Recovering Rare Earth Metals from Coal Fly Ash

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Outline

Background
- Rare Earth Elements
- Coal Fly Ash

Objectives and Hypotheses

Research Approach and Methods
- Ash characterization
- Sequential extractions and XAS
- Extraction methods

Intellectual Merit and Broader Impacts
Rare Earth Elements

Consist of lanthanides and yttrium

Not particularly rare, just diffuse
- $10^3$ times more abundant than precious metals
- Crustal concentration (220 ppm) comparable to carbon (200 ppm)

Heavy rare earths less common
Critical Materials

REE in defense, energy, and electronics industries:

- Guidance/control systems
- Petroleum cracking catalysts
- Permanent magnets
- LEDs/glass additive
- Motors/generators
- Catalytic converters
- Flat panel displays
- Hard drives
- Batteries
- Hybrid/electric vehicles
REE Criticality

Classifications from Seredin (2010)

The “Balance Problem”
- REE utility does not match abundance
- Shortage of critical REE

Conventional ores have low C/E ratio (outlook coefficient)

<table>
<thead>
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<th>Category</th>
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<tr>
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<td>Lu</td>
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Rare Earth Production

Supply and Demand

2013: 86% of REE production took place in China
China controls 48% of global REE supply

2010: demand exceeds supply by 3000 T
Demand projected to increase consistently

<table>
<thead>
<tr>
<th>Country</th>
<th>2010 Production (t)</th>
<th>2011 Production (t)</th>
<th>Estimated Reserves (t)</th>
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<td>China</td>
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<td>130,000</td>
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<td>United States</td>
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<td>13,000,000</td>
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<tr>
<td>Rest of world</td>
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<td>3,000</td>
<td>42,000,000</td>
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<tr>
<td>Total</td>
<td>133,000</td>
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<td>110,000,000</td>
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</table>
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  - Sequential extractions and XAS
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Intellectual Merit and Broader Impacts
Environmental Hazard

53.4 million tons produced annually in the U.S.

Over 40% is recycled, primarily in cement

The remaining 30 million tons is landfilled or held in wet ash impoundments
  ◦ Often unlined
  ◦ Prone to failure

Toxic trace elements: As, Se, Cr, Cd, Pb, etc.

Contaminate groundwater and surface waters
Ash Spills

TVA Kingston Fossil Plant in December 2008

- **3.7 million m³** of mixed fly ash and bottom ash released
- **300 acres** contaminated

Dan River (Eden, NC) in February 2014

- **30,000-39,000 tons** of ash released
Strategic Metals in Ash

Some ashes exceed ore grade (over 1000 mg/kg)

NIST SRM 1633b has 420 mg/kg REE

Enriched 10x during combustion

Precedent for metal recovery from coal and fly ash

- Uranium source after World War II
- Germanium source since 1960s
- Aluminum recovery research in 1970s and 1980s
- Recent gallium recovery from fly ash
Advantages

Reuses a waste product
  ◦ Coal will be an important energy source for decades
  ◦ Worldwide scope

No excavation, beneficiation, and milling required
  ◦ Ideal form for chemical processing
  ◦ Eliminates a major part of the cost and environmental impact of REE production

Need for additional mines less urgent
  ◦ Thorium associated with conventional ores
Disadvantages

REE separation and purification still difficult
  ◦ Energy and chemical intensive
  ◦ Based largely in China

Coal ash has much lower REE content than concentrated ore

Metals entrained within ash particles

Ash composition heavily dependent on coal geology
Research Objectives

1. Characterize REE content of American fly ashes and correlate with ash attributes
2. Investigate structure and location of REE within fly ash using sequential extractions and XAS
3. Test industrially-relevant extraction methods, quantify extractable REE, and measure residual trace elements in fly ash after extraction
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Hypotheses

A. Appalachian Basin coal ashes will have higher REE content than Illinois Basin or Powder River Basin ashes.

B. Na$_2$O$_2$ sintering will be as effective as HF digestion for quantifying REE in fly ash. For other elements, HF digestion will be more accurate.

C. REE content will be correlated with BET surface area, particle size, and major oxide content.
Ash Characterization

Test characterization methods using NIST SRM 1633c as a standard

Determine REE concentration in coal ash samples

**ALKALINE SINTERING**
- Bake sample in Zr crucible with sodium peroxide
- Leach with nitric acid
- USGS method for REE analysis

**HF/HNO₃ DIGESTION**
- Whole rock digestion
- Evaporate HF and re-dissolve in nitric acid
- Quantification of metals remaining after extraction
Other Parameters

**Objective 1:** Correlate ash characteristics with total and extractable REE data

**BET surface area**
- Measure gas adsorption
- More porous fly ash may have higher extractable REE content regardless of particle size

**Analyses already performed by CAER:**
- Major oxide content
- Mineralogy
- Ash content of source coal
Preliminary Results

1. HF digestion and Na$_2$O$_2$ sintering are accurate quantification methods
2. Many fly ashes contain 500-600 ppm REE
3. Clear clustering by coal basin; Appalachian Basin ashes seem most promising

Note: Additional ash samples will be collected from plants in the Carolinas
Prioritizing Ashes

Coal ashes compare favorably with REE ore deposits

Fig. 6. Classification of REE-rich coal ashes by outlook for individual REY composition in comparison with selected deposits of conventional types: 1 = REE-rich coal ashes; 2 = carbonatite deposits; 3 = hydrothermal deposits; 4 = weathered crust elution-deposited (ion-adsorbed) deposits. Clusters of REE-rich coal ashes distinguished by outlook for REY composition (numerals in figure): I = unpromising, II = promising, and III = highly promising.
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Hypotheses

D. REE will be entrained in the glassy matrix of the fly ash particles rather than surface-bound. The majority of the REE will be present in the HF-leachable fraction of the ash (i.e. silicates).

