Coupled Hydrothermal Extraction and Ligand-Associated Swellable Glass Media Recovery of Rare Earth Elements from Coal Fly Ash

T.M Dittrich, M. Dardona, J. Hovey, and M.J. Allen
Wayne State University
S.K. Mohanty
University of California-Los Angeles
H. Boukhalfa, A. Migdissov
Los Alamos National Laboratory
Purpose of Project

- AOI 2: DE-FOA-0001718 Award DE-FE-0031565 (Maria Reidpath)
- Couple a novel application of hydrothermal extraction with the advancement of a state-of-the-art SOMS Osorb® platform by engineering ligand selectivity
- Supported liquid extraction (SLE) or extraction chromatography (EXC)
- GOAL: Economical REE separation that minimizes use of solvents and acids (>2 wt% recovery)
- DRIVING QUESTION: Can we use hydrothermal extraction to reduce need for acid, while engineering ligands to extract REEs from the resulting solution?
- Technology benchmarking - nitric acid dissolution and liquid-liquid extraction (solvent extraction)

Current Status of project

- <13 months into project - exceeded most milestones so far
- Project goals remain same as originally proposal - transition from new concept to bench scale (in prep for pilot-scale)

Industry/input or validation - Just reaching stage to reach out for feedback with preliminary results
Accomplishments

- ACS Fall National Meeting (Boston, MA)
- SME National Conference (Denver, CO)
- ACS Spring National Meeting (Orlando, FL)
- Bilal Syed (2nd of 74) Design & Innovation Day
- Mohammed Dardona (Best poster award)
Outline

- **Overall Objective**
  - Economically feasible dissolution, concentration, and recovery (REEs)
  - Minimize use of solvents and acids, where possible
  - Fly ash (and FGD sludge)

- **Project Team**

- **Sample Collection and Experimental Setup**
  - (Obj. 1a) Trenton Channel and Monroe Power Plants near Detroit, MI
  - (Obj. 1b) Hydrothermal digestion process
  - (Obj. 2) Selection and synthesis of ligands
  - (Obj. 3) DIPEX and DTPA ligand association to organosilica (media)
  - (Obj. 4) REE sorption to ligand-organosilica media (capacity, selectivity)

- **Milestones**

- **Future Work**
Project Objectives and Partners

INTERDISCIPLINARY TEAM

Wayne State U., UCLA, and LANL

1) Hydrothermal extraction of REEs
   - Similar process for trinitite dissolution (LANL)

2) Select lanthanide-specific ligands to associate with solid support (organosilica)
   - Dr. Allen (WSU) - lanthanide coordination chemistry for MRI and catalysis applications (AAAS Fellow 2018-Chem)

3) Optimize attachment of ligands to the solid support to allow for flow-through separations (EXC)
   - Drs. Dittrich and Mohanty - similar to CBT-associated activated carbon for hazardous waste treatment

4) Test pH conditions for back-extraction

5) Evaluate resilience of material through cycling
Leveraging similarities to actinides

Periodic Table of Elements

For elements with no stable isotopes, the mass number of the isotope with the longest half-life is in parentheses.
Project Flow-chart

Detroit Coal Power Plant → Coal or fly ash with REEs → Characterization (WSU) → Hydro-thermal extraction (LANL) → Supernatant with REEs → Osorb-ligand optimization (WSU) → Loading of REEs on Ligand-Osorb packed columns (WSU) → REE-free solution

Strong Acid → Leaching of REEs from Ligand-Osorb packed columns (WSU) → Concentrated REEs

Optimization of sorption/desorption of REE from ligands (UCLA)
Ligand-associated Osorb (TBP)

- Osorb® (ABS Materials, Wooster, OH)
  - Swellable organically modified silica (SOMS)
  - Bridged silane
  - ~600 m²/g surface area
  - Can accumulate >4x mass in nonpolar ligands (Edmiston and Underwood, 2009)

