



**Environmental Research
& Education Foundation**
Lighting a path to sustainable waste management practices



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

Crustal concentration (220 ppm) comparable to carbon (200 ppm)

Heavy rare earths less common

57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	3
La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	IIIb
138.91	140.12	140.91	144.24	(145)	150.36	151.96	157.25	158.93	162.50	164.93	167.26	168.93	173.04	174.97	44.956

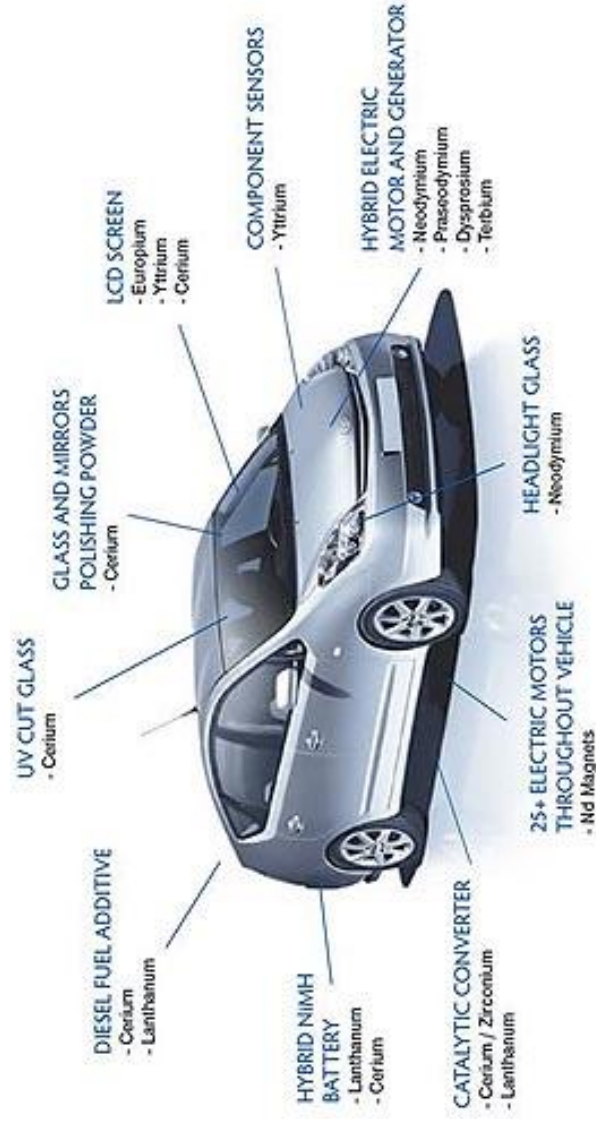
LREE

HREE

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”

