R&IC Rare Earth Overview

Sampling, Characterization & Recovery of Rare Earths from Coal By-Products

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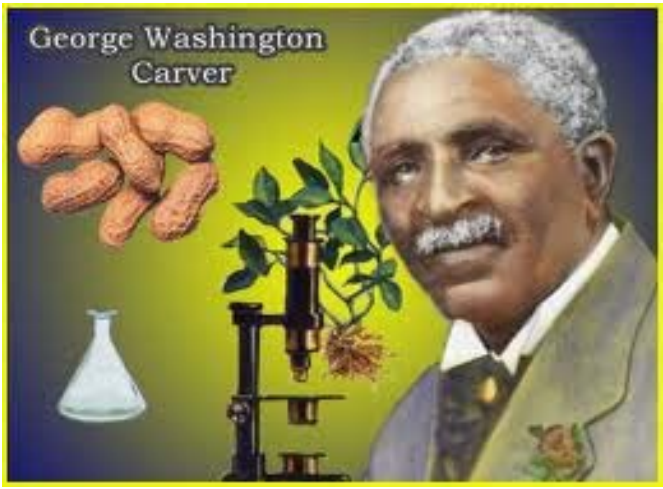
Coal – A Precious Domestic Resource

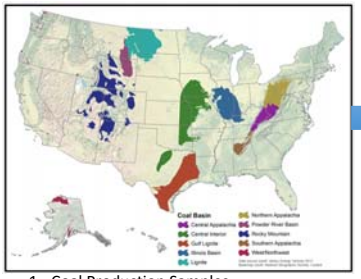
- **Typically Mine One Billion Tons/Year (738 MM tons in 2016)**
- **275 Year Supply**
- **90% Burned in United States to Make Electricity (Power, Mining, Rail)**
- **Rest – Steel, Activated Carbon, Chemicals**
- **We Can Do So Much More With Coal & By-Products**
- **Inspiration**



Integrated Field Sampling, Characterization, Separations, & Modeling

NATIONAL ENERGY TECHNOLOGY LABORATORY

U.S. Coal Basins



1. Coal Production Samples
2. Coal Processing Samples
3. Coal Utilization Samples

Screen Field Samples

Portable XRF
Sensitized Fluorescence – sensor development
Portable LIBS
Well Logs
Gamma Detection
Magnetic Detection
Database Interpretation (USGS CoalQual), EDX
Literature Review
Geochemistry interpretation

Collect Field Samples >300ppm REE+Y

Collectors and Agreements
LTI, DOE, NETL, EPRI, USGS, and Individual Coal Industry Companies

Characterization

Elemental Concentrations
ICP-MS, ICP-OES, CHNS, TGA

Mineralogy and Mineral Size
SEM/EDS, XRD, Advanced Microscopy, etc

REE Associations (Minerals and Elements)
Sequential Extraction
Laser Ablation ICP-MS
SEM/EDS, XRD, Advanced Microscopy
ICP-MS, ICP-OES, CHNS, TGA

Techno Economic Analysis (TEA)

Separations: Chemical/Thermal

2Wt% REE+Y Solid

Sorbents

Polymer fibers/sorbents
Amines on organic and inorganic supports

Clays intercalated with organics
Ionic Exchange Resins

Inorganic Clays

REE+Y Solution (Chemical Separations or Field Samples)

Thermal Energy
Melt, Precipitation, Roasting

Photophoretic Separation

Sequential Extraction

Ion Exchangeability Tests
(Ammonium Sulfate/Chloride)

Novel Solvents (Deep Eutectic and Ionic Liquids, etc)

Alkaline/Acid Leaching, Reactive Ball Milling, Microwave, Ultrasound

Solid Product REE 4,000 – 20,000ppm

Integrate Modeling Techniques with Separation Projects

Separations: Physical Beneficiation

Ultrasiever

Flotation Column

Organic/Coal Flotation

Size Separation/Sieving (wet or dry)

Density Separation (Heavy Liquid, Cross-flow Separator, etc)

