High Yield and Economical Production of Rare Earth Elements from Coal Ash

Dorin V. Preda (PI), [a] Prakash B. Joshi, [a] David P. Gamliel, [a] Jeffrey Y. Yee, [a] Russell D. Lambert, [a]
James C. Hower, [b] John G. Groppo, Jr., [b] Todd Beers, [c] Mike Schrock [c]
[a] Physical Sciences Inc., [b] University of Kentucky, Center for Applied Energy Research, [c] Winner Water Services

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Program Topic:
11. RARE EARTH ELEMENTS (REE) IN FOSSIL FUEL DERIVED SOLIDS AND LIQUIDS

DOE/NETL Project Team

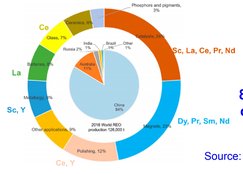
- **Physical Sciences Inc. (PSI), Andover, MA**
  - Project lead
  - Rare earths recovery technology development (micropilot)
  - Techno-economic modeling
- **University of KY/Center for Applied Energy Research (CAER), Lexington, KY**
  - Coal/coal ash surveys and physico-chemical characterization
  - Coal ash selection for REE recovery processes
  - Physical processing plant design and pilot development
  - Produce selected ash fraction for chemical processing
- **Winner Water Services (WWS), Sharon, PA**
  - REE recovery chemical plant design and pilot development
  - Process selected ash fraction from physical processing
  - Technology transition and commercialization

Rare Earth Elements (REEs)

- **Group 3B Elements (Scandium, Yttrium) and lanthanides**
- **Classified into light (LREE), medium, and heavy (HREE)**

Sc	Rare Earth Elements (REE)													Y
21														39
La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
57	58	59	60	61	62	63	64	65	66	67	68	69	70	71

Light REE LREE — Med. REE MREE — Heavy REE HREE



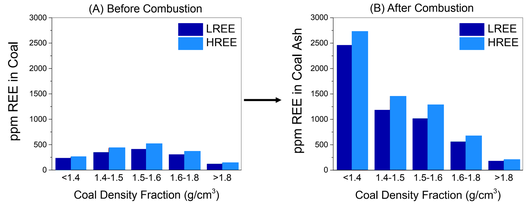
REEs are used in a variety of applications, 84% of U.S. REEs come from China

Source: Zhou et al., Minerals, 2017

Coal Combustion Enriches REE Content in Ash by ~ X10

- **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 tons annually)**

Example of Russian Far East Coal (Black Stone Deposit)



- **Coal Ash LREE + HREE Concentration = ~ 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%

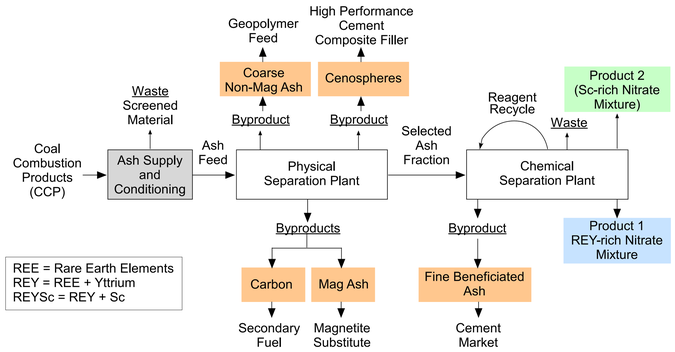
- **U.S. coals from PA, WV, KY, AL and ND meet threshold**

- **TREE = (Y+REE) > 500**
- **HREE/LREE > 10%**

Source: USGS COALQUAL Database

Outline REE Extraction Process

- **Physical separation stage, followed by a chemical separation stage, followed by a post-processing stage**
- **Proposed Product:** **REYSc-enriched mixture (dry concentrate)**
- **Higher Value Products: REY-rich & Scandium-rich concentrates**
- **By-products: Cement substitute, cenospheres, secondary fuel carbon**



PSI has successfully developed and optimized processes; Pilot plant development in progress

Overall Goals of DOE Project

- **Develop and demonstrate a pilot scale plant to economically produce salable rare earth element-rich concentrates from coal ash feedstock**
  - Includes yttrium, scandium, and commercially viable co-products
  - Environmentally safe and high-yield physical and chemical enrichment processes
- **Project Metrics**

Performance Parameter	Threshold Value	Objective Value
Feedstock REYSc[¶] Content	>300 ppm (Whole Mass Basis)	>500 ppm (Whole Mass Basis)
Total REYSc Enrichment in Final Concentrate	>10 wt% (Elemental Basis)	>20 wt% (Elemental Basis)
Return on Investment[*]	<7 y	<5 y
Delivered Concentrate Quantity[&]	~50 g[$]	~0.5 kg[$$]

REYSc = Rare Earth Elements Plus Yttrium and Scandium, *Scale-dependent ~ 600 tpd, &Ten 5g split samples, 5g split sample required per solicitation.

