Fate of Rare Earth Elements during Lab-Scale Combustion of Lignite Coal

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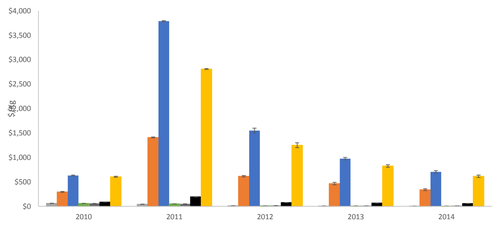
REE Background and Challenges

- Roughly 87% of REEs came from China in 2014
- National security and supply risk for critical RE
  - Y, Nd, Eu, Dy, Tb
- Not typically found in concentrated ores
- Difficult to extract and separate
- Integrated Recovery of REEs at Power Stations
- Resource Determination
- Enhanced Utilization of REEs

Approximate Composition of Beneficiated Commercial Rare Earth Ores on a 100% Rare Earth Oxide Basis

Oxide	Bastnasite	Monazite	Xenotime
ThO_2	<0.05	3-9	4-6
Total rare earth oxides	60-70	~60	~60
La_2O_3	32	22	0.5
CeO_2	49	45	5
Pr_6O_{11}	4.4	5	0.7
Nd_2O_3	13.5	17	2.2
Sm_2O_3	0.5	4	1.9
Eu_2O_3	0.1	0.1	0.2
Gd_2O_3	0.3	2	4
Tb_2O_7		0.2	1
Dy_2O_3		1	8.6
Ho_2O_3		0.1	2
Er_2O_3	0.1	0.4	5.4
Tm_2O_3		trace	0.9
Yb_2O_3		0.2	6.2
Lu_2O_3		trace	0.4
Y_2O_3	0.1	3	61

Cost Estimates



Fate of Rare Earth Elements during Coal Combustion

- Coal is typically burned at power plants in twenty percent excess air at temperatures of around 1370°C.
- A couple of common rare earth salts do have relatively low melting temperatures compared to the average combustion temperature reached in a coal fired power plant.
- It would be informative to know what form the rare earth elements are in, after combustion at high temperature.
- Significance of form is due to rare earth oxides having different solubility characteristics than rare earth phosphates or carbonates.
- Determining the form and location (encapsulated in glassy fraction, deposited on the surface, etc.) can greatly help develop separation processes

Hypothesis

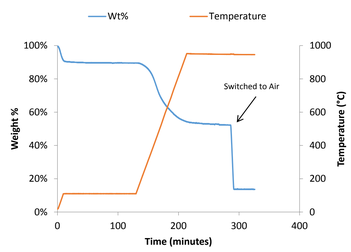
- Most rare earth element (REE) compounds are non-volatile at coal combustion temperatures.
- Rare earth elements are concentrated in the coal ash after the combustion of coal.
- Will rare earth minerals such as monazite, xenotime, basnasite, ion adsorption clays, etc, react with gases produced during the coal combustion process?

Procedure

- Concentration of rare earth elements in a lignite coal and lignite coal ash was determined using Inductively Coupled Plasma Mass Spectrometry (ICP-MS).
- Combustion of lignite coal in air at 750°C.
- Thermogravimetric analysis was conducted on the coal, as well as some rare earth phosphates, to determine if the rare earth phosphates at high temperatures ~900°C in air.

Characterization of Lignite Coal

- TGA analysis for lignite characterization
  - Initial experiment run in nitrogen
  - Switch to Air at 950°C after weight stabilizes for fixed carbon and ash



BET SA Results for Lignite Coal

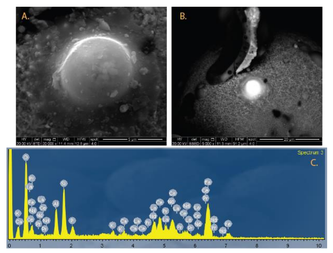
Mesh Size	BET SA (m^2/g)	Total Pore Volume (cc/g)	Average Pore Diameter (nm)
73-200	1.7	0.019	44.2

TGA Results for Lignite Coal

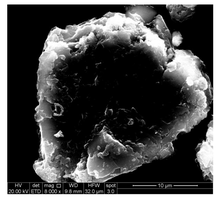
% Moisture	% Volatiles	% Fixed Carbon	%Ash
11	37	39	13

SEM Analysis

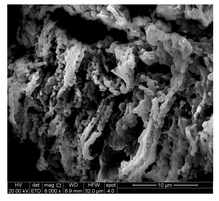
- Coal is relatively flat and smooth
  - (Low SA)
- Low temperature lab ashing is not the same as "real" ash from a power plant
- Monazite minerals have been shown to survive the combustion process in power plant coal ash



Power Plant Ash. Secondary (A.) and Backscatter (B.) images of a La, Ce, Nd, Pr, and P -rich grain. EDS spectra shown in (C.). This chemistry is consistent for the mineral monazite.