Electrostatic

Magnetic Separation

REE Froth Flotation

Mini Lab Crusher

Hammermill

Crushing/Coarse Grinding

Fine Grinding

Lab Attrition Mill
Union Processing Mill

Sample Divider

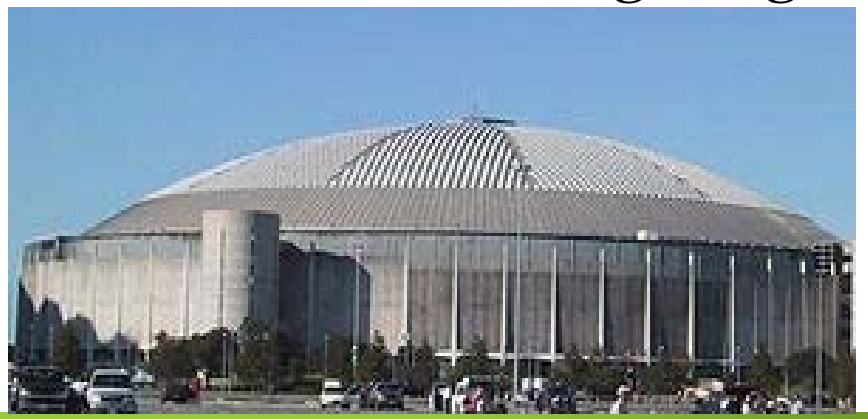
Rare Earth Element Challenges

- **Approximately 90% of REEs come from China**
- **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**
- **Modest Concentrations in Coal and By-Products**
- **Difficult to extract and separate**
- **REs are not distributed evenly**
  - Causes excess supply for some REs and shortages for other REs
  - Price significantly different for individual REs

Rare Earth Element Challenges

The Modest Concentrations in By-Products

- Imagine the Houston Astrodome
- Holding 30 Billion Ping Pong Balls Representing Fly Ash (470 ppm RE+Y)
- Remove Many of 14 Million Different Colored Rare Earth Ping Pong Balls
- Can We Do This?
- Yes



Coal – Precious Domestic Resource

Opportunity

- 275 billion tons – Resource
- Typical REE Concentration of 62 ppm
- $275*10^{9}$ tons coal * ($62*10^{-6}$ parts REE/coal) = 17 million tons REE in US coal
- US consumes around 16 – 17 thousand tons REE annually
- **Over 1,000 year supply of REEs in US Coal at Current Rate of Consumption**

Coal By-Products - Opportunities

- Everything in the earth's crust, good and bad, is found to some extent in coal and coal by-products

- The US typically produces 1 billion tons of coal a year (1990-2014)
  - 100-150 million tons of coal ash/year with concentration of ~470 ppm REE+Y
  - Coal ash produced yearly based on average concentrations contains ~47,000-70,500 tons of REE+Y or 2.8 - 4 times the US consumption
  - Coal mining and coal prep by-products provide additional opportunities
  - Other critical or valuable elements could also be extracted
  - Provide a stable source of REEs and other critical metals
  - Extraction of REEs can be environmentally friendly by utilizing already mined materials and potentially treating and utilizing by-product materials

Field Sampling

- Identification of Promising By-Products for Rare Earths
- Rare Earth Archive houses over 1,000 samples
- 768 samples collected since June 30, 2015 (nearly all solids, a few aqueous)
- 258 sample analyses uploaded onto EDX website
- Promising Materials identified with over 500 ppm RE+Y on dry whole basis (more than 27)
- Geochemistry – origins and mobilization mechanisms
- Marker Elements (such as Th) and Element Associations

Characterization

- Over 1,000 assays – bulk elemental analyses
- More than 100 SEM-EDX, 200 XRD analyses
- 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; No Digestion
- Ion Exchange Capacities and pH – novel technique developed
- Stanford Synchrotron – several awards of beam time – identified sulfates, oxides, phosphates in ash – now examining 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, SHRIMP-RG

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 – Over 90% recovery
- High Temperature Phase Separations - 100% Recoveries as Monazite
- REE Selective Sorbents – 100% Capture
- Photophoresis – Novel Particle Separation
- Reactive Grinding