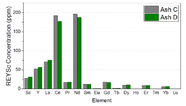
Ash Source Selection

- **Ash from Eastern KY coal selected for project developments**
- **The average REYSc content of 556 ppm measured by ICP-OES/MS from a composite of 20 ash samples > 300 ppm (DOE requirement)**
- **Example:**

Sample	Sc	Y	ΣREE	ΣREY	LREE/HREE
Composite	33 ppm	59 ppm	457 ppm	516 ppm	7.46

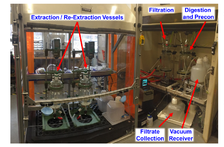
CAER Physical Processing Pilot Plant

- **CAER physical pilot plant operational and ~8 tons of coal ash processed to date; >50% yield for ash mass fraction for chemical processing**

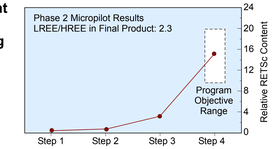


- **Significant content of Nd (~180 ppm), Y (~50 ppm), and Sc (~25 ppm) Reasonable (~10 ppm) content of Pr, Gd, Dy**

PSI Micropilot Facility



- **PSI Micropilot facility operational & has demonstrated target yield and enrichment performance requirements. Currently being used for validating/troubleshooting chemical pilot processes.**
- **REYSc concentration sequentially increased as material moves through chemical processing**



Total REYSc relative content in final micropilot concentrate is >10 wt.%, meeting threshold program objective.

- **Developed chemical processes for the selected ash fraction to recover REYSc with high yield and high enrichment in two final concentrate products of commercial value.**
  - Concentration expressed on elemental basis i.e. the content of REY or Sc relative to that of all elements)

Product 1: REY-rich concentrate:
- REY Yield > 10.5%, REY Concentration > 15 wt%
- Sc Yield ~ 5%, REY:Sc 100:1
- LREE:HREE ratio = 2.3:1
- REY concentration >> threshold target (10 wt%)

Product 2: Sc-rich concentrate:
- REY Yield > 0.5%
- Sc Yield ~ 10%, REY:Sc 6:1

Process improves LREE:HREE Ratio by 2X in Product 1
Starting Coal Ash LREE:HREE Ratio = 5:1

Pozzolanicity Testing – Strength Activity Index

Post-digestion fine ash is a significant source of commercial revenue as cement substitute, the current traditional use of fly ash

Testing performed at CAER Cement Lab Per ASTM C-618 Procedures

- **Strength Activity Index or SI:** **how the coal ash contributes to the strength of concrete.**
- **Typically measured as the compressive strength of a standard mortar mix with fly ash substituting at a defined level for Portland cement after a defined period of curing (Blue Line).**
- **SI is then compared as a ratio percent to a mortar with all Portland cement (Green Line).**
- **ASTM-C618 SI criterion is 75% at 7 days or 28 days (Red line).**

WWS Chemical Processing Pilot Plant

- **Detailed design completed March 2019**
- **Plant assembly started May 2019**
- **Start up operations ongoing**

Deliverable REE Concentrate Production To begin ~ October 2019

Process Economics

- **Plant Size: 1200 tpd ash physical processing/600 tpd chemical processing plant**
- **Plant Attributes:**
  - Co-located at ash source to significantly reduce transportation costs; Decoupled operations
  - Modular designs for operational flexibility and transportability
- **Ash fractions shipped to local markets**
  - Carbon, magnetic ash, > 200 mesh non-magnetic ash
- **Annual production of major REE salts, Sc salt, and byproducts:**

Component	Quantity Produced* tons/year	Portion of Revenue (%) 2018 REE Pricing	Portion of Revenue (%) 2011 REE Pricing	Worldwide Market tons/year	Market Application
REEs	38.2	1.0	10.8	170K	Batteries, Magnets, Alloys, Catalysts
Scandium	5.6[¶]	26.1	35.0	10-15	Alloys, Catalysts
Carbon	96K	6.2	4.6		Low-grade Fuel
Magnetic	20K	5.4	4.0		Magnetite Substitute
Non-Magnetic >200 Mesh	40K	1.0	0.8		Geopolymer Feed
Non-Magnetic <200 Mesh	186K	23.9	17.8	71.8M	Cement Substitute (Pozzolan)
Cenosphere Product	2K	36.4	27.1	~51K	High Performance Concrete Additive /Advanced Composites

[¶]Sc_2O_3 market demand expected to reach 25,000 kg by 2023 (Mordor Intelligence, April 2018)

Payback period 4-8 years dependent on REYSc prices

- **Non-REE products significantly offset effects of REYSc commodity price fluctuations**
  - Pricing of non-REYSc products varies with general economic conditions

Conclusions

- **US fly ash is a suitable source for economical recovery of rare earth elements, particularly, heavy rare earth elements**
- **Demonstrated operational pilot plant (0.4 tpd) for physical separation processes**
  - Optimized processes to produce selected ash fraction as feedstock for the chemical processing
  - Valuable by-products: cement substitute, cenospheres, secondary fuel carbon
- **Pilot plant for chemical processing (0.5 tpd) under start-up**
  - Optimized processes validated in micropilot plant operations
  - REYSc concentrates as main products
  - Beneficiated ash as valuable by-product
- **Commercially viable processes demonstrated by techno-economic analysis**
  - Currently AACE Class 2/3

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