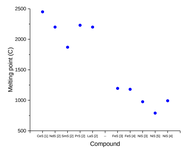


Lignite Coal

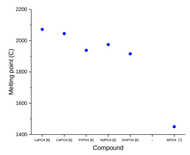


Lignite Coal Ashed at 750°C

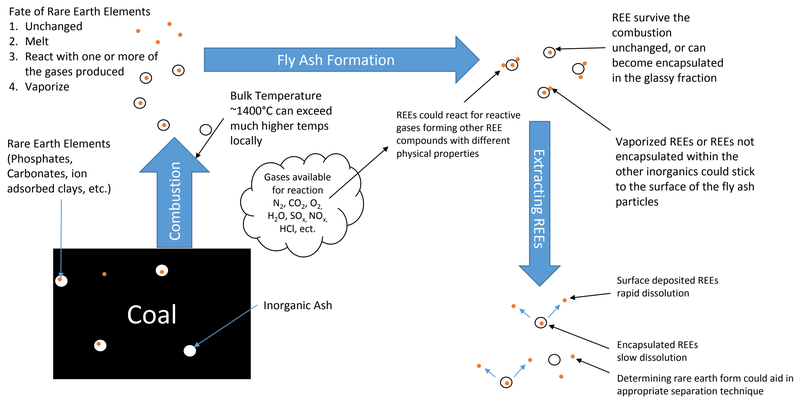
Melting Points of RE Sulfides



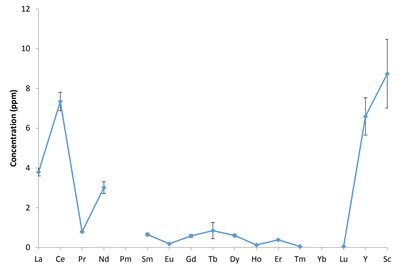
Melting Points of RE Phosphates



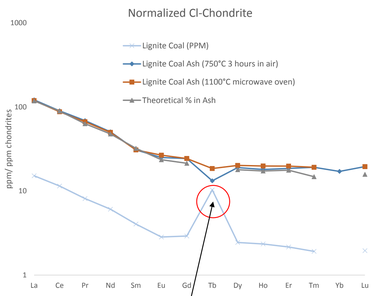
Fate of Rare Earth Minerals during Coal Combustion



REE Concentration in Lignite Coal



Concentration of rare earth elements in lignite coal. Error bars are the standard deviation between the seven samples.



- **REEs usually form a smooth line (exceptions are Ce and Eu)**
- **Tb is probably an ICP-MS measurement error**
- **The two ashing temperatures for lignite coal give very similar results and indicate that nearly all of the REEs are concentrated in the ash**

TGA Results with Model Phosphates in Air and Nitrogen

Lanthanum III Phosphate	% wt loss/air	%wt loss/N_2
110°C	2.05	2.06
110°C to 900°C	5.38	5.36
Yttrium III Phosphate		
110°C	0.89	0.32
110°C to 900°C	4.77	4.87
Holmium III Phosphate		
110°C	0.9	0.37
110°C to 900°C	4.93	4.61

Ramp 10°C/min 1 hour isothermal at 110°C and 900°C

- **TGA results showed two weight loss steps**
- **One below 110°C which is typical for water**
- **Another weight loss step occurred at higher temperatures**
- **Air and Nitrogen both had similar weight losses**
  - **More investigation needs to be conducted to determine what is being released at these high temperatures**

Conclusion

- It was determined that even with the difficulty of measuring the small concentrations of rare earth elements in the coal, that all of the rare earth elements are concentrated in the coal ash. Additionally, a mass balance shows that most of the REE elements in the parent lignite end up in the resulting ash when ashed at relatively low temperatures of 750°C and 1100°C
- REEs are concentrated in the coal ash after the combustion of coal due to their typically high melting temperatures and low volatility.
- TGA results on model phosphates in air and in nitrogen showed two degradation steps

Future Work

- Initiate experimental and modeling efforts to determine likely forms of REEs at various points within coal-fired power stations.
- Perform TGA testing on model compounds such as phosphates in environment more similar to Flue-Gas streams
- Determine if common rare earth minerals react with flue gases produced during coal combustion
- Determine if high temperature separations could be used on different rare earth compounds

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