- Tri-butyl phosphate (TBP-associated Osorb)
- Similar behavior to liquid/liquid extraction

Extraction of Pu(IV) onto a polypropylene membrane with immobilized TBP

Uranium extraction with Osorb-TBP media
- 94% recovery from 1000 ppm U
- Successful strip/cycle
Project Flow-chart

Detroit Coal Power Plant → Coal or fly ash with REEs → Characterization (WSU)

Supernatant with REEs → Hydro-thermal extraction (LANL)

Loading of REEs on Ligand-Osorb packed columns (WSU)

Osorb-ligand optimization (WSU)

Strong Acid → Concentrated REEs

Leaching of REEs from Ligand-Osorb packed columns (WSU)

REE-free solution → Optimization of sorption/desorption of REE from ligands (UCLA)
Detroit, MI
Trenton Channel and Monroe Power Plants

- **Trenton Channel**
  - 536 MW plant (Unit 9)
  - Mostly low sulfur western coal

- **Monroe Power Plant**
  - 3,066 MW plant
  - FGD process
  - Low sulfur/high sulfur blends
  - Up to 15% petcoke

- **ALL ash and wastewater sludge disposed in Sibley Quarry**
Sibley Quarry Landfill (Trenton, MI)

- 300’ deep limestone quarry (mid 1800’s)
- 1951 - DTE acquired (Type III Industrial Waste Landfill)
- 10,000-15,000 yd³/mo of CCR
- 1.5 MGD pumping rate to isolate CCR from groundwater
Sibley Landfill