Modeling

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

- CFD Modeling
- Mass/Heat Transfer
- Kinetic/Reaction Modeling
- REE Extraction Simulations

Techno-Economic Modeling

- Various Separation and Sampling Techniques

Recent Highlights: Sampling

- Identification of promising coal by-products for rare earths
- Unique rare earth archive houses over 1,000 samples
- 768 samples collected since June 30, 2015 (nearly all solids, a few aqueous)
- All samples analyzed (ICP-MS) for rare earths and many other elements
- 258 sample analyses uploaded onto EDX website
- Promising materials (≥ 27) identified with over 500 ppm RE+Y on dry whole basis

Geochemistry

- Marker elements (Th, Y) identified using portable x-ray fluorescence (XRF)
- Element Associations; Geological Origins; & Geomobilizations Identified
- 2 Memorandums of Agreement (MOAs) for sampling (United States Geological Survey (USGS), Electric Power Research Institute (EPRI), others pending) and collaborations

Recent Highlights: Characterizations

- Development of digestion methods for accurate determination of trace REE contents by inductively coupled plasma mass spectrometry (ICP-MS) – minimize uncertainty in trace RE determinations.
- Use of geologic interpretation and elemental characterization results to identify geochemical markers that may assist in identifying high REE zones.
- Distribution and speciation of Ce in coal combustion by-products, rock materials, and clays was determined using synchrotron-based techniques.
- REE-containing minerals were identified in various coal-related materials using advanced microscopic methods. The distribution of those minerals was examined, including their 3-D volume images.
- Feasibility of using high-temperature confocal microscopy for studying the reaction of dispersed REEs and phosphate to produce distinct monazite phases for later separation was demonstrated.
- Advances were made in the development of techniques that would lead to field probes for REEs in solid and liquid matrices. Progress was made in overcoming interferences with qualitative detection of REEs in solids by laser induced breakdown spectroscopy (LIBS), while the concept of using a fluorescence-based fiber-optic coupled probe integrated with sensitizers was demonstrated for detection of REEs at low-ppm and high-part-per-billion (ppb) in aqueous liquids under ideal conditions.

