Background, Oversight Issues, and Options for Congress", V. Grasso, Congressional Research Service, 5 September 2012

REE Applications in Clean Energy Technologies

Electric Vehicles (Nickel Metal Hydride Batteries)	La_2O_3
Wind Turbines & Disk Drives (Permanent Magnets)	Nd_2O_3, Pr_6O_{11}, Tb_2O_7, Dy_2O_3
Catalytic Converters	CeO_2
Compact fluorescent lights (CFL)	Y_2O_3, Eu_2O_3,Tb_2O_7
Flat panel displays	Eu_2O_3,Tb_2O_7, CeO_2
Magnetic Resonance Imaging Machines	Gd Compounds

Criticality of Rare Earth Elements to Clean Energy

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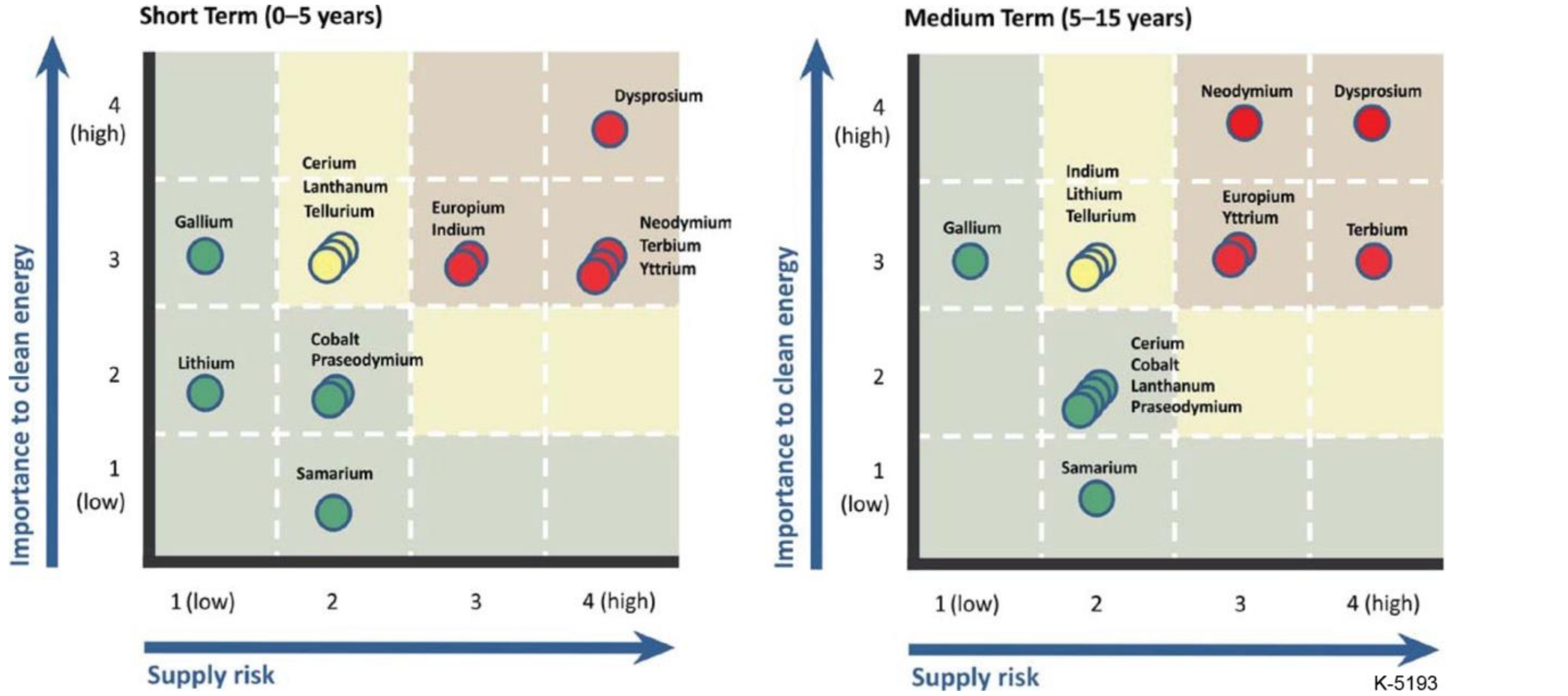
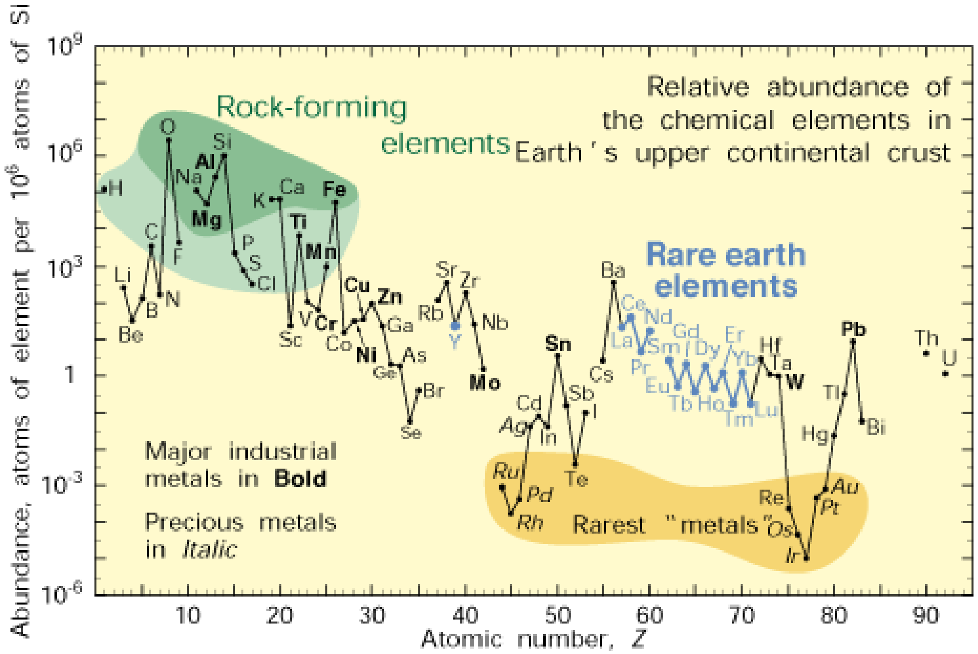