CAT 980H Front-end loader
Fly ash and sludge collection - Detroit, MI
<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Sc 45 (ppm)</th>
<th>Ce 140 (ppm)</th>
<th>Dy 164 (ppm)</th>
<th>Er 166 (ppm)</th>
<th>Eu 153 (ppm)</th>
<th>Ho 165 (ppm)</th>
<th>La 139 (ppm)</th>
<th>Lu 175 (ppm)</th>
<th>Nd 142 (ppm)</th>
<th>Pr 141 (ppm)</th>
<th>Sm 152 (ppm)</th>
<th>Gd 158 (ppm)</th>
<th>Tb 159 (ppm)</th>
<th>Yb 174 (ppm)</th>
<th>Total REE minus Y (ppm)</th>
<th>Th 232 (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Trenton Channel, Detroit</td>
<td>NA</td>
<td>100.21</td>
<td>7.16</td>
<td>4.50</td>
<td>2.49</td>
<td>1.48</td>
<td>51.04</td>
<td>0.59</td>
<td>46.09</td>
<td>11.90</td>
<td>10.08</td>
<td>9.18</td>
<td>1.26</td>
<td>0.61</td>
<td>3.77</td>
<td>NA</td>
</tr>
<tr>
<td>DI water blank</td>
<td>0.022</td>
<td>0.0008</td>
<td>0.0006</td>
<td>0.0004</td>
<td>7E-04</td>
<td>0.0006</td>
<td>0.0004</td>
<td>0.00068</td>
<td>0.0005</td>
<td>0.0006</td>
<td>0.0004</td>
<td>0.0006</td>
<td>0.0008</td>
<td>0.0006</td>
<td>0.0006</td>
<td>0.03</td>
</tr>
<tr>
<td>WSU-1A (Monroe 75/25)</td>
<td>61.65</td>
<td>121.40</td>
<td>9.40</td>
<td>5.49</td>
<td>2.67</td>
<td>1.94</td>
<td>57.13</td>
<td>0.77</td>
<td>55.42</td>
<td>12.76</td>
<td>11.16</td>
<td>11.35</td>
<td>1.66</td>
<td>0.78</td>
<td>4.97</td>
<td>258.56</td>
</tr>
<tr>
<td>WSU-2A (Monroe 75/25)</td>
<td>61.10</td>
<td>124.26</td>
<td>9.65</td>
<td>5.64</td>
<td>2.66</td>
<td>1.89</td>
<td>57.60</td>
<td>0.71</td>
<td>56.03</td>
<td>13.01</td>
<td>11.11</td>
<td>11.71</td>
<td>1.64</td>
<td>0.81</td>
<td>4.84</td>
<td>362.67</td>
</tr>
<tr>
<td>WSU-3A (Monroe 75/25)</td>
<td>57.91</td>
<td>117.81</td>
<td>9.51</td>
<td>5.16</td>
<td>2.57</td>
<td>1.81</td>
<td>55.39</td>
<td>0.71</td>
<td>54.01</td>
<td>12.33</td>
<td>10.76</td>
<td>11.19</td>
<td>1.55</td>
<td>0.75</td>
<td>4.86</td>
<td>346.31</td>
</tr>
<tr>
<td>WSU-4A (Monroe 75/25)</td>
<td>57.33</td>
<td>123.12</td>
<td>9.59</td>
<td>5.79</td>
<td>2.68</td>
<td>1.86</td>
<td>57.93</td>
<td>0.74</td>
<td>58.53</td>
<td>13.04</td>
<td>11.02</td>
<td>11.84</td>
<td>1.58</td>
<td>0.77</td>
<td>4.96</td>
<td>360.79</td>
</tr>
<tr>
<td>WSU-1B (Monroe 70/15/15)</td>
<td>52.15</td>
<td>94.01</td>
<td>7.42</td>
<td>4.19</td>
<td>2.00</td>
<td>1.45</td>
<td>44.83</td>
<td>0.59</td>
<td>43.83</td>
<td>9.91</td>
<td>8.28</td>
<td>8.40</td>
<td>1.16</td>
<td>0.58</td>
<td>3.69</td>
<td>282.49</td>
</tr>
<tr>
<td>WSU-2B (Monroe 70/15/15)</td>
<td>49.18</td>
<td>94.01</td>
<td>7.07</td>
<td>4.03</td>
<td>2.16</td>
<td>1.41</td>
<td>44.81</td>
<td>0.55</td>
<td>43.58</td>
<td>9.83</td>
<td>8.34</td>
<td>8.58</td>
<td>1.23</td>
<td>0.58</td>
<td>3.63</td>
<td>279.00</td>
</tr>
<tr>
<td>WSU-3B (Monroe 70/15/15)</td>
<td>50.58</td>
<td>93.72</td>
<td>6.68</td>
<td>4.04</td>
<td>2.14</td>
<td>1.36</td>
<td>45.17</td>
<td>0.55</td>
<td>41.86</td>
<td>9.72</td>
<td>8.14</td>
<td>8.58</td>
<td>1.15</td>
<td>0.55</td>
<td>3.69</td>
<td>277.92</td>
</tr>
<tr>
<td>WSU-4B (Monroe 70/15/15)</td>
<td>50.53</td>
<td>98.79</td>
<td>7.45</td>
<td>4.25</td>
<td>2.16</td>
<td>1.48</td>
<td>47.79</td>
<td>0.59</td>
<td>46.04</td>
<td>10.41</td>
<td>8.89</td>
<td>8.91</td>
<td>1.22</td>
<td>0.62</td>
<td>3.90</td>
<td>293.03</td>
</tr>
</tbody>
</table>
Project Flow-chart

1. Detroit Coal Power Plant
2. Coal or fly ash with REEs
3. Characterization (WSU)
4. Hydro-thermal extraction (LANL)
5. Supernatant with REEs
6. Osorb-ligand optimization (WSU)
7. Loading of REEs on Ligand-Osorb packed columns (WSU)
8. REE-free solution
9. Optimization of sorption/desorption of REE from ligands (UCLA)
10. Strong Acid
11. Concentrated REEs
12. Leaching of REEs from Ligand-Osorb packed columns (WSU)
Hydrothermal Extraction

