Recovery of the REE from Coal Fly Ash *via* the combination of Physical Separations and Chemical Extraction Methods

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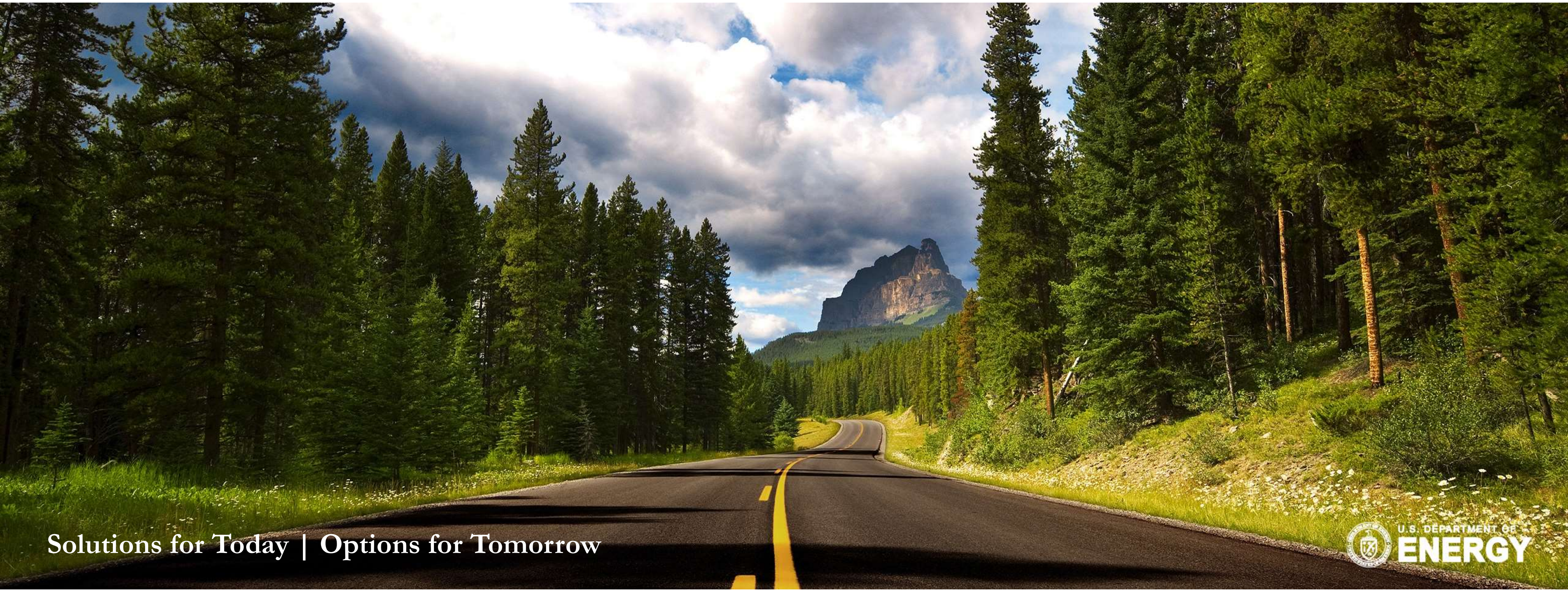
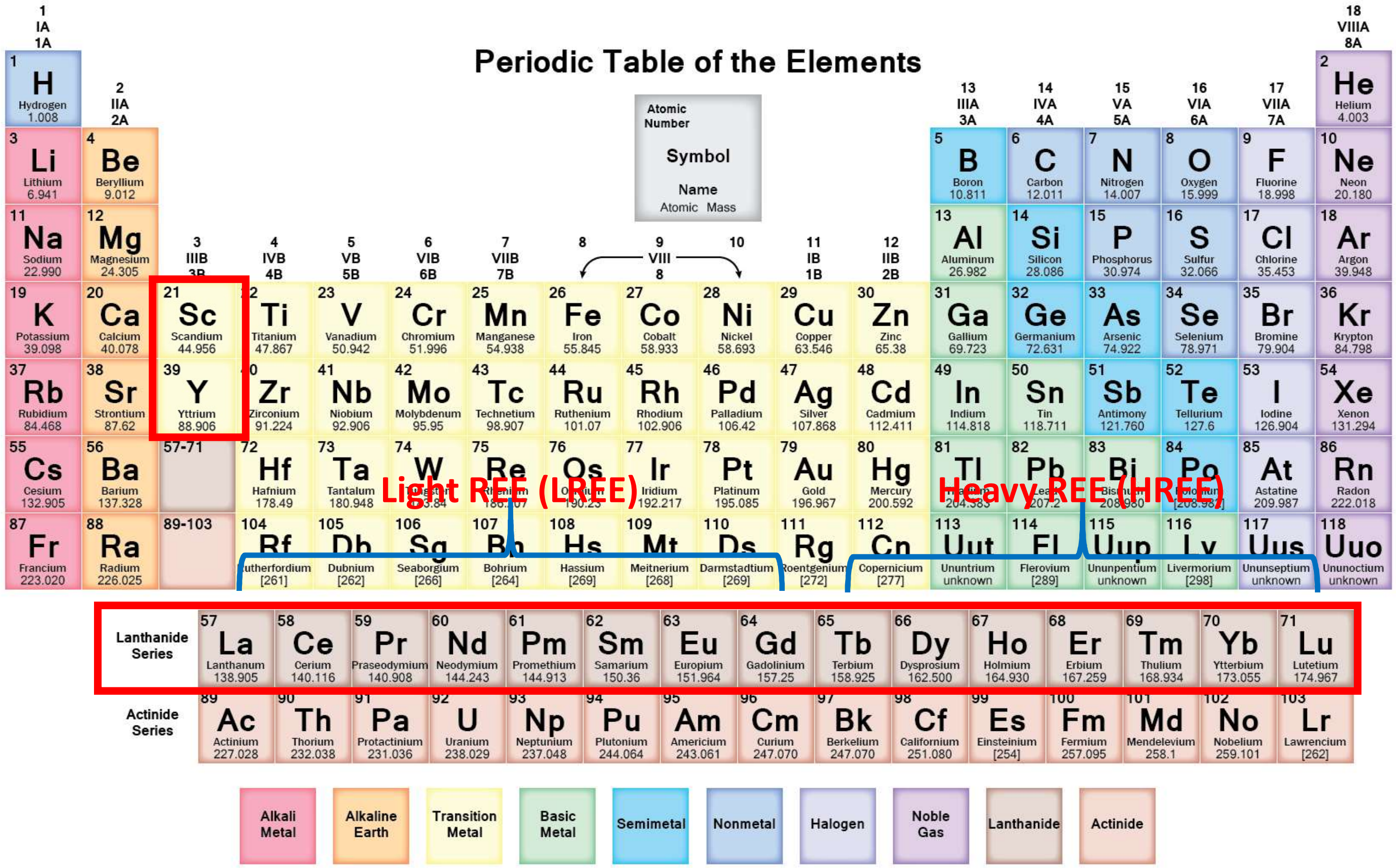