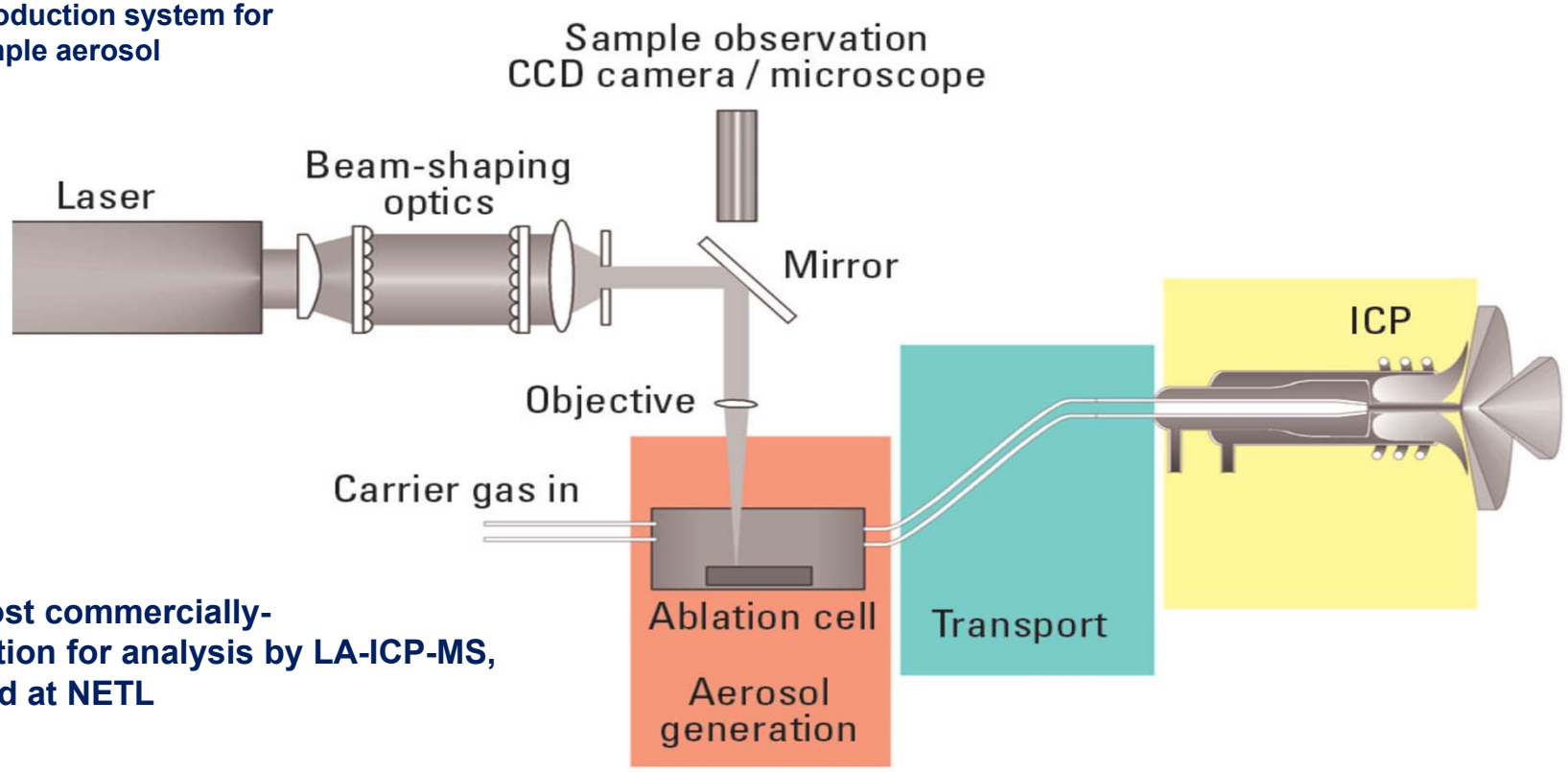
Characterization of Rare Earths in Coal and By-Products

Sampling and Characterization Techniques

- Identify Abundant By-Products Containing Highest Concentration of Extractable Rare Earths
- Improve Rapid & Accurate Characterization Techniques for Concentration & Species
- *Obtain Predictive Capabilities for Geological Location of High RE Content*
- Accomplishments for Sampling
- 768 samples collected since June 30, 2015 (nearly all solids, a few aqueous)
- Promising materials (≥ 27) identified with over 500 ppm RE+Y on dry whole basis
- 2 Memorandums of Agreement (MOAs) for sampling (United States Geological Survey (USGS), Electric Power Research Institute (EPRI), others pending) and collaborations
- Development of digestion methods for accurate determination of trace REE contents by inductively coupled plasma mass spectrometry (ICP-MS) – minimize uncertainty in trace RE determinations
- Identified Rare Earth Phosphate in Coals& Ashes; Rare Earth Phosphate, Sulfate and Oxides in Fly Ashes – Important for Developing Extraction Processes