- Artas Migdissov and Hakim Boukhalfa (LANL)
- Optimize variables
  - $T$ (150-350°C)
    - Isothermal/variable
  - Ligand system
    - Cl, $SO_4^{2-}$, $CO_3^{2-}$
  - Leaching conditions
    - pH, time
  - Quenching conditions
    - Cooling cycle, pH adj.
- Compare to HF digestion
  - DTE ash and NIST SRM 1633C
Hydrothermal Extraction

(A) high pressure pump
(B) influent solution [e.g., 0.5 M CO$_3^{2-}$]
(C) stainless steel column in oven
(D) fraction collector

Hydrothermal Leaching Method

- Column is packed with fly ash (~8g)
- 250°C Furnace Temperature
- 0.5 M carbonate pumped
  0.1 mL/min flow rate, ~8 hours
- Hydrothermally Altered Fly Ash extruded from column
**Acid Leaching Method**

0.5g fly ash (dry)

Ash is leached with nitric acid (0.8 M to 4 M)

Leaching ~24hours

ICP-MS analysis of leachate

---

**Hydrothermal + Acid Leaching Method**

0.5g hydrothermally altered fly ash

Ash is leached with nitric acid (0.8 M to 4 M)

Leaching ~24hours

ICP-MS analysis of leachate
SEM verification of alteration

Unaltered Ash

Hydrothermally Altered Ash

Hydrothermally Altered Ash after acid leached
Project Flow-chart

Detroit Coal Power Plant

Coal or fly ash with REEs

Characterization (WSU)

Hydro-thermal extraction (LANL)

Supernatant with REEs

Osorb-ligand optimization (WSU)

Loading of REEs on Ligand-Osorb packed columns (WSU)

REE-free solution

Optimization of sorption/desorption of REE from ligands (UCLA)

Concentrated REEs

Leaching of REEs from Ligand-Osorb packed columns (WSU)

Strong Acid
Obj. 2 - Ligands of investigation

- Commercial ligands
  - P-P'-di(ethylhexyl)methanediphosphonic acid (DIPEX) from Eichrom, LLC.
  - Dipentyl pentylyphosphonate

- Synthesized ligands (char. w/ NMR and LC-MS)
  - Diethylenetriaminepentaacetic acid (DTPA) (denticities from 1-8)
    - functionalized with hydrophobic groups
  - Bis(butylamido) DTPA
    - 4NH2 DTPA
  - Bis(ethylhexylamido) DTPA
    - EHNH2 DTPA
Bis(2-ethylhexylamido) DTPA-\(^1\)H NMR

\(^1\)H NMR (400 MHz, CD\(_3\)OD): \(\delta = 3.83\) (s, 2H; NCH\(_2\)CO\(_2\)H, central), 3.50 (s, 4H; NCH\(_2\)CO\(_2\)H, terminal), 3.46 (s, 4H; NCH\(_2\)CONH), 3.40 (t, \(J = 8\) Hz, 4H; NCH\(_2\)CH\(_2\)N), 3.10–3.21 (m, 8H; NCH\(_2\)N, 4H; NCH\(_2\)CH(CH\(_2\)CH\(_3\))CH\(_2\)CH\(_2\)CH\(_2\)CH\(_3\)), 1.52 (m, 2H; CH), 1.46–1.56 (m, 16H; NCH\(_2\)CH(CH\(_2\)CH\(_3\))CH\(_2\)CH\(_2\)CH\(_2\)CH\(_3\)), 0.85–0.98 (m, 12H; CH\(_3\)).