- **Criticality = Importance to Clean Energy Tech X Risk of Supply Disruption**
- **HREE - Tb, Dy, Y; MREE – Gd, Eu; and and LREE – La, Ce, Nd critical/near critical**

"Rare" Earths Are Really Not that Rare

- Relative abundance of rare earths >> precious metals
- Crustal concentration (220 ppm) is higher than that of carbon (200 ppm)



- Widely distributed in the earth's crust with some highly enriched concentration in certain minerals
- Common rare earth minerals: Bastnaesite (La, Ce, Y) , Monazite (Th, La, Ce), Xenotime (Dy, Er, Tb, Yb), Ion adsorption clays (Y, Gd, Dy)
- Bastnaesite is considered most desirable due to high LREE concentrations with relatively low thorium content

U.S. Mineral Resources Scarce in Heavy REEs

TYPE	LOCATION (S)	LIGHT				MEDIUM			HEAVY							
		Lanthanum (La)	Cerium (Ce)	Praseodymium (Pr)	Neodymium (Nd)	Samarium (Sm)	Europium (Eu)	Gadolinium (Gd)	Terbium (Tb)	Dysprosium (Dy)	Holmium (Ho)	Erbium (Er)	Thulium (Tm)	Ytterbium (Yb)	Lutetium(Lu)	Yttrium(Y)
Currently active:																
Bastnäsite	Bayan Obo, Inner Mongolia	23.0	50.0	6.2	18.5	0.8	0.2	0.7	0.1	0.1	0.0	0.0	0.0	0.0	0.0	0.0
Xenotime	Lahat, Perak, Malaysia	1.2	3.1	0.5	1.6	1.1	0.0	3.5	0.9	8.3	2.0	6.4	1.1	6.8	1.0	61.0
Ion adsorption clays	Longnan, Jiangxi Province, China	1.8	0.4	0.7	3.0	2.8	0.1	6.9	1.3	6.7	1.6	4.9	0.7	2.5	0.4	65.0
Possibly online in the next 5 years:																
Bastnäsite	Mountain Pass, California, United States	33.2	49.1	4.3	12.0	0.8	0.1	0.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1
Monazite	Mount Weld, Australia	26.0	51.0	4.0	15.0	1.8	0.4	1.0	0.1	0.2	0.1	0.2	0.0	0.1	0.0	0.0
	Eastern coast, Brazil	24.0	47.0	4.5	18.5	3.0	0.1	1.0	0.1	0.4	0.0	0.1	0.0	0.0	0.0	1.4
Fergusonite	Nechalaco, Canada	16.9	41.4	4.8	18.7	3.5	0.4	2.9	1.8	0.7	0.0	0.0	0.0	0.0	0.0	7.4