LA-ICP-MS Analysis: Instrumentation

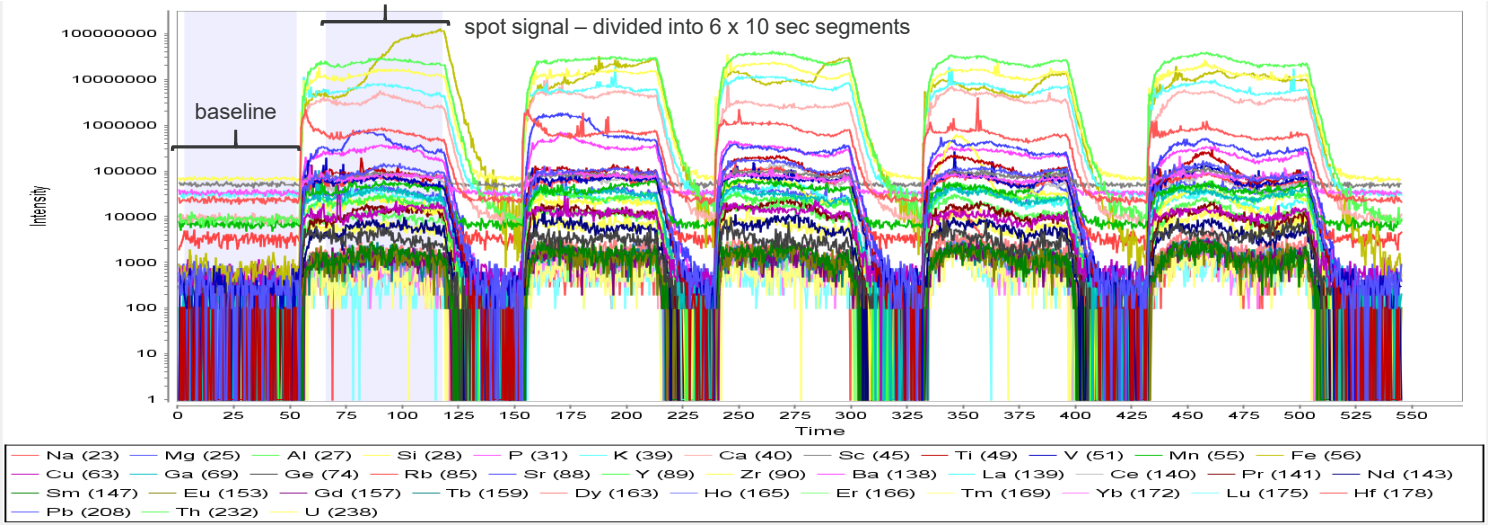
laser acts as sample introduction system for ICP-MS by providing sample aerosol



principal setup for most commercially-available instrumentation for analysis by LA-ICP-MS, including the one used at NETL

Typical Laser Sequence

SRM 1633b epoxy mounted – all 60 μm spots



- Each sample was analyzed in multiple spots for approximately 1 min per spot
- Each spot was then segmented into 6 x 10 sec slices to see if trends could be observed
- Different spot sizes from 32 μm to 60 μm were used
- Elemental content of 10 sec. segments were compared to 1 min spot
- 3 mounted samples were measured, with a total of 46 spots sampled
- Pearson's correlation matrices were calculated for each set of 6 spot segments

Recent Highlights: Separations

- **Physical Separations – Size, Density, Magnetic, Flotation**

  500 ppm by-product → 4,000 ppm in an early non-optimized fashion

  Anticipate enrichment to > 2% shortly

- **Sorbents – 100% Removal of REs from lab aqueous solutions**
- **Acid Digestion – Over 90% Recovery of Rare Earths from Fly Ashes**
- **Thermal – 100% Recovery as Monazite from Synthetic Lab Slags**
- **Chemical – High Conversion of RE Phosphates to More Amenable Species**
- **Novel – Photophoresis shows great early promise**