What Are Rare Earth Elements (REE)

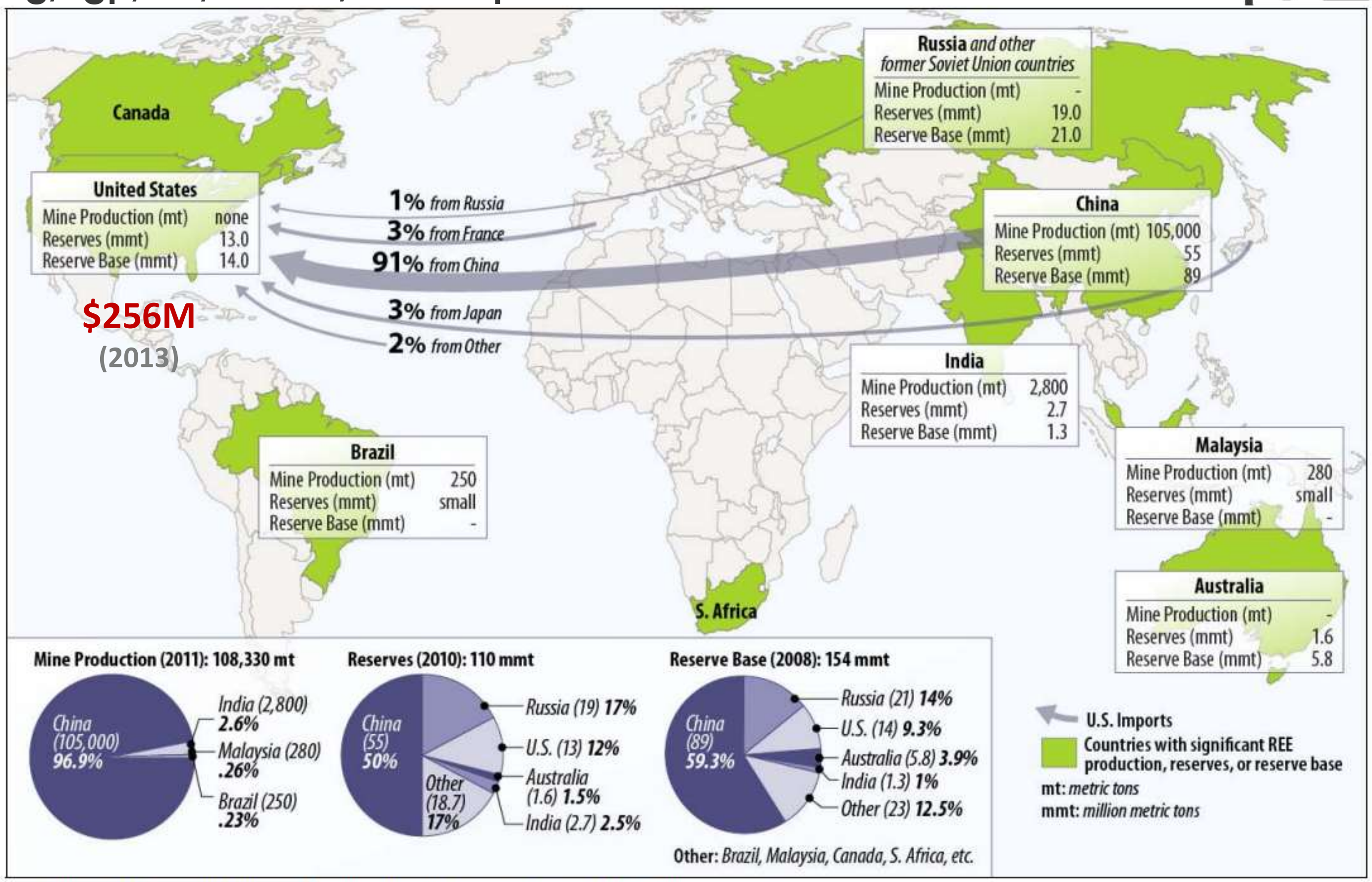


- http://sciencenotes.org/wp-content/uploads/2015/01/PeriodicTableMuted.png

REE applications

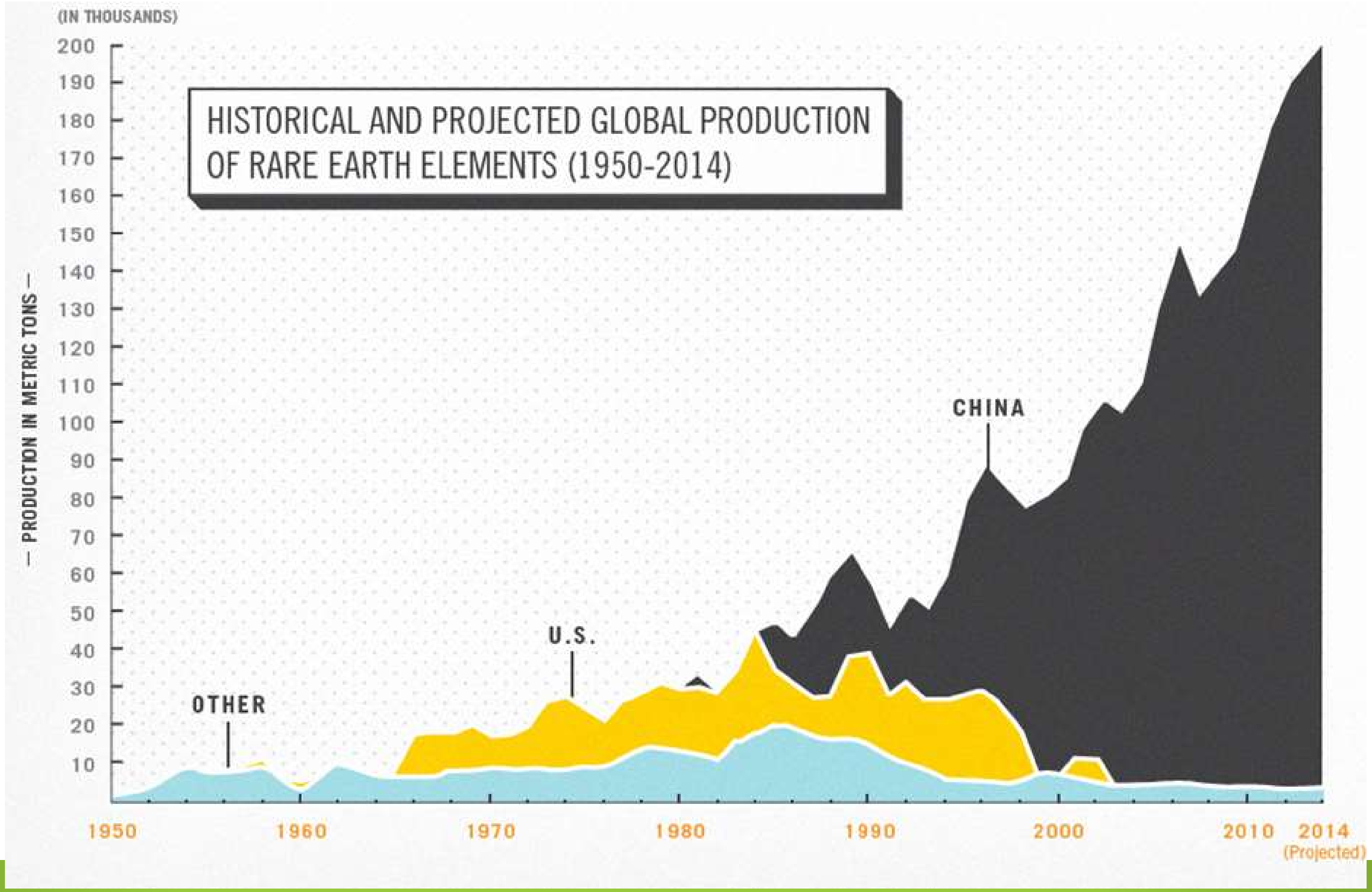
U.S. 100% Depends On REE Imports

https://www.fas.org/sgp/crs/natsec/R41347.pdf



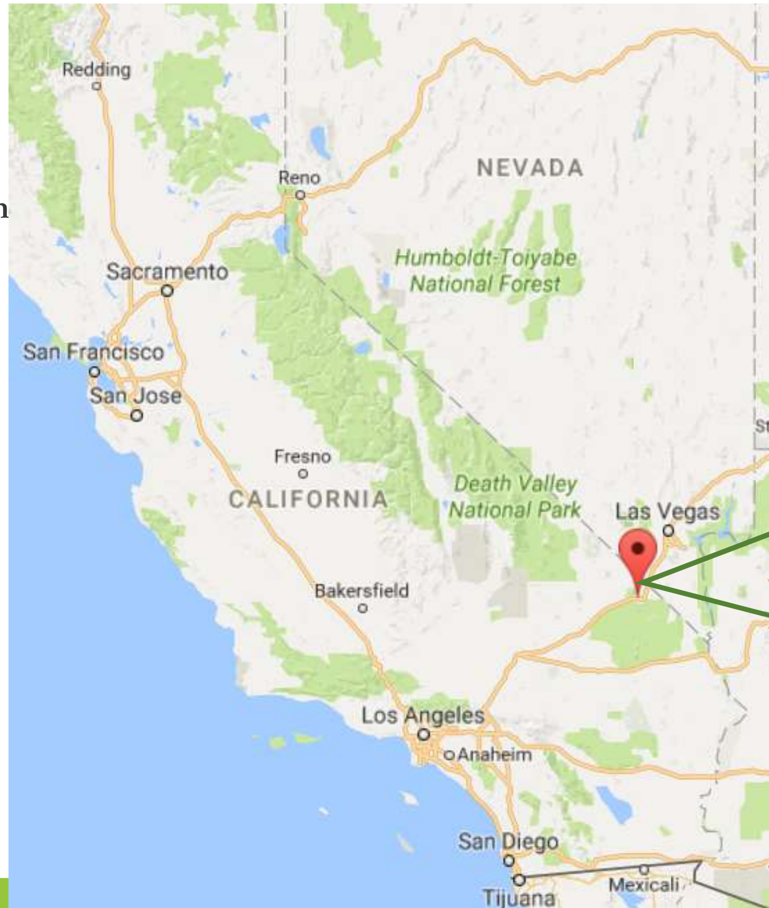