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- **Wt% data: U.S. DoE Critical Material Strategy Reports Dec. 20l0/11**

Coal Ash: A Resource with Substantial REE Content

- **Russian and US literature:**
  - ~ 1 wt% (10,000 ppm) in Russian Far East coal ash*
  - Rich in HREE

- **Fly ash: An abundant waste product from coal-fired power plants in U.S. (~ 100M t annually)**

***Seredin, V. V., "Rare earth element-bearing coals from the Russian Far East Deposits," *Int. J. Coal Geology*, 30, pp. 101-129 (1996).**

Coal Combustion Enriches REE Content in Ash by ~ X10

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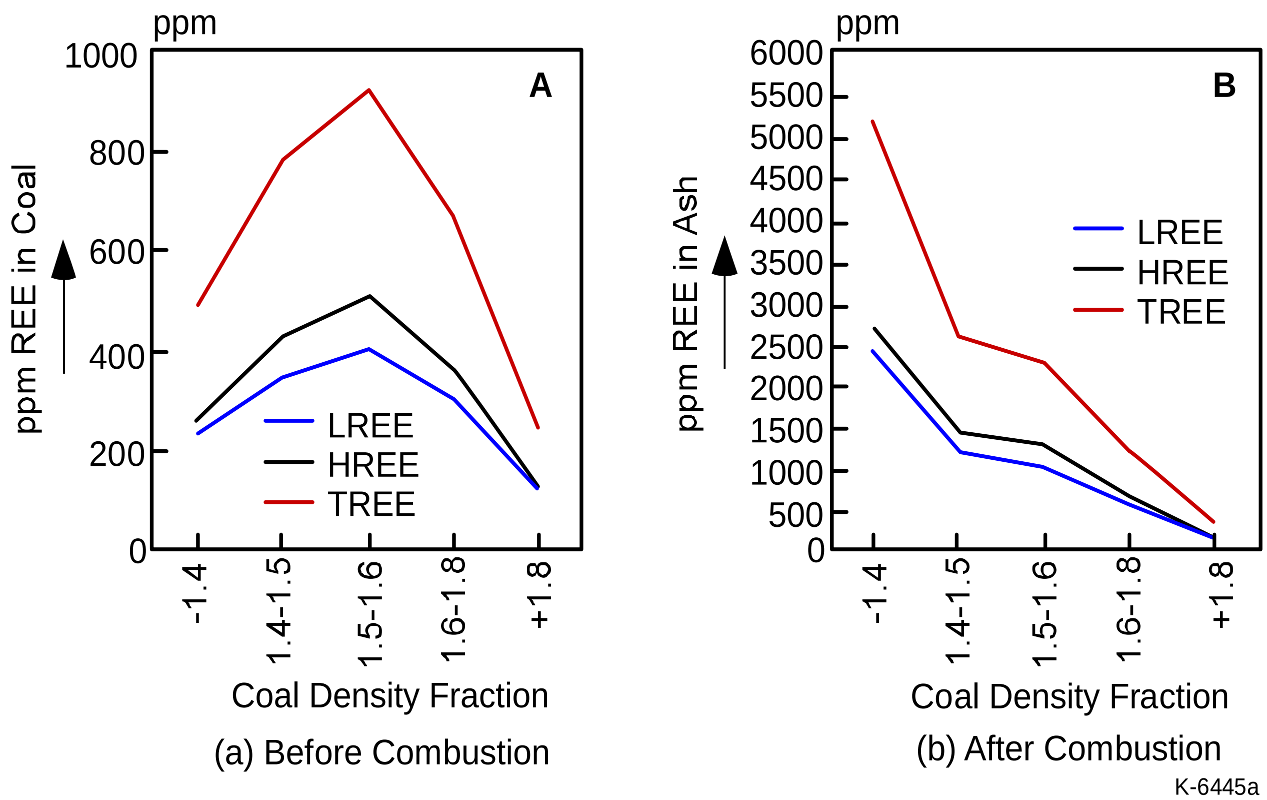
- **Example of Russian Far East Coal (Black Stone Deposit)**