Physical Separation Methods

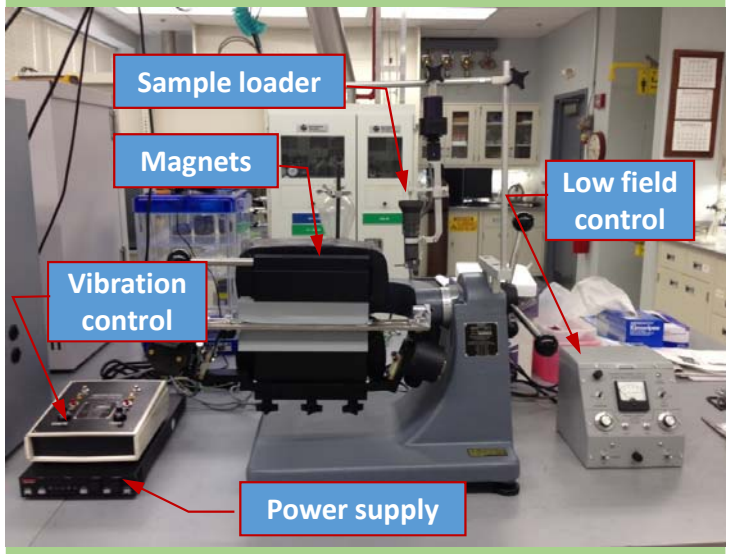
Density Separation

Float-sink separation
Bottom dense fraction

Size Separation

Ultrasound Shaker
Sieve size down to 5 micron

Magnetic Separation

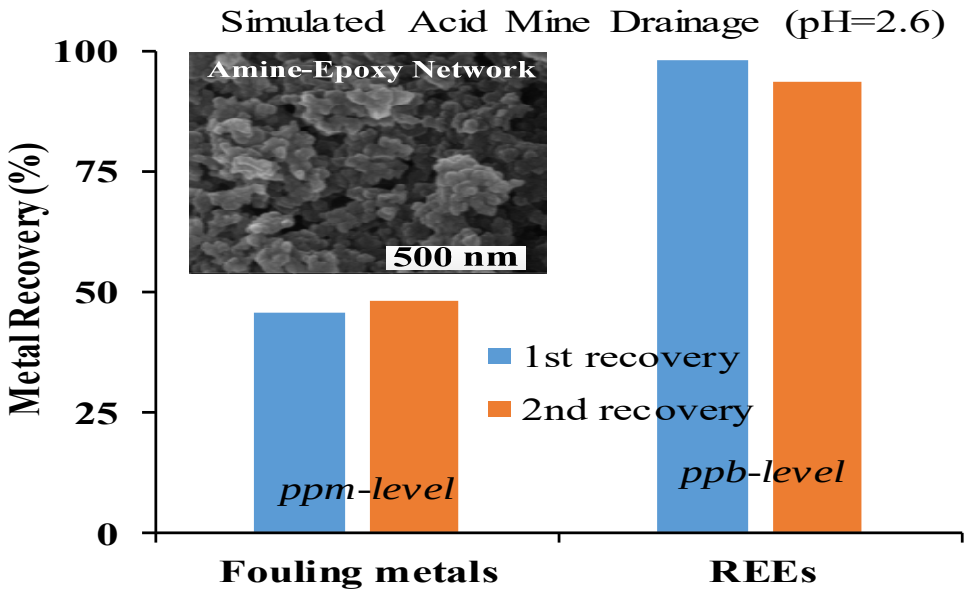


The Frantz Magnetic Barrier Laboratory Separator

Recent Highlights: Sorbents

