ELECTRO-ASSISTED EXTRACTION OF CRITICAL RAW MATERIALS FROM COAL ASH

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<table>
<thead>
<tr>
<th>Element</th>
<th>Symbol</th>
<th>Atomic Number</th>
<th>Atomic Mass</th>
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<tbody>
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**Rare Earth Elements (REEs)**

‘Rare’ because they mix diffusely with other minerals underground therefore difficult and costly to extract.
REEs applications

MAGNETICS
- Computer Hard Drives
- Disk Drive Motors
- Anti-Lock Brakes
- Automotive Parts
- Frictionless Bearings
- Magnetic Refrigeration
- Microwave Power Tubes
- Power Generation
- Microphones & Speakers
- Communication Systems
- MRI

DEFENSE
- Satellite Communications
- Guidance Systems
- Aircraft Structures
- Fly-by-Wire
- Smart Missiles

CATALYSTS
- Petroleum Refining
- Catalytic Converter
- Fuel Additives
- Chemical Processing
- Air Pollution Controls

METAL ALLOYS
- NiMH Batteries
- Fuel Cells
- Steel
- Super Alloys
- Aluminum/Magnesium

CERAMICS
- Capacitors
- Sensors
- Colorants
- Scintillators
- Refractories

PHOSPHORS
- Display phosphors-CRT,LCD,LED
- Fluorescents
- Medical Imaging
- Lasers
- Fiber Optics

GLASS & POLISHING
- Polishing Compounds
- Pigments & Coatings
- UV Resistant Glass
- Photo-Optical Glass
- X-Ray Imaging

Nd Eu Tb Dy Y Lu Sm Pr La
Nd La Ce Pr
Nd Gd Er Ho La Ce Pr
Nd Gd Er Ho La Ce Pr

Chart by netl.doe.gov
Problem
EU overview

- EU is almost entirely dependent upon imports from China
- The 2011 REE-price crisis pointed to the need to reduce the dependence on China’s imports
- Substitution Index**: 0.96 (HREE) & 0.90 (LREE)
- End of life recycling rate: 8% (HREE) & 3% (LREE)

** 0 - 1: 1 means non-substitutable

EU, 2017
Geopolitical strategy

Final List of 35 Minerals deemed critical to U.S. National Security and Economy

2018 May (Dep. of Interior)

List of Critical Raw Materials for the EU – 27 CRMs

2017 September (European Commission)

- 2025

Criticality matrix (2015)

- Supply challenges for 5 REE may affect clean energy technology deployment in the years ahead.

2011 Critical Materials Strategy - by the U.S. Department of Energy - includes criticality assessments:

- Supply challenges for 5 REE may affect clean energy technology deployment in the years ahead.

(Based on the US Dept. of Energy, 2011)
Aim

Recovery of REEs from a secondary resource (e.g., coal by-product) through electro-based technologies

Efficient & environmentally-friendly separation and processing technology

In progress:
- Assessment and analysis of the feasibility of electrodialytic recover of REEs from anthracite ash
- Proof of concept

Electrodialytic Process

Recover of REEs from fine anthracite coal ash under the influence of an applied low level direct current

Matrix compartment: anode
Anthracite origin

• Blaschak Coal Corporation, Centralia, PA, USA
• Northern Pennsylvania
  • Lat. 40.8° N, Long. 76.36° W
• Mammoth Vein
Methodology

Processing

Characterization

- Cut
- Crush
- Grinding
- Ashing

ICP
EDX
SEM-EDS

pH desorption test

Extraction/Analysis

Fluxing
ICP

REE recovery

Anthracite

Anthracite ash
ASTM (D3174-12)

Electrodialytic cell

Fluxing

Cut Crush Grinding Ashing
Characterization
Relative REE content in anthracite ash

- Scandium (Sc)
- Yttrium (Y)
- Lanthanum (La)
- Cerium (Ce)
- Praseodymium (Pr)
- Neodymium (Nd)
- Samarium (Sm)
- Europium (Eu)
- Gadolinium (Gd)
- Terbium (Tb)
- Dysprosium (Dy)
- Holmium (Ho)
- Erbium (Er)
- Thulium (Tm)
- Ytterbium (Yb)
- Lutetium (Lu)

- Critical
- Near Critical
- Not Critical
- Other REE

REE
LREE
HREE

38.07%
19.35%
14.61%
10.09%
3.71%
Characterization
Particle morphology of anthracite ash

• Disperse
• Angular
• Size range: 1 to 10 um

SEM microphotograph of anthracite ash
Characterization
Particle morphology of anthracite ash

Trace elements
• Carbon
• Oxygen
• Aluminum
• Silicone
• Phosphorus
• Titanium
• Iron

REEs
• Lanthanum
• Neodymium
• Cerium

SEM microphotographs and respective EDS spectra of a) REE particle; b) agglutination of minerals
pH desorption from anthracite ash

Sc, Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu

LREE
HREE
Outlier
ED experiments

- 2C-ED cell
- L/S = 15
- CEM = cation exchange membrane
- MMO coated titanium bar
- Time: 3 days
- Current intensity: 10 mA
- pH: no adjustment

## Results

**Desorped REEs after ED**

<table>
<thead>
<tr>
<th>REE</th>
<th>Mass Number</th>
<th>Percentages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sc</td>
<td>44.956</td>
<td>1.1%</td>
</tr>
<tr>
<td>Y</td>
<td>88.906</td>
<td>4.9%</td>
</tr>
<tr>
<td>La</td>
<td>138.905</td>
<td>15.5%</td>
</tr>
<tr>
<td>Ce</td>
<td>140.116</td>
<td>12.7%</td>
</tr>
<tr>
<td>Pr</td>
<td>140.908</td>
<td>3.0%</td>
</tr>
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**LREE**