Bis(2-ethylhexylamido) DTPA-HRMS

\[
[M+Na]^+ = C_{30}H_{57}N_5O_8Na \\
\text{Calcd: } 638.4099 \\
\text{Found: } 638.4096
\]
Preliminary Osorb®-DIPEX media

- Add 0.2 g Osorb to 50 mL centrifuge tubes
- Add 40 mL methanol with DIPEX
  - Methanol dissolves DIPEX and wets Osorb
- Rotate for 24 h, vacufuge, and DI rinse
Project Flow-chart

Detroit Coal Power Plant → Coal or fly ash with REEs → Characterization (WSU) → Hydro-thermal extraction (LANL) → Supernatant with REEs → Osorb-ligand optimization (WSU) → Loading of REEs on Ligand-Osorb packed columns (WSU) → REE-free solution → Optimization of sorption/desorption of REE from ligands (UCLA)

Concentrated REEs

Leaching of REEs from Ligand-Osorb packed columns (WSU) → Strong Acid
Neodymium sorption

- 40 mL 300 ppm Nd (pH ~2)
- Rotate 24 h (0.2 g media)
- Measure Nd concentration via ICP-MS
  - Agilent 7700 (He and H₂ collision gas)
Nd sorption to DIPEX-Osorb

- 300 ppm Nd in pH 2 HNO₃
- 40 mL per 0.2 g media
- No competing ions (e.g., Fe³⁺, Al³⁺)

<table>
<thead>
<tr>
<th>DIPEX/Osorb</th>
<th>mg Nd/g dry media</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.3</td>
<td>59.712</td>
</tr>
<tr>
<td>1.1</td>
<td>50.58</td>
</tr>
<tr>
<td>0.5</td>
<td>25.056</td>
</tr>
<tr>
<td>0.05</td>
<td>6.798</td>
</tr>
</tbody>
</table>

Reversibility of Nd sorption

ND Sorbed to the Osorb

Recovered Nd
Nd sorption as function of HNO₃ conc (M)

- 300 ppm Nd (40 mL for 0.2 g media)
Sorption isotherms

\[ y = 20.594 \ln(x) - 41.255 \]
\[ R^2 = 0.992 \]

\[ y = 18.716 \ln(x) - 75.176 \]
\[ R^2 = 0.8332 \]

\[ y = 10.4 \ln(x) - 52.946 \]
\[ R^2 = 0.8855 \]
16 REEs; 2.5 ppm each (pH 2 HNO₃)
Breakthrough column

- 0.2 ml/h
- 0.075 g media
- Nd, Eu, and Sc (100 ppm each)
Bis(ethylhexylamido) (EHNH$_2$) DTPA

EHNH$_2$ DTPA binding of 300 ppm Nd on Osorb resin at different pH

4NH$_2$-Osorb Binding Kinetics
Project Flow-chart

1. Detroit Coal Power Plant
   → Coal or fly ash with REEs
   ↓
   Characterization (WSU)

2. Hydro-thermal extraction (LANL)
   ↓
   Supernatant with REEs
   → Osorb-ligand optimization (WSU)
   ↓
   Loading of REEs on Ligand-Osorb packed columns (WSU)
   → REE-free solution

3. Strong Acid
   ↓
   Leaching of REEs from Ligand-Osorb packed columns (WSU)

4. Concentrated REEs

Optimization of sorption/desorption of REE from ligands (UCLA)
## Project Timeline