Source: U.S. Geological Survey, Mineral Commodity Summaries, 2008-2013. (Figure created by CRS.)

Top REE Suppliers In The World: Then and Now
U.S. consumed 17,000 ton REE in 2015 (estimated $ 246 million)



Mountain Pass: America's Only REE Mine

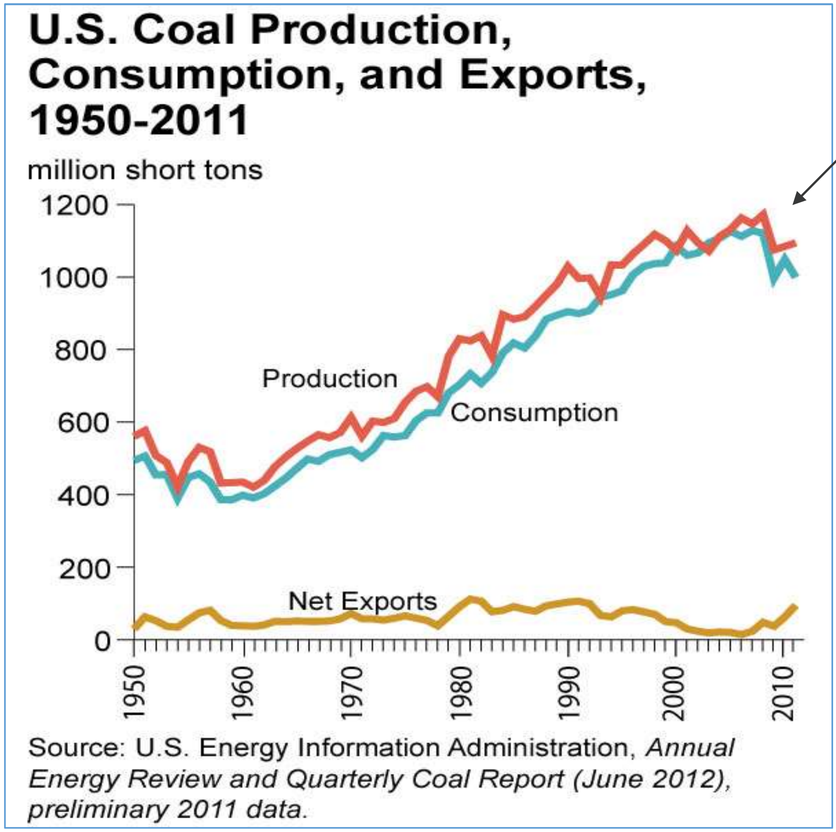
- 1949: discovered
- 1952: small-scale production
- 1960s-1990s: large-scale production
- 2002: closed
- 2012: restarted
- 2015: shut down