E. The mineral phase of the rare earth elements in fly ash will determine how easily they can be extracted and which acid is most effective.
Sequential Extractions

4 g ash sample, 20 mL of extractant, 15 hours

1. Deionized water (water soluble fraction)
2. 1 M ammonium acetate (ion exchangeable)
3. 3 M HCl (carbonate-bound)
4. 8.8 M H$_2$O$_2$ and 4 M HNO$_3$ (oxidizable)
5. 1:1 mixture of HF and HNO$_3$ (silicate-bound)

Adapted from Huggins et al., 2000 / Modes of occurrence of Cr in four US coals
<table>
<thead>
<tr>
<th>Extraction step</th>
<th>Fraction</th>
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<td>2</td>
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<td>Acid-soluble</td>
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<td>5 mL H₂O₂, 85°C, 2 h, 1 M CH₃COONH₄, pH 2, 16 h</td>
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<td>5</td>
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<td>5 mL aqua regia (1:3 HNO₃:HCl), 3 mL HF, microwave digestion, 160°C 10 min, 180°C 30 min</td>
<td>Residual</td>
<td>Metals bound in lithogenic minerals</td>
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X-ray Methods

X-ray Absorption Spectroscopy (XAS)
Requires synchrotron radiation source

**XANES**

- Near-edge (±50 eV)
- Three-dimensional geometry
- Coordination environment
- Oxidation state

**EXAFS**

- Extended fine structure (100-1000 eV beyond edge)
- Coordination environment
- Nearest neighboring atoms
Figure 1. Normalized and background K-edge XANES spectrum of copper(0) foil.
Interferences

Absorption edges of other elements in sample may lie in XANES/EXAFS region

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Huggins et al., 2000 / Modes of occurrence of Cr in four US coals
Yttrium XAS

Most promising REE

- Second most abundant (up to 100 mg/kg)
- No notable interferences
- Critical REE

Reference materials should mimic fly ash samples (e.g. yttrium minerals embedded in glass)

**Objective 2** results will influence extraction method selection in **Objective 3**
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Hypotheses

F. Sonication or sintering of samples prior to acid digestion will improve REE recovery and enable the use of more dilute acids.

G. Recovering REE from fly ash will simultaneously remove the majority of the leachable toxic elements (e.g. As, Se, Cr, Pb).
Initial Methods

Direct Acid Leaching
◦ 8 M HCl at 105°C for 2 hours

Pressure-Digestion Acid Leach
◦ Pre-treat with NaOH solution at 200-245°C
◦ Ambient temperature leach with 12.5 M HCl

Sulfuric Acid Leaching
◦ 10% v/v H₂SO₄ at 30-80°C for 2 hours
◦ Specifically for REE in fly ash
Extraction Variables

1. Temperature (25-200°C)
2. Solid-to-liquid ratio (up to 1:2)
3. Acid type and concentration
4. Pretreatments (e.g. sintering)
5. Duration (30 minutes to overnight)
Sintering

Converts minerals to acid soluble forms

Allows leaching with dilute acid

◦ 25% HNO$_3$ after sintering (Objective 1)
◦ Twice as effective as concentrated HNO$_3$ alone

Variables to be tested:

◦ CaO and FGD waste instead of Na$_2$O$_2$
◦ Ratio of flux to sample
◦ Leaching acid and concentration
Post-Extraction

Quantify REE and trace elements in remaining solids
  ◦ Evaporate acid
  ◦ HF digestion (Objective 1)

Calculate extraction efficiencies by method

Correlate ash parameters (Objective 1) with extraction efficiency
Preliminary Results

HCl is the most effective acid

Effects of acid and sonication vary considerably between samples
  ◦ May depend on ash characteristics (Objective 1)
  ◦ High total REE does not imply high extractable REE

Sonication appears to hinder REE recovery in many cases (HCl and HNO$_3$)
  ◦ Inconsistent results for H$_2$SO$_4$
Preliminary Results

HCl is the most effective acid

Effects of acid and sonication vary considerably between samples

- May depend on ash characteristics (Objective 1)
- High total REE does not imply high extractable REE

Sonication appears to hinder REE recovery in many cases (HCl and HNO₃)

- Inconsistent results for H₂SO₄
Intellectual Merit

Objective 1
◦ REE totals for broad sample of American fly ashes
◦ Ash parameters linked to total/extractable REE

Objective 2
◦ Use of XAS to examine REE in fly ash
◦ Better understanding of REE structure in fly ash

Objective 3
◦ Application of relevant extraction methods to REE in fly ash
Broader Impacts

Environmental
- Beneficial reuse of fly ash
- Reduction in toxic trace elements

Economic
- Waste monetization
- Alternative source for crucial REE

National Security
- Stable domestic supply of strategic metals
- Considered critical elements by DOE
Conclusion

Fly ash is a promising alternative source of REE

Strong need for further research on fly ash REE content, structure, and extraction

Upcoming work
- Collect additional ash samples from Duke Energy and Santee Cooper
- Begin acquiring XAS standards
- Sequential extractions
Acknowledgements

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References