<table>
<thead>
<tr>
<th>Task</th>
<th>6 months</th>
<th>12 months</th>
<th>18 months</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>Hydrothermal extraction</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td></td>
<td>Ligand selection</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td></td>
<td>Ligand attachment to OSORB</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td></td>
<td>Evaluate REE sorption</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td></td>
<td>Evaluate REE Recovery from solid phase</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td></td>
<td>Model ligand-OSORB-REE system components</td>
<td></td>
</tr>
<tr>
<td>Milestone</td>
<td>Quantitative Measurement</td>
<td>Planned Completion Date</td>
<td>Investigator</td>
</tr>
<tr>
<td>--------------------------------------------------------------------------</td>
<td>------------------------------------------------------------------------------------------</td>
<td>-------------------------</td>
<td>----------------------------------</td>
</tr>
<tr>
<td>Obj. 1. Establish feasibility of hydrothermal extraction</td>
<td>&gt; 300 ppm T-REEs in hydrothermal extraction liquid</td>
<td>8/15/2018</td>
<td>Boukhalfa &amp; Migdissov</td>
</tr>
<tr>
<td>Obj. 2. Select/characterize two commercial ligands</td>
<td>Two commercial ligands are &gt;99% pure to identity</td>
<td>8/15/2018</td>
<td>Allen</td>
</tr>
<tr>
<td>Obj. 3. Load ligands to Osorb platform</td>
<td>Achieve surface coatings of ~50% by wt with first 2 ligands</td>
<td>12/1/2018</td>
<td>Dittrich</td>
</tr>
<tr>
<td>Obj. 4. Successful test of ligand-Osorb system with 2 commercial ligands</td>
<td>Achieve &gt;95% sorption of REEs from extraction liquid (by mass)</td>
<td>4/1/2019</td>
<td>Mohanty</td>
</tr>
<tr>
<td>Obj. 5. Successful pH-optimized strip with 2 commercial ligands</td>
<td>Recover minimum of 2wt% T-REE concentrate</td>
<td>8/1/2019</td>
<td>Dittrich</td>
</tr>
<tr>
<td>Obj. 6. Successful modeling of the ligand-Osorb-REE system</td>
<td>List of modeled/calculated system parameters/coefficients</td>
<td>9/1/2019</td>
<td>McElmurry</td>
</tr>
</tbody>
</table>
Future Work - Associate ligands to Osorb

1) Need to verify REE extraction efficiency from hydrothermal solutions
2) Test REE recovery from hydrothermal solutions
3) Column experiments for ligand-SOMS media prep
4) Stripping and precipitation to metal oxides
Conclusions

- Successfully loaded DIPEX on organosilica by >400% (wt)
- DTPA derivatives have been synthesized, successfully loaded to Osorb, and have recovered Nd at pH 6 and 2
- More complex solution chemistry (and Fe competition) must be tested
Acknowledgement and Questions

- DOE/NETL grant #FE-0031565 (Maria Reidpath)
- Support from Oak Ridge National Lab
  - Ralph E. Powe Junior Faculty Enhancement Award
- LANL graduate staff (EES-14)
  - A. Strzelecki
- DTE and DTE Staff
  - Amanda Kosch, Kayla Maas, and Lisa Lockwood
**Figure 1**

Uptake of Various Elements by Ln Resin

**Figure 2.**

The uptake of actinide elements by Actinide Resin

*Horwitz et al. (1975)*
Figure 6
Effect of Fe(III) on Am uptake by Actinide Resin

Horwitz, et al. (HP197)
Iron/ Nd competition

Based on 300 ppm Nd & 1000 ppm Fe

Based on 300 ppm Nd & 10 ppm Fe
Kinetics

- Ligands to Osorb (via NMR)
- Nd to DIPEX-Osorb
Rare-earth elements are leached from fly ash using hydrothermal extraction:
- High pressure
- High temperature
- High pH

A column of organically-modified silica (Osorb™) is loaded with ligands

The ligands are designed to:
- Irreversibly associate with the silica via alkyl chain interaction in the silica network
- Extract metals from the hydrothermal leachate using phosphonate and carboxylate groups as metal-binding ligands

An acidic environment will be used to elute the rare-earth elements from the column
What are Rare Earth Elements

- Lanthanides +Y +Sc -Pr (16 elements)
- Many high tech uses
  - Permanent magnets (power generation)
  - Electric car batteries
  - Petroleum refining catalysts
  - Phosphors
  - Electronic components (cell phones)
- ~$4 billion annual market ($4 trillion/yr in products associated with REEs)
Background