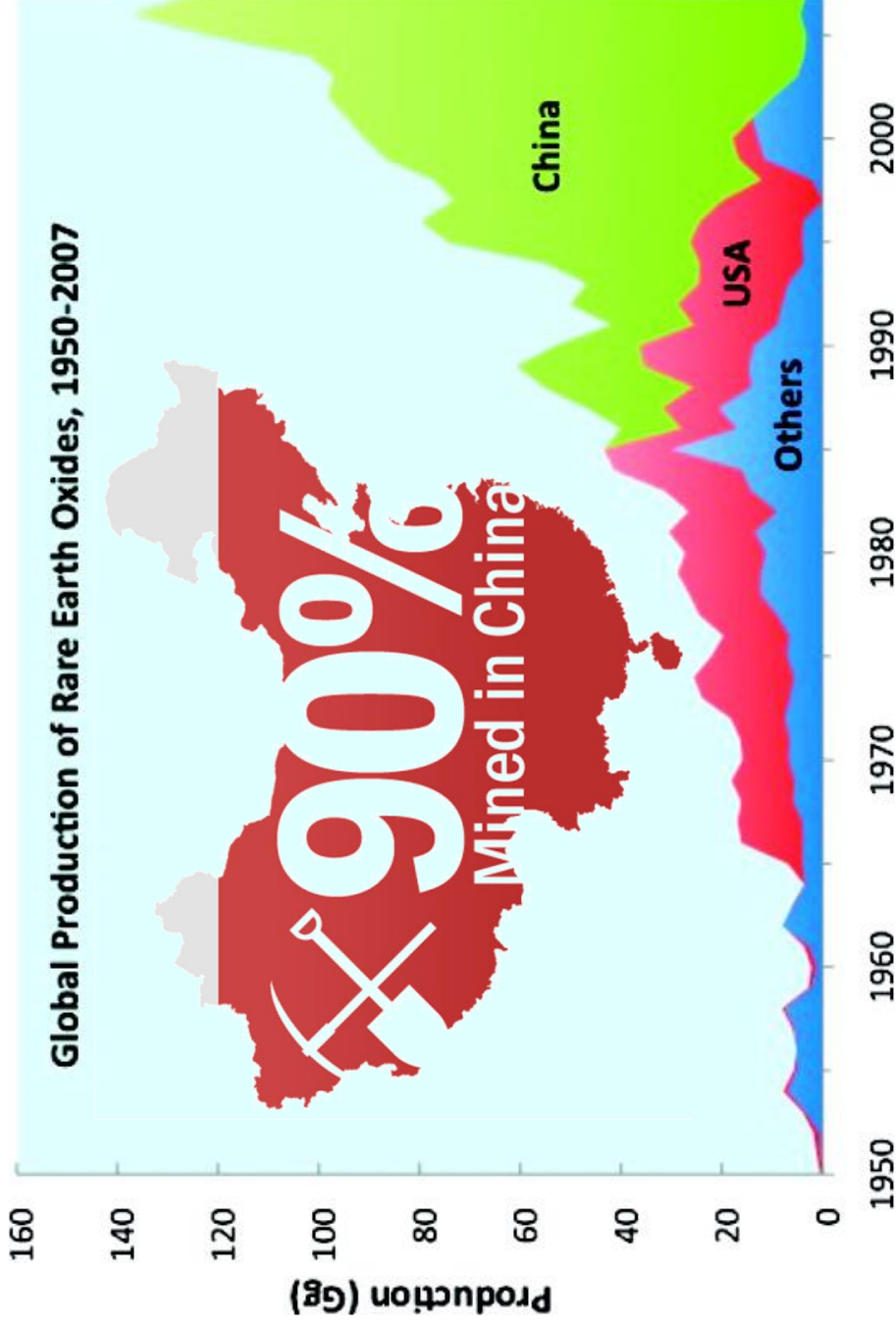
- REE utility does not match abundance
- Shortage of critical REE

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



Category	Symbol	Name
Critical	Nd	Neodymium
	Eu	Europium
	Tb	Terbium
	Dy	Dysprosium
	Y	Yttrium
	Er	Erbium
Uncritical	La	Lanthanum
	Pr	Praseodymium
	Sm	Samarium
	Gd	Gadolinium
Excessive	Ce	Cerium
	Ho	Holmium
	Tm	Thulium
	Yb	Ytterbium
	Lu	Lutetium

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

Country	2010 Production (t)	2011 Production (t)	Estimated Reserves (t)
China	130,000	130,000	55,000,000
United States	0*	0*	13,000,000
Rest of world	3,000	3,000	42,000,000
Total	133,000	133,000	110,000,000

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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

Aerial Image of Kingston Ash Slide 12/23/2008



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_2O_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_2O_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