- **LREE, HREE Conc. ~ 0.25 wt%**
- **LREE/HREE ~ 1**

***Seredin, V. V., "Rare earth element-bearing coals from the Russian Far East Deposits," *Int. J. Coal Geology*, 30, pp. 101-129 (1996).**

U.S. Coal Deposits with Total REE Content > 500 ppm and HREE/LREE Ratio > 10%

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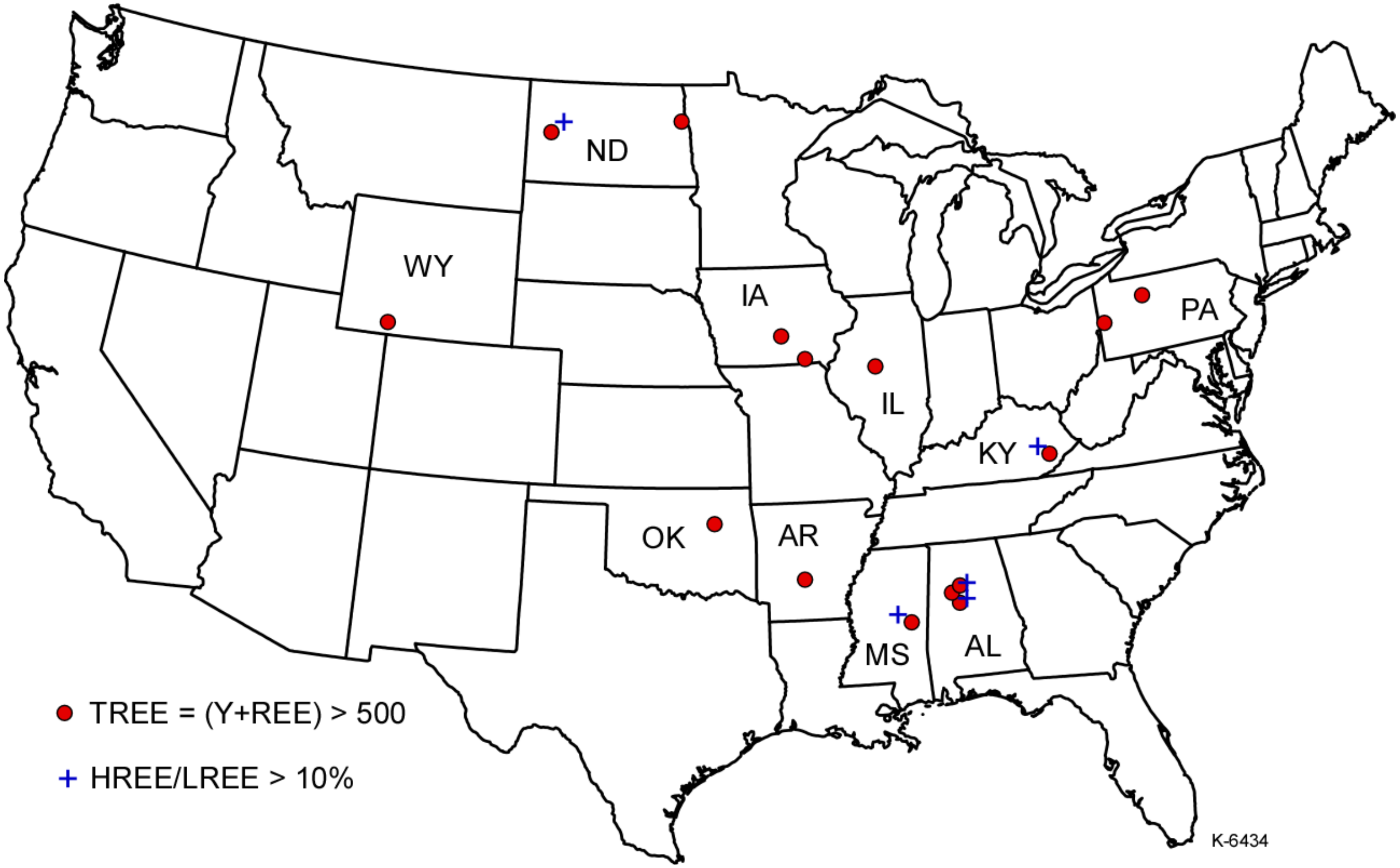