- 10% REO
- Bastnasite
  - Cerium
  - Lanthanum
  - Neodymium
  - Europium
- Estimated Reserve: 1.5 M tons

- https://en.wikipedia.org/wiki/Mountain_Pass_rare_earth_mine

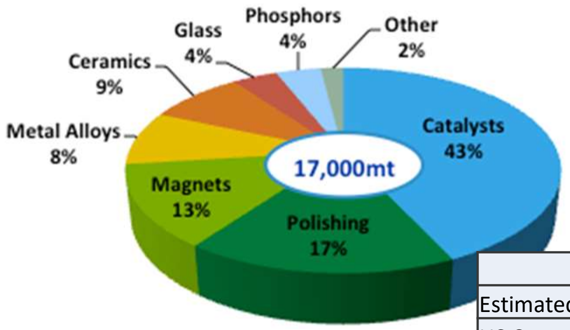
REE from Coal and Coal By-Products: Opportunities



~ 1 B ton/year

REE: 56ppm

~ 56,000 ton REE/year



> 3 times of U.S. demand

Year	2015	2016
Estimated Cost of imports	$ 160,000,000	$ 120,000,000
US Consumption Tons	17,000	16,000
Import %	65	100
Import tons	11,050	16,000
Cost/Ton Import	$ 14,480	$ 7,500

Existing REE Extraction Processes

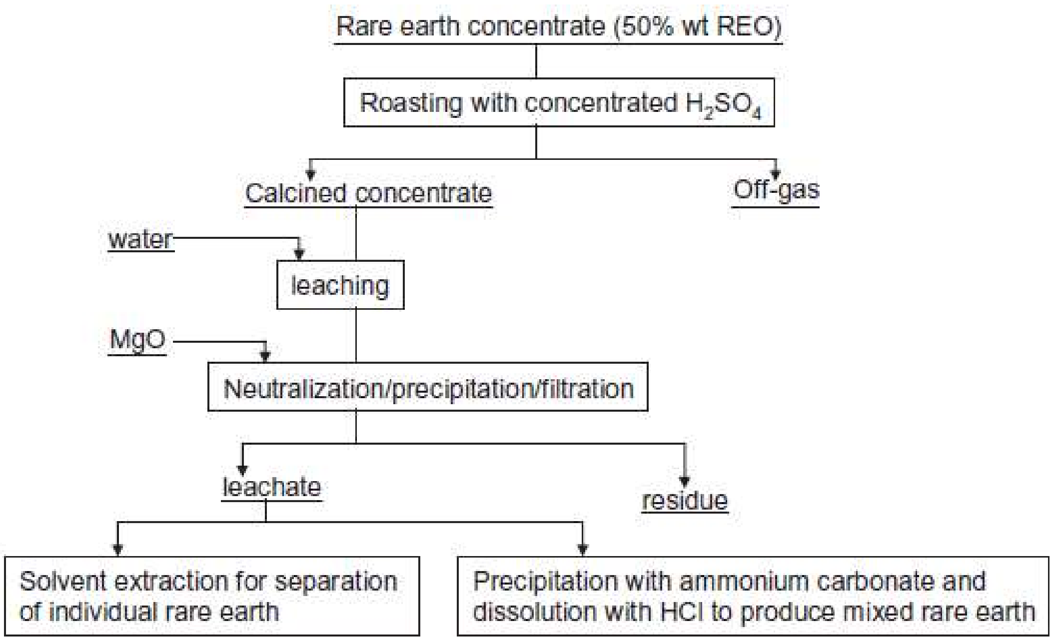


Fig. 1. Schematic leaching process used for Baotou rare earth concentrates (after Huang et al., 2006).