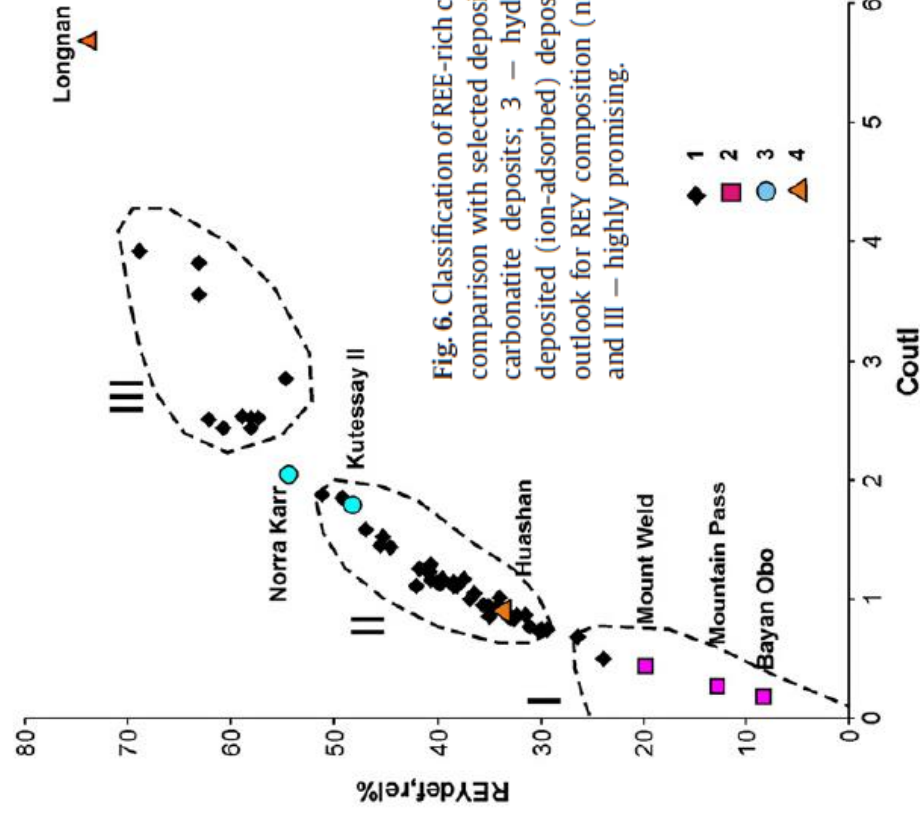


Fig. 6. Classification of REE-rich coal ashes by outlook for individual REY composition in comparison with selected deposits of conventional types. 1 – REE-rich coal ashes; 2 – carbonatite deposits; 3 – hydrothermal deposits; 4 – weathered crust elution-deposited (ion-adsorbed) deposits. Clusters of 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_2O_2 and 4 M HNO_3 (oxidizable)
5. 1:1 mixture of HF and HNO_3 (silicate-bound)



Extraction step	Fraction	Extraction procedure	Fraction	Fraction description
1	F1	H ₂ O, ultrasonic, 2 h	Water-extractable	Extractable by water
2	F2	0.11 M CH ₃ COOH, pH 2.85, 16 h	Acid-soluble	Exchangeable ions and carbonates
3	F3	0.1 M CH ₂ OH·HCl, pH 2, 16 h	Reducible	Iron–manganese oxides
4	F4	5 mL H ₂ O ₂ , 85°C, 2 h, 1 M CH ₃ COONH ₄ , pH 2, 16 h	Oxidizable	Sulfides/organics
5	F5	5 mL aqua regia (1:3 HNO ₃ :HCl), 3 mL HF, microwave digestion, 160°C 10 min, 180°C 30 min	Residual	Metals bound in lithogenic minerals