- **What are REEs?**
  - >85% of REE supply from China (undiversified global supply)
  - Global supply susceptible to supply shocks - 2010 RE magnets for wind turbine raised from $80,000 to $500,000 before dropping below $80,000 again
  - US DOE has deemed 6 REEs critical materials (Y, Nd, Eu, Tb, Dy)
  - Not typically found in concentrated ores (bastnaesite, monazite, xenotime, and ion-adsorbed clays commercially mined)
    - Difficult to extract and separate

Hower et al., 2016. Minerals
Coal Use and Fly Ash Supply

- ~1/3rd of US energy production from coal-fired plants
- US burns ~1 billion tons of coal /yr
- 100-150 million tons of CCPs / yr (~45 million tons of fly ash)
- 1.5 billion tons of fly ash in storage basins/landfills
- ~40-50% of fly ash is reused (concrete and BMs), rest is landfilled
- Other elements/resources possible
Why is this “waste to product”?

- **Fly ash disposal problems**
  - Bulk storage spills (e.g., Kingston FP, TN)
    - 1.1 billion gallons fly ash slurry that covered 300 acres
  - Groundwater contamination
    - Arsenic, barium, beryllium, boron, cadmium, chromium, thallium, selenium, molybdenum and mercury
    - 10× concentration of trace elements (e.g., 10-30 ppm U)

- **Environmental pollution from REE mining**
  - Large volumes of contaminated acids and solvents (and concentrated radionuclides, i.e., U and Th)

- **REEs required for many advanced “green” technologies**
Hydrothermal results

- ~8 g of ash
- ~20 mL 0.5 M TotCO$_3^{2-}$
- High pH (>9)
- Currently low yield (<1% of recovery from HF digestion)
What is Fly Ash?

- 0.5-300 µm particles
  - amorphous glass spheres
  - refractory crystals remain
  - alkali silica reaction?

- **Minerology**
  - silicon dioxide (SiO₂)
  - aluminum oxide (Al₂O₃)
  - calcium oxide (CaO)
  - calcium silicates

- ~200-500 ppm REE+Y

<table>
<thead>
<tr>
<th>Component</th>
<th>Bituminous</th>
<th>Subbituminous</th>
<th>Lignite</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂ (%)</td>
<td>20-60</td>
<td>40-60</td>
<td>15-45</td>
</tr>
<tr>
<td>Al₂O₃ (%)</td>
<td>5-35</td>
<td>20-30</td>
<td>20-25</td>
</tr>
<tr>
<td>Fe₂O₃ (%)</td>
<td>10-40</td>
<td>4-10</td>
<td>4-15</td>
</tr>
<tr>
<td>CaO (%)</td>
<td>1-12</td>
<td>5-30</td>
<td>15-40</td>
</tr>
<tr>
<td>LOI (%)</td>
<td>0-15</td>
<td>0-3</td>
<td>0-5</td>
</tr>
</tbody>
</table>