- U.S. coals from PA, WV, KY, AL and ND meet threshold

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Fire Clay Coal Deposits in Eastern Kentucky: High Total REE Content in Ash

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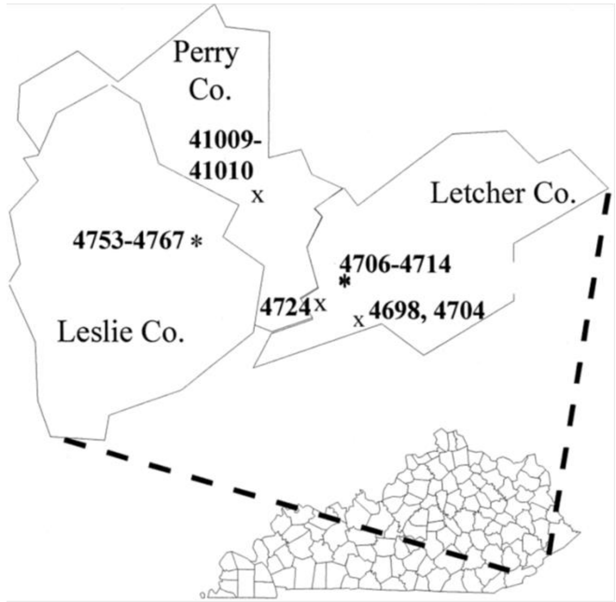
Location (County)	LREE				MREE			HREE								Y+REE	LREE	HREE	LREE/ HREE
	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Y					
Hyden East, (Leslie)	790	1500	190	660	150	13	130	22	130	25	75	11	72	430		4251	3140	765	4.10
Tilford, (Letcher)	430	820	96	350	71	6	70	10	67	13	40	6	38	330		2380	1696	504	3.36
Tilford, (Letcher)	360	740	89	340	72	7	60	9	57	10	30	4	27	160		2018	1529	297	5.16
Hazard South, (Perry)	390	770	94	350	73	6	70	10	66	13	40	6	37	280		2238	1604	452	3.55