Porous Amine Epoxy Particles

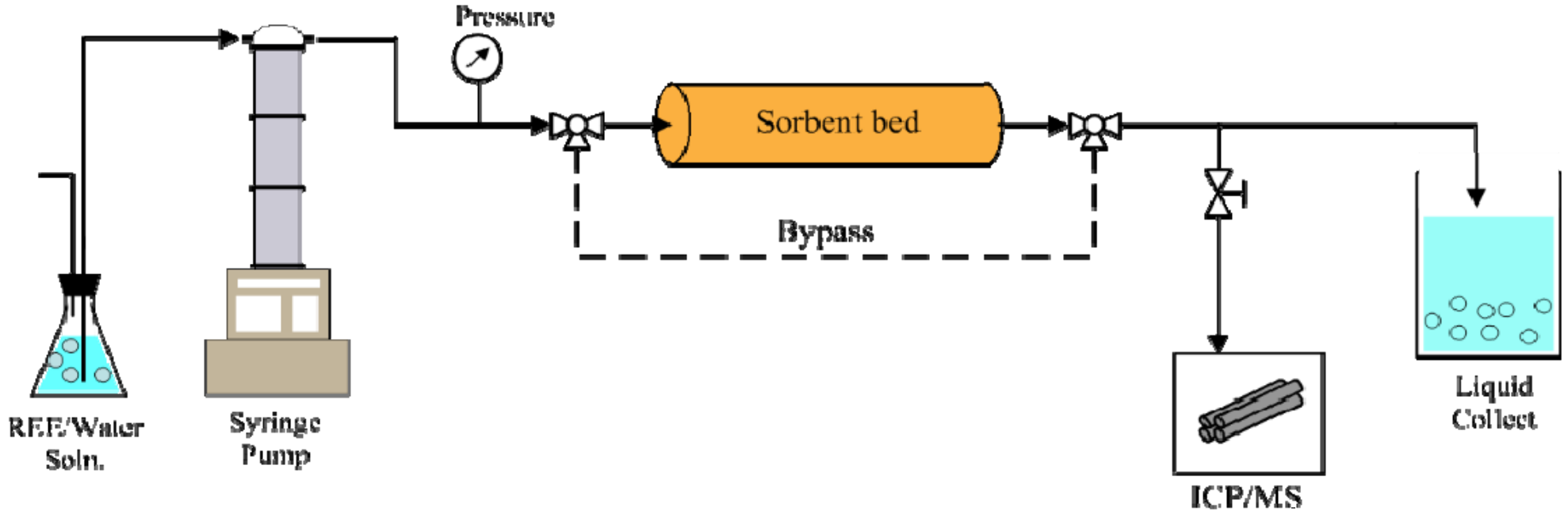
- **Near 100% Removal of Rare Earths from Simulated Acid Mine Drainage**
- **Some Capture of Heavy Metals**



Recent Highlights: Sorbents

Organoclay Particles

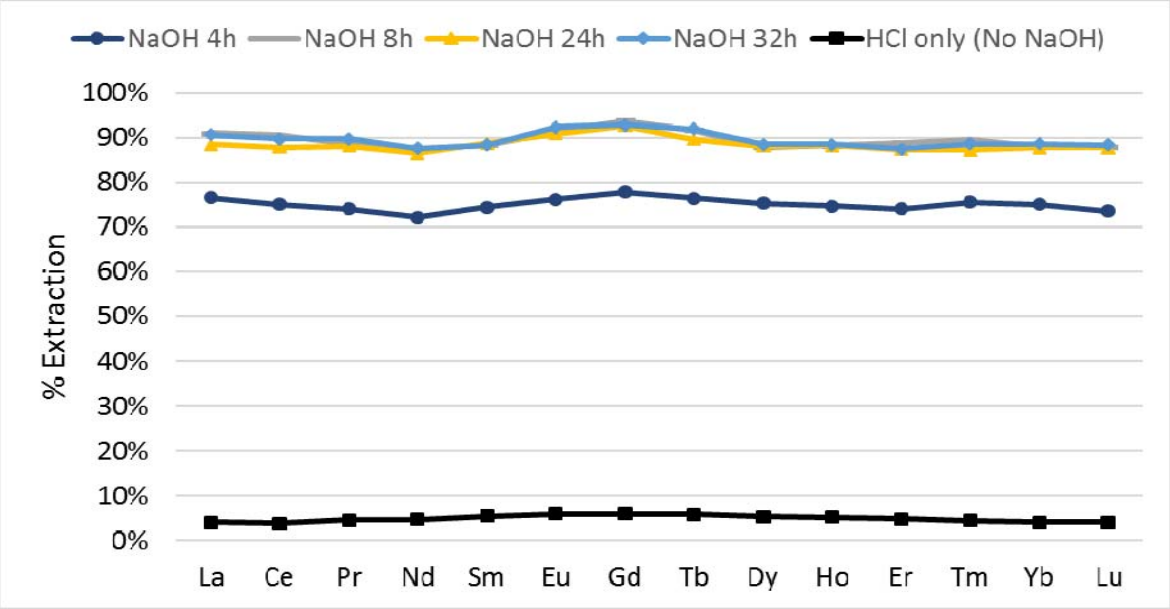
- **Near 100% Removal of Rare Earths from Lab Solutions**