- $200-$400 REO/ metric ton
- ~50,000-70,000 tons of REE+Y in fly ash (2-4x US consumption)
<table>
<thead>
<tr>
<th>Oxide name</th>
<th>oxide</th>
<th>oxide molar mass</th>
<th>$/kg Dec. 2015</th>
<th>SRM 1633C Ash mg Metal/kg ash</th>
<th>mg oxide/mg metal</th>
<th>mg oxide/kg ash</th>
<th>$/kg</th>
<th>$/metric ton</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lanthanum Oxide</td>
<td>La₂O₃</td>
<td>325.81</td>
<td>$2</td>
<td>87</td>
<td>1.172737744</td>
<td>102.0281837</td>
<td>$0.00</td>
<td>$0.12</td>
</tr>
<tr>
<td>Cerium oxide</td>
<td>Ce₂O₃</td>
<td>172.115</td>
<td>$2</td>
<td>180</td>
<td>1.22839994</td>
<td>221.101139</td>
<td>$0.00</td>
<td>$0.12</td>
</tr>
<tr>
<td>Praseodymium oxide</td>
<td>Pr₂O₃</td>
<td>329.813</td>
<td>$52</td>
<td>$94</td>
<td>1.170296643</td>
<td>$0.00</td>
<td>$3.00</td>
<td></td>
</tr>
<tr>
<td>Neodymium oxide</td>
<td>Nd₂O₃</td>
<td>388.48</td>
<td>$42</td>
<td>87</td>
<td>1.166389851</td>
<td>101.4758735</td>
<td>$0.00</td>
<td>$2.42</td>
</tr>
<tr>
<td>Samarium oxide</td>
<td>Sm₂O₃</td>
<td>348.72</td>
<td>$14</td>
<td>19</td>
<td>1.159616919</td>
<td>22.03272147</td>
<td>$0.00</td>
<td>$0.00</td>
</tr>
<tr>
<td>Europolium oxide</td>
<td>Eu₂O₃</td>
<td>351.926</td>
<td>$150</td>
<td>4.67</td>
<td>1.157956041</td>
<td>5.40765712</td>
<td>$0.01</td>
<td>$8.66</td>
</tr>
<tr>
<td>Gadolinium oxide</td>
<td>Gd₂O₃</td>
<td>362.5</td>
<td>$32</td>
<td>$47</td>
<td>1.152623211</td>
<td>0</td>
<td>$0.00</td>
<td>$1.85</td>
</tr>
<tr>
<td>Terbium oxide</td>
<td>Tb₂O₃</td>
<td>747.7</td>
<td>$400</td>
<td>$949</td>
<td>3.12</td>
<td>3.695577802</td>
<td>$0.02</td>
<td>$23.08</td>
</tr>
<tr>
<td>Dysprosium oxide</td>
<td>Dy₂O₃</td>
<td>372.998</td>
<td>$230</td>
<td>$540</td>
<td>18.7</td>
<td>21.4817318</td>
<td>$0.01</td>
<td>$13.27</td>
</tr>
<tr>
<td>Holmium oxide</td>
<td>Ho₂O₃</td>
<td>377.86</td>
<td></td>
<td></td>
<td>1.14551628</td>
<td>0</td>
<td>$0.00</td>
<td>$0.00</td>
</tr>
<tr>
<td>Erbium oxide</td>
<td>Er₂O₃</td>
<td>382.56</td>
<td>$34</td>
<td>$34</td>
<td>1.143608753</td>
<td>0</td>
<td>$0.00</td>
<td>$1.96</td>
</tr>
<tr>
<td>Thulium oxide</td>
<td>Tm₂O₃</td>
<td>385.866</td>
<td></td>
<td></td>
<td>1.142088439</td>
<td>0</td>
<td>$0.00</td>
<td>$0.00</td>
</tr>
<tr>
<td>Ytterbium oxide</td>
<td>Yb₂O₃</td>
<td>394.08</td>
<td>7.7</td>
<td>1.138690255</td>
<td>8.767961165</td>
<td>$0.00</td>
<td>$0.00</td>
<td>$0.00</td>
</tr>
<tr>
<td>Lutetium oxide</td>
<td>Lu₂O₃</td>
<td>397.932</td>
<td>0.498</td>
<td>1.13714351</td>
<td>0.566297458</td>
<td>$0.00</td>
<td>$0.00</td>
<td>$0.00</td>
</tr>
<tr>
<td>Scandium oxide</td>
<td>Sc₂O₃</td>
<td>137.91</td>
<td>$4,100</td>
<td></td>
<td></td>
<td></td>
<td>$5.00</td>
<td>$242.34</td>
</tr>
<tr>
<td>Yttrium oxide</td>
<td>Y₂O₃</td>
<td>225.81</td>
<td>6</td>
<td>25</td>
<td>1.266670654</td>
<td>0</td>
<td>$0.00</td>
<td>$0.35</td>
</tr>
<tr>
<td><strong>TOTAL</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>445.288</td>
<td>544.1781928</td>
</tr>
</tbody>
</table>