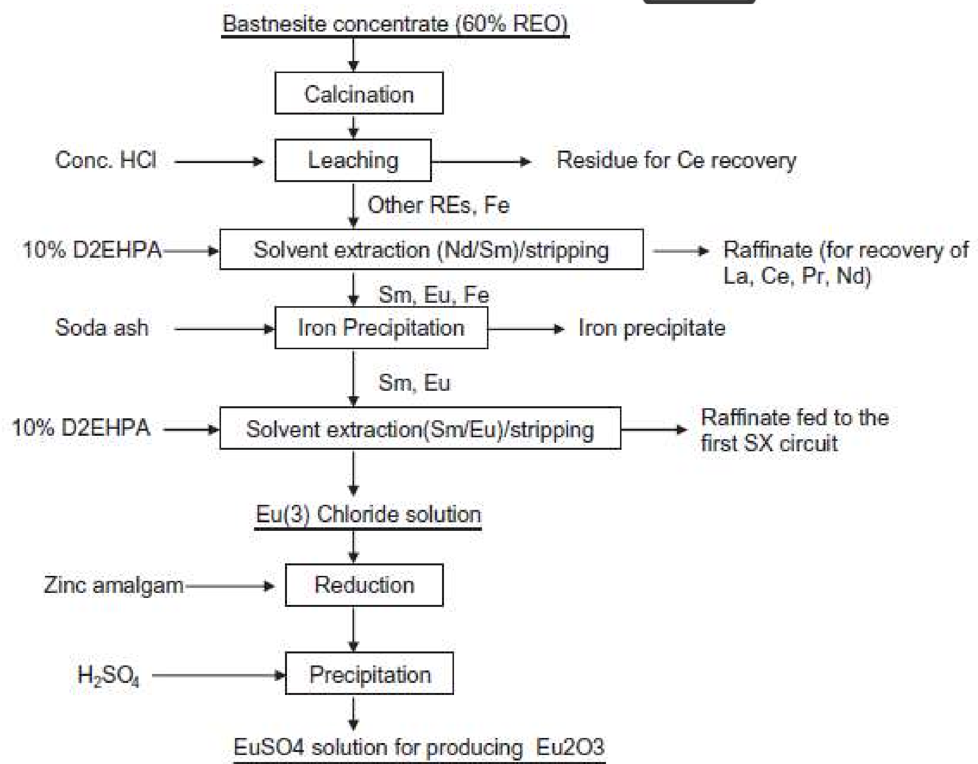


Fig. 2. Molycorp process for producing europium oxide from the bastnesite concentrate (after Gupta and Krishnamurthy, 2005).

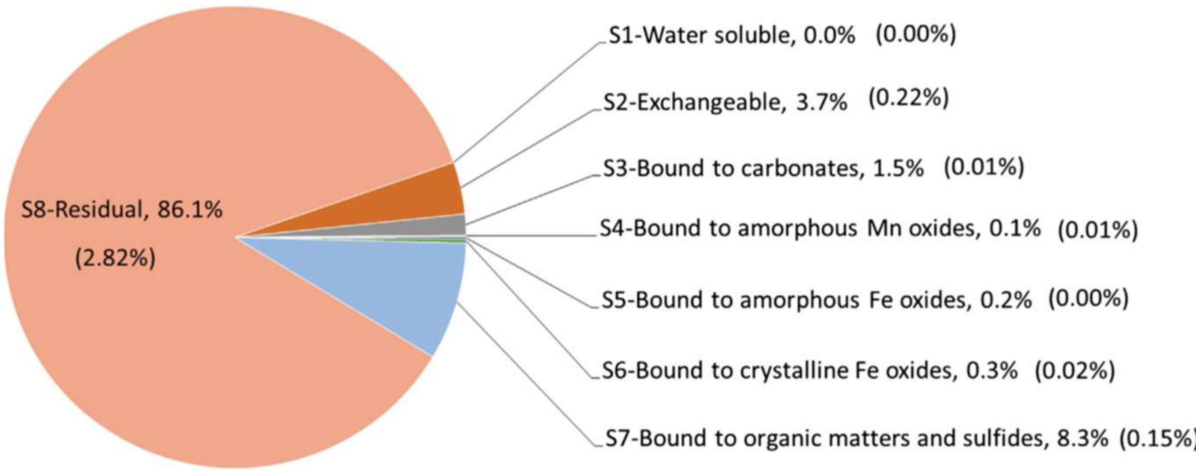
Extraction reagents and conditions used in 7-step sequential extraction to recover REE from coal fly ash

Taggart et al ., *Enviro Sci Tech* 2016, 50, 5919-5926.

Step #	Targeted Fraction	Reagents	L:S ratio	L (mL)	S (g)	Temp (°C)	Duration (h)	pH
1	Water soluble	MilliQ water	10:1	40	4	25	24	
2	Exchangeable	1 M ammonium sulfate	10:1	40	4	25	24	5.0
3	Carbonate	0.11 M acetic acid	10:1	35	3.5	25	24	3.0
4	Mn oxides	0.1 M hydroxylammonium chloride	50:3	50	3	25	0.5	3.5
5	Amorphous Fe oxides	0.2 M ammonium oxalate + 0.2 M oxalic acid in dark	20:1	50	2.5	25	4	3.0
6	Crystalline Fe oxides	0.2 M ammonium oxalate + 0.2 M oxalic acid + 0.1 M ascorbic acid	20:1	40	2	80	0.5	2.3
7	Organics and sulfides*	1) 30% H_2O_2	10:1	10	1.0	25/85	1 + 1	2-3
		2) 30% H_2O_2	10:1	10	1.0	85	1	2-3
		3) 1M ammonium acetate wash	50:1	50	1.0	25	16	2.0
8	Residual	$LiBO_2$ digestion	-	-	0.1	-	-	-

Follow Taggart et al ., 7- step sequential process to recover REE from fly ash

- **Material Fly ash 345**
  - Dry fly ash from a pulverized coal power plant in Ohio.
  - Coal seams unidentified.
  - Class F fly ash (>70%)
    - SiO_2+Al_2O_3+Fe_2O_3: ~87%
  - Phases:
    - Major: quartz, glass
    - Intermediate: hematite, mullite, magnetit
  - 92% of REE in glassy phase



Sequential extraction of REE from fly ash 345

By Mengling Stuckman and Christina Lopano

Summary of 7-step sequential extraction

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- 86% of REE associated with residual phase
- 8.3% of total REE was bound to organic matters and sulfides
- 3.7% was ion exchangeable
- 1.5 % was associated with carbonate
- Majority of REE deposited in residual phases were mostly embedded in glassy phases and/or associated with Al-Si-oxides.
- Can we extract more REE from fly ash ?
- Can we combine physical separation and chemical extraction to recover more REE from fly ash ?

Prior study *via* size, density and magnetic separation of REE from fly ash 345

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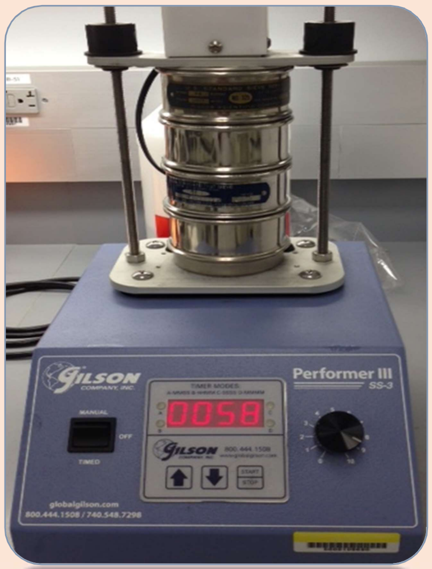
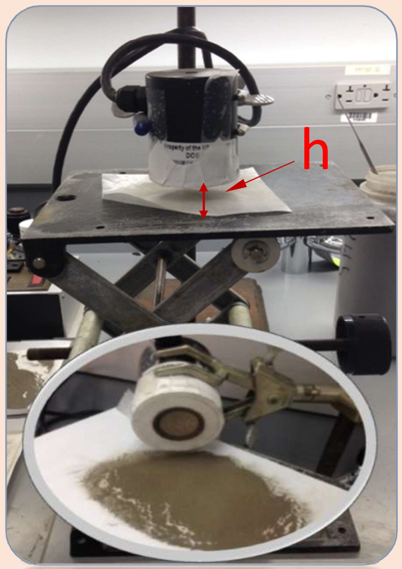
Size Separation