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

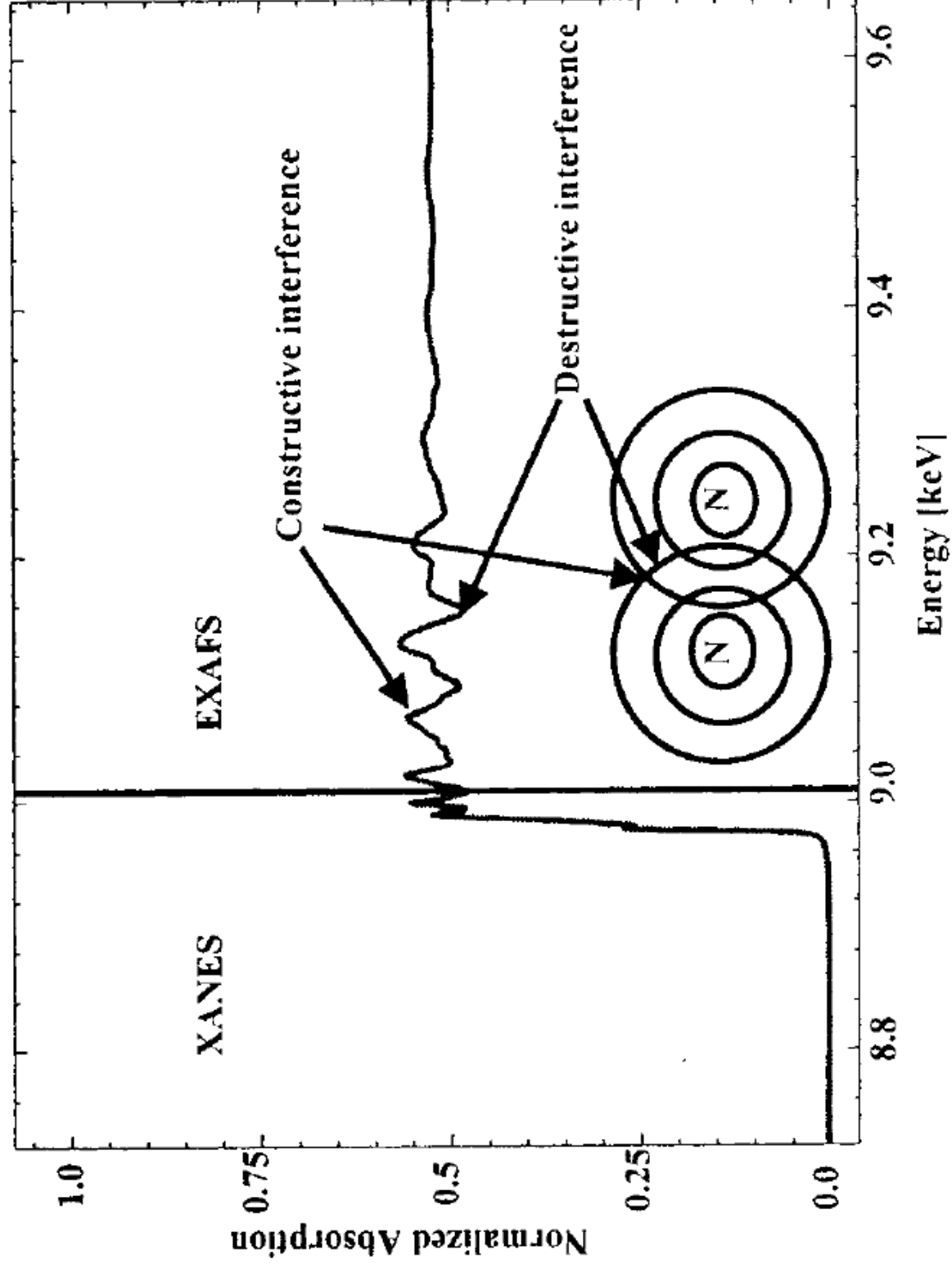
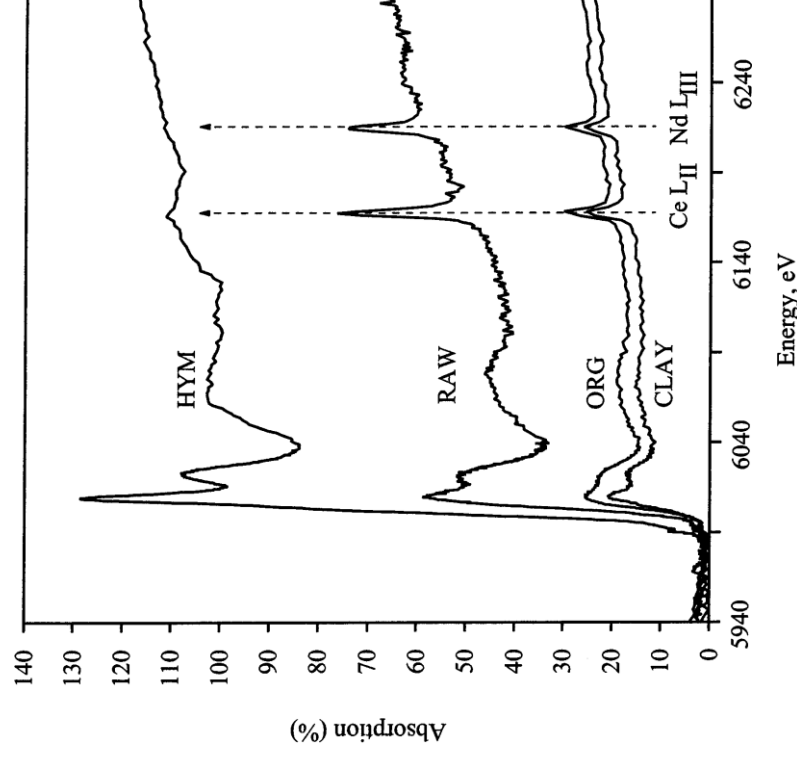


Figure 1. Normalized and background K-edge XANES spectrum of copper(0) foil.

Interferences

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

No.	Elem.	Binding energy (eV)		Emission (eV)	
		K-edge	L _{III} -edge	Kα1	Lα1
22	Ti	4966		4510.8	4504.9
23	V	5465		4952.2	
24	Cr	5989		5414.7	
25	Mn	6539		5898.8	
39	Y	17038		14958.4	
55	Cs	35985	5012	4619.8	
56	Ba	37441	5247	4466.3	4827.5
57	La	38925	5483	33441.8	4651.0
58	Ce	40443	5732	34719.7	4840.2
60	Nd	43569	6208	37361.0	5230.4
92	U		17166	13614	



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_2O_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 HNO₃)

- Inconsistent results for H₂SO₄

Preliminary Results

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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



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