# Characterization and Recovery of Rare Earths from Coal and By-Products

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## Rare Earth Element Challenges

- Roughly 87% of REEs came from China in 2014
- Potential national security and supply risk for critical rare earths for defense and clean energy
  - Y, Nd, Eu, Dy, Tb
- Not typically found in concentrated ores
- Difficult to extract and separate
- REs are not distributed evenly
  - Causes excess supply for some REs and shortages for other REs



## REE Extraction Opportunities for Coal and Coal By-Products

- Everything in the earth's crust, good and bad, is found to some extent in coal and coal by-products
- The US burns almost 1 Billion tons of coal a year
  - Producing 100-150 million tons of coal ash with an average concentration of ~470ppm REE+Y
  - Coal ash produced yearly based on average concentrations contains ~47,000-70,500 tons of REE+Y or 2 - 4 times the US consumption
  - Coal mining and coal prep by-products could provide additional opportunities for REE extraction and recovery.
  - Other critical or valuable elements could also be extracted from coal and coal by-products during the extraction of REEs
  - Extraction of REEs from coal and coal by-products could provide a stable source of REEs and other critical metals
  - Extraction of REEs could also be environmentally friendly by utilizing already mined materials and potentially treating and utilizing by-product materials

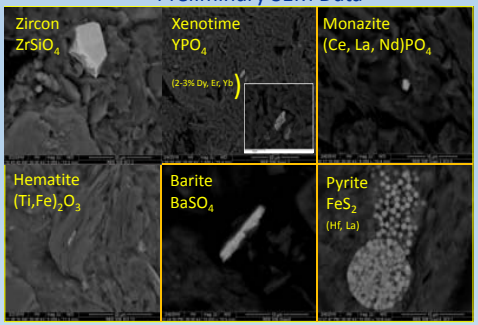
## Field Sampling Effort

- Identification of Promising By-Products for Rare Earths
- Rare Earth Archive houses approximately 1,000 samples
- 470 samples collected since June 30, 2015 (nearly all solids, a few aqueous)
- 164 sample analyses uploaded onto EDX website March 2016
- Promising Materials identified with over 500 ppm RE+Y on dry whole basis
- Geochemistry
- Marker Elements and Element Associations

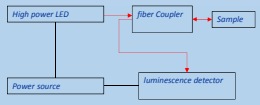
## Characterization Effort

- Over 1,000 assays – bulk elemental analyses
- Approximately 40 SEM-EDX, 40 XRD
- ICP-MS – best in class - digestion, uncertainty, publications
- ICP-OES – bulk multi-elemental analysis (supplementary)
- C, H, N, S, Ash, and Moisture
- SEM-EDX – identified phosphates in by-products, possible Ca-association in ash
- XRD – determine minerology of the sample
- LA-ICP-MS – Spot and Depth Analyses; State-of-the-Art Mass Spectrometer to Resolve Overlapping Peaks
- Ion Exchange Capacities and pH – novel technique developed
- Stanford Synchrotron – several awards of beam time – identified sulfates, oxides, phosphates in ash – now focusing on mine by-products
- Sequential Extractions – current – form of RE in coal and by-products
- LIBS: Laser Induced Breakdown Spectroscopy
- Sensitized Fluorescence
- Portable XRF
- Gamma Detection

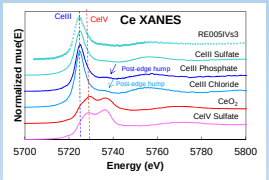
Preliminary SEM Data




Sensitized Fluorescence Sensor Diagram




XANES and Synchrotron

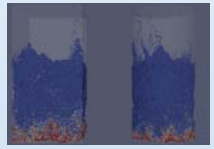



## Separations

Mineral Processing and Physical Beneficiation

- Density Float-Sink
- Magnetic
- Size
- Froth Flotation – Shakedown and commercial interest
- Bench/Pilot Scale Process Design

- Ammonium Sulfate
- Deep Eutectic Solvents/Ionic Liquids
- Acid dissolution
- High Temperature Phase Separations
- REE Selective Sorbents – Aqueous Feeds
- Photophoresis
- In-situ $CO_2$ Brine injection and extraction
- Reactive Grinding



## Modeling

Extraction of REEs from clays and other coal and coal by-products

- CFD Modeling
- Mass/Heat Transfer
- Kinetic/Reaction Modeling
- Modeling Physio-Chemical properties and REE Extraction Simulations

## Tech Transfer

- 21 presentations to date
- At least 10 presentation at upcoming meetings
- 7 publications
- Several ROI
- MOUs for Sample Acquisitions
- Possible CRADA for Lab Froth Flotation
- Sessions Organized on Rare Earths at International Conferences

## Conclusions and Future Work

Much of the recent research on coal utilization in the United States has focused upon the capture of pollutants such as acid gases, particulates, and mercury, and the greenhouse gas carbon dioxide. The possible recovery of rare earth elements from abundant coal and byproducts is an exciting new research area, representing a dramatic paradigm shift for coal. Additional data is needed on the rare earth contents of coals and byproducts in order to determine the most promising potential feed materials for extraction processes. Future work will likely focus on the characterization of coals and byproducts, as well as separation methods for rare earth recovery.