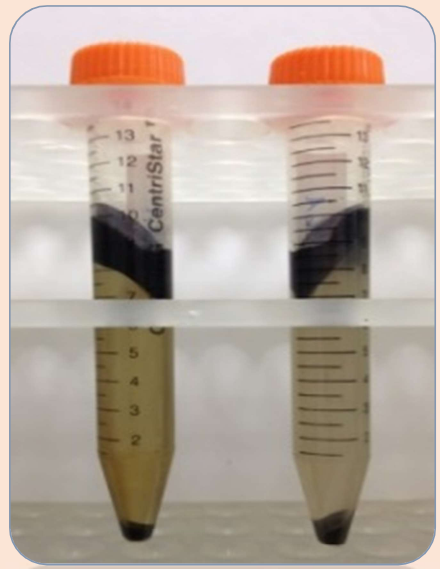
100 - 635 mesh

Magnetic Separation



h= 0.3, 0.5, 1.0, 1.5, 2.0 cm

Density Separation



Bottom Dense Fraction

Enrichment Factor and REE Recovery

Sample ID	Size		Magnetic		Density	
	EF_{max}	R (%)	EF_{max}	R (%)	EF_{max}	R (%)
345 (FA)	1.04	13.14	1.13	49.79	1.27	37.15

Enrichment Factor:

$$EF_i = \frac{REE_i}{\sum_{i=1}^{n}(REE_i W_i)}$$

Recovery:

$$\mathrm{R}(\%) = \frac{REE_i W_i}{\sum_{i=1}^{n}(REE_i W_i)}$$

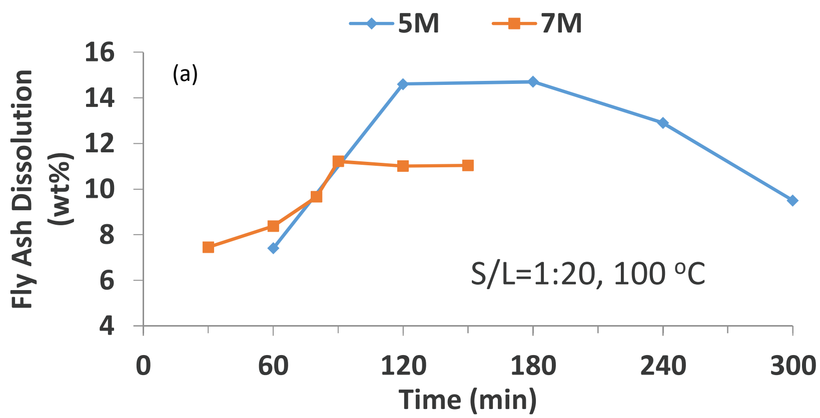
Lin et al. (2017), Fuel 200, 506-520

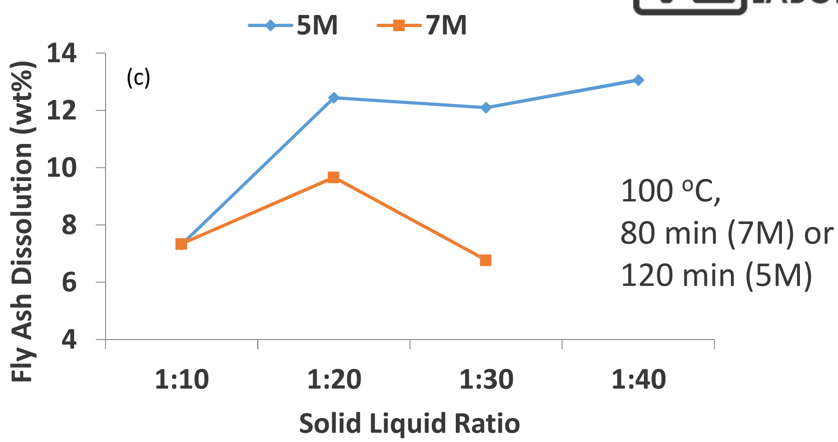
Approaches in current study

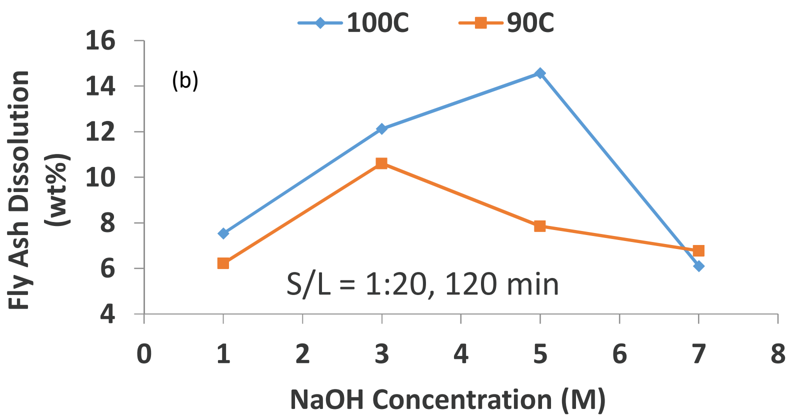
- The combination of physical separation (size, density, and magnetic) with alkaline treatment (NaOH) to dissolve glassy phases of separated fly ash
- Goal : to determine the optimum conditions of alkaline treatment such as concentrations, temperature, treatment time and solid to liquid ratios

  - NaOH concentration: 1-7M
  - S/L ratio: 1:10 – 1:40
  - Temperature: 90 and 100 ^{o}C
  - Time of treatment : 30-300 min

Optimal NaOH HT Conditions







Key findings:

- High temperature favors dissolution
- Low temperature favors zeolitization
- High concentration favors both dissolution and zeolitization
- Optimal conditions
  - 5M NaOH, 100 °C, 2hr, 1:20