- **TREE > 0.2 wt%, HREE/LREE > 20%**

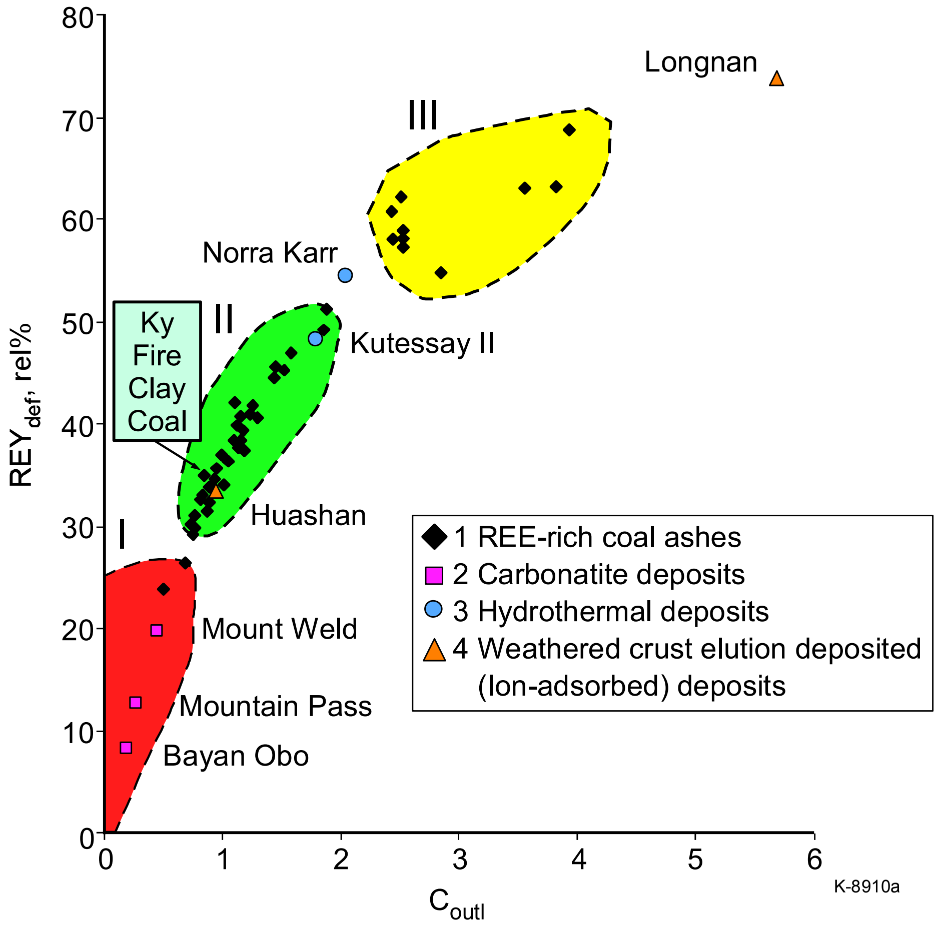


Comparative Evaluation of High-REE Content Coal Ash Relative to Traditional REE-rich Mineral Resources

- **Coal ashes are better critical REE deposits than minerals:**
  - Coal Ash: Clusters II and III including eastern KY Fire Clay coal deposits
  - Minerals: Cluster I Mountain Pass (US), Bayan Obo (PRC), and Mount Weld (Australia)

- **Outlook Coefficient:***

$$C_{outl} = ((Nd+Eu+Tb+Dy+Er+Y)/\Sigma REY)/(Ce+Ho+Tm+Yb+Lu)/\Sigma REY)$$



*Seredin, V. V., Dai, S., "Coal deposits as potential alternative sources for lanthanides and yttrium," *International Journal of Coal Geology*, 94, 67-93 (2012).

Advantages of Coal Ash Over Minerals for REE Extraction – I

- High costs and relative scarcity of REE are due to high costs of separation, concentration, and extraction from ores
- A very large fraction of the cost (~ 60%) is incurred in excavation, pulverization, and grinding of the minerals to a fine powder necessary for chemical processing
- Starting with good REE abundance in coal, the combustion of coal further concentrates the non-volatile REEs into fly ash by ~ 10X
- Fly ash is already available as fine powder (~ 100 micron scale), readily processable by chemical means, avoiding the mine-to-mill expenditures associated with mining

Advantages of Coal Ash Over Minerals for REE Extraction – II

- **Coal ash use as REE resource will significantly reduce energy use and accompanying CO_2 emission relative to conventional mining by ~ 75%**

- **PSI's REE extraction process will remove metals, including the hazardous elements arsenic, cadmium, and thorium from the coal ash, rendering it non-hazardous**
  - **A value-added co-product of commercial importance used in cement and construction materials**
  - **Beneficiation of coal ash**

- **Preprocessing prior to chemical extraction will also separate valuable commercial byproducts**

10% – 15% of Available Fly Ash Estimated to Meet U.S. REE Demand by 2020

- **REE content of ash ~ 1/40th compared to minerals**

	Catalytic Cracking	Permanent Magnets		Batteries		Compact Fluorescent Lighting	
	La + Ce	*Nd*	*Dy*	*La*	*Ce*	*Y*	*Tb*
Annual U.S. Demand (metric tons)	2200	2400	270	1560	1944	1079	73
Coal Ash Needed (metric tons)	1.30.E+06	4.80.E+06	2.87.E+06	2.71.E+06	1.74.E+06	3.66.E+06	4.56.E+06
% of Annual U.S. Coal Ash Production	1.30%	4.80%	2.87%	2.71%	1.74%	3.66%	4.56%

➢ **Estimate accounts for process yield and REE content variability**

Developments Needed:
Technological and Economic Feasibility Evaluation

- **PSI has shown feasibility of efficient REE recovery from coal ash on laboratory scale**
  - Company funded project
- **Seeking to further develop and scale up process**
  - Increase overall REE extraction efficiency
    - Identify ash with high total REE content (>1000 ppm) and high HREE/LREE ratio (>10%)
    - Enrich REE content via preprocessing
  - Separation of REE and other elements separation
  - Identify utility of byproducts and co-products
    - Environmentally beneficiated ash
    - Other elements of value
- **Model process economics, energy use and environmental impact**