Recent Highlights: Acid Digestions

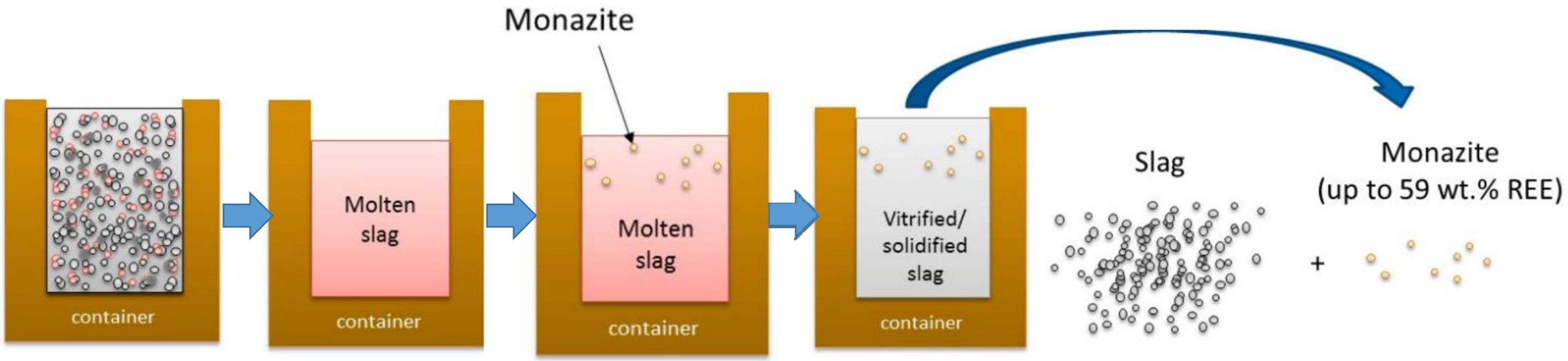
Extraction of Rare Earths from Fly Ash

- **Often Difficult Due to Glassy Matrix**
- **NaOH Pretreatment Greatly Enhances Recovery of Rare Earths**



Recent Highlights: Thermal Separations

Capture of Rare Earths from Slag



- **Additive to Slag**
- **Forms Monazite**
- **100% Rare Earth Recovery in Lab as Monazite**

Recent Highlights: Technology Transfer

Inventions, Patent Applications, and Licenses

- Bennett, J., Nakano, J., and Nakano, A., "Thermal Separation of Rare Earths," Report of Invention filed, June 2016.
- Gray, M., Wilfong, C., and Kail, B., "Regenerable Immobilized Amine Sorbents for REE and Heavy Metals Recovery from Liquid Sources," approved for filing US Patent Application, June 2016.
- Ohodnicki, P., Baltrus, J., Ahern, J., and Poole, Z., "A Luminescense Based Fiber Optic Probe for the Detection of Rare Earth Elements," Provisional Patent Application, filed July 21, 2016.
- Siriwardane, R., "Organo Clays for Recovery of Rare Earth Metals," approved for filing Patent Application, September 21, 2016.

Other Products

- 43 Presentations at National Conferences; 13 Publications; 1 book chapter; 2 MOAs; and 6 Sessions Organized at International Conferences
- The information developed by NETL R&IC is made available to the public through the EDX website, updated regularly with all NETL R&IC publications, presentations, sessions, and field data listed.
- Many Visitors to Web Site
- Rare Earth EDX website: https://edx.netl.doe.gov/ree/.

The NETL Rare Earth EDX Database

A Great Resource for Rare Earth Information

- Coal Materials
- Rare Earth Content - DOE's Coal-Based Rare Earth Element (REE) Data Bank
- Reports
- Publications and Presentations
- Upcoming Meetings
- Latest News
- Solicitations/Funding Opportunity Announcements
- Receive E-Mail Updates
- Submit Questions to NETL Experts
- https://edx.netl.doe.gov/ree/

Conclusions and Future Research

- 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 focus on the characterization of coals and byproducts, and separation methods for rare earth recovery.
- Co-recovery/Co-production of other products may be needed.

Questions

- **Visit Our Labs**

- **Contact:** evan.granite@netl.doe.gov

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