Precipitation In NaOH solution with conditions of 5M NaOH, 120 min, 100 °C, S/L=1:20

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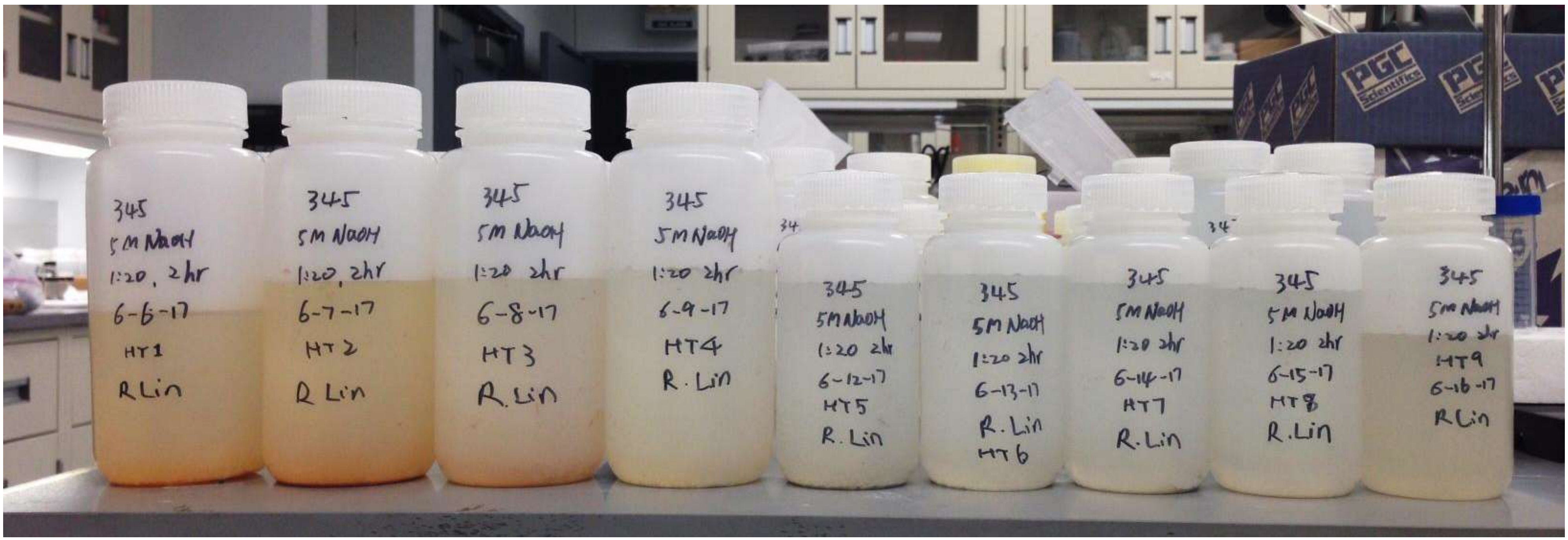
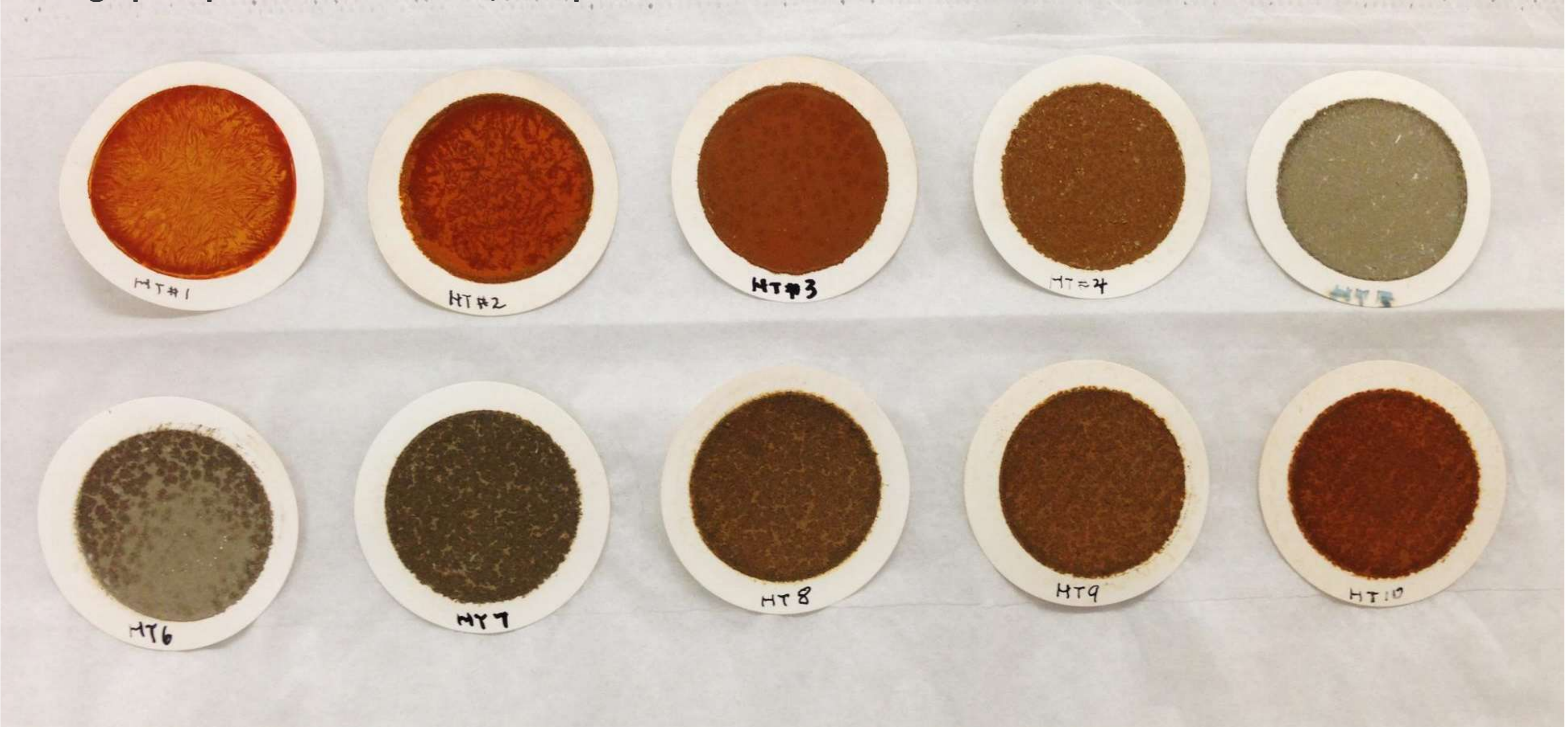