- Scandium (Sc)
- Yttrium (Y)
- Lanthanum (La)
- Cerium (Ce)
- Praseodymium (Pr)
- Neodymium (Nd)
- Samarium (Sm)
- Europium (Eu)
- Gadolinium (Gd)
- Terbium (Tb)
- Dysprosium (Dy)
- Holmium (Ho)
- Erbium (Er)
- Thulium (Tm)

**HREE**

- Ytterbium (Yb)
- Lutetium (Lu)

**Critical REEs**

- Scandium (Sc)
- Yttrium (Y)
- Lanthanum (La)
- Cerium (Ce)
- Praseodymium (Pr)
- Neodymium (Nd)
- Samarium (Sm)
- Europium (Eu)
- Gadolinium (Gd)
- Terbium (Tb)
- Dysprosium (Dy)
- Holmium (Ho)
- Erbium (Er)
- Thulium (Tm)

**Near Critical REEs**

- Scandium (Sc)
- Yttrium (Y)
- Lanthanum (La)
- Cerium (Ce)
- Praseodymium (Pr)
- Neodymium (Nd)
- Samarium (Sm)
- Europium (Eu)
- Gadolinium (Gd)
- Terbium (Tb)
- Dysprosium (Dy)
- Holmium (Ho)
- Erbium (Er)
- Thulium (Tm)

**Not Critical REEs**

- Scandium (Sc)
- Yttrium (Y)
- Lanthanum (La)
- Cerium (Ce)
- Praseodymium (Pr)
- Neodymium (Nd)
- Samarium (Sm)
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- Gadolinium (Gd)
- Terbium (Tb)
- Dysprosium (Dy)
- Holmium (Ho)
- Erbium (Er)
- Thulium (Tm)

**Other REEs**

- Scandium (Sc)
- Yttrium (Y)
- Lanthanum (La)
- Cerium (Ce)
- Praseodymium (Pr)
- Neodymium (Nd)
- Samarium (Sm)
- Europium (Eu)
- Gadolinium (Gd)
- Terbium (Tb)
- Dysprosium (Dy)
- Holmium (Ho)
- Erbium (Er)
- Thulium (Tm)

**Key Values**

- 1,1% for Scandium (Sc)
- 4.9% for Yttrium (Y)
- 15.5% for Lanthanum (La)
- 12.7% for Cerium (Ce)
- 3.0% for Praseodymium (Pr)
- 12.0% for Neodymium (Nd)
- 10.8% for Samarium (Sm)
- 13.5% for Europium (Eu)
- 8.9% for Gadolinium (Gd)
- 10.5% for Terbium (Tb)
- 14.4% for Dysprosium (Dy)
- 14.4% for Holmium (Ho)
- 12.7% for Erbium (Er)
- 13.0% for Thulium (Tm)
- 12.0% for Ytterbium (Yb)
- 10.8% for Lutetium (Lu)
- 3.1% for Scandium (Sc)

**Graph**

- The graph visually represents the percentages of different REEs, with critical REEs highlighted in red, near critical REEs in blue, not critical REEs in green, and other REEs in gray.
Results

REEs criticality analysis of relative content after ED
**Conclusions**

ED process is a promising extraction technique for rare earth elements recover from coal ash

- REE desorption improved with the ED process
- LREE show higher desorption rates
- HREE show promising capabilities of passing through the CEM

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<thead>
<tr>
<th>Critical REEs</th>
<th>Relative % of REEs desorped by ED</th>
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<td>Dy</td>
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This work has received funding from the European Union’s Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No. 778045, and from FCT/MEC through grant UID/AMB/04085/2019 to the Research unit CENSE – Center for Environmental and Sustainability Research. N. Couto also acknowledges FCT Investigator Contract CEECIND/04210/2017.
pH desorption
LREE

REE desorption at acidic pH

- Stable complexes are the first to desorb
- Higher desorption rates compared to HREE

Tendency
- Desorption starts from lower to higher atomic number (i.e. inversely related with ionic radius)

Scandium
- Different electronic and magnetic properties

LREE

Desorption (%) vs pH

Scandium (Sc), Lanthanum (La), Cerium (Ce), Praseodymium (Pr), Neodymium (Nd), Samarium (Sm), Europium (Eu)
Results

Relative distribution of REEs in the ash

Before ED

- Critical: 15.16%
- Near critical: 27.31%
- Other REE: 57.53%

After ED

- Critical: 31.57%
- Near critical: 50.93%
- Other REE: 17.50%
Results

REE distribution within the cell

<table>
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<th>Mass Number</th>
<th>Mass (amu)</th>
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Results
Relative distribution of REEs in the liquid phase after ED

![Anolyte](chart)

- Critical: 11
- Near critical: 20
- Other REE: 14

![Catholyte](chart)

- Critical: 5
- Near critical: 11
- Other REE: 7
Results
REE in the catholyte after ED

Critical
Near Critical
Not Critical
Other REE

LREE
HREE

REE

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2,8% 4,7%
0,7% 0,5%
2,5% 0,6%
2,2%
12,3%
24,0%
24,4%
12,3%
32,6%
33,5%
Future Work

**Experiment duration**
- 7 days
- Higher desorption rates

**pH adjustment**
- In the catholyte (pH ~2)
- Prevention of ion element precipitation
- Prevention of the formation of aggregated elements around the electrodes and the membrane
- Prevent membrane obstruction

**Increase current intensity**
- 50 mA
- Higher desorption rate
- Higher migration speed of the REE from the anolyte to the catholyte