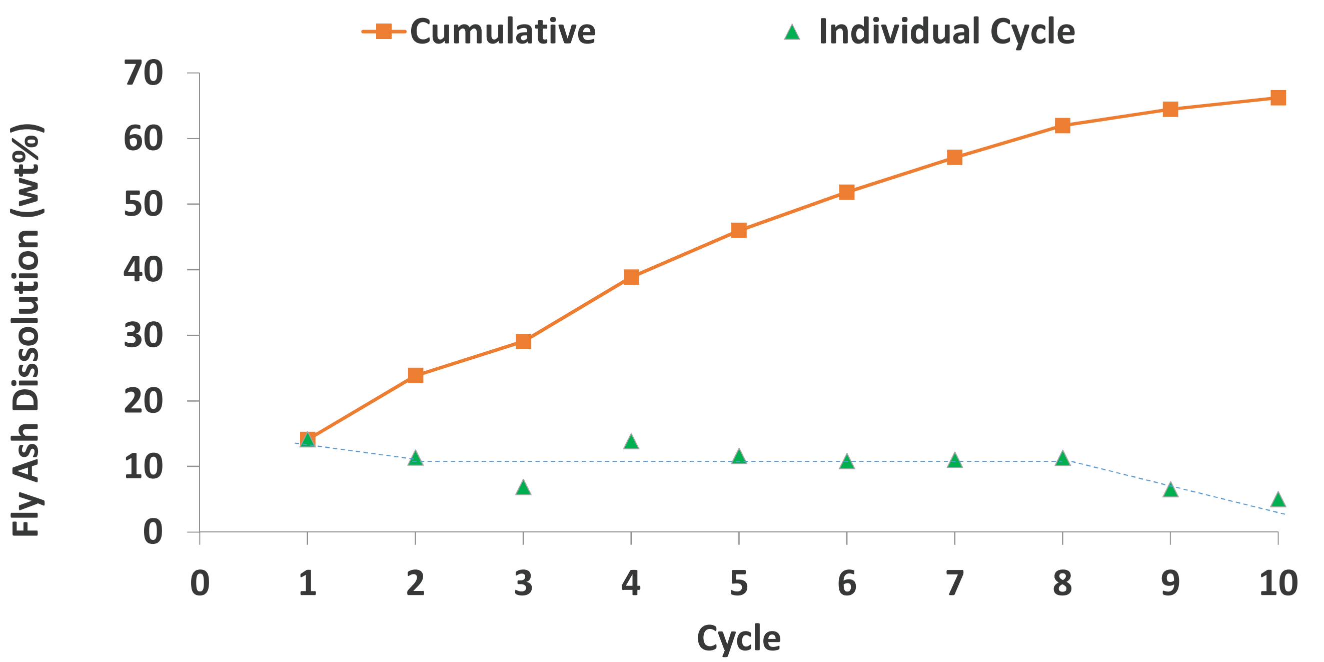
Precipitation and Ash from NaOH Solution after each treatment

Orange precipitation: Fe:Ti = 3:1, composition and structure to be determined.



Fly ash dissolution vs. cycle of NaOH HT

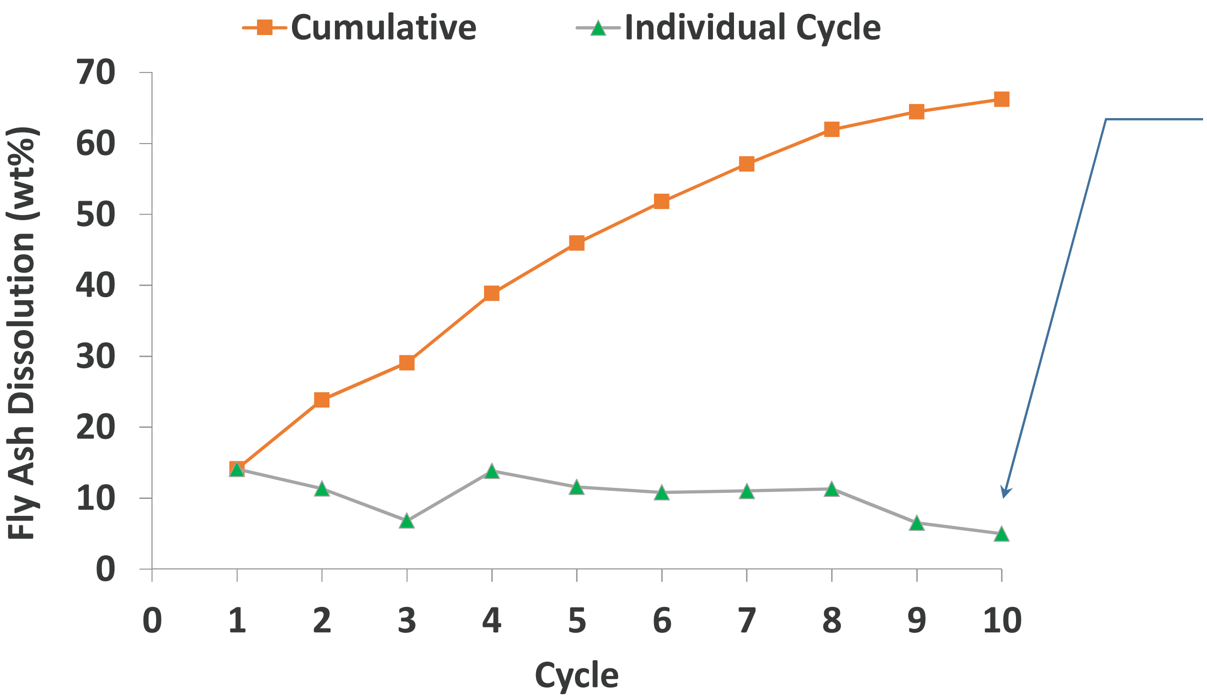
After 10 cycles, 66 wt.% of the ash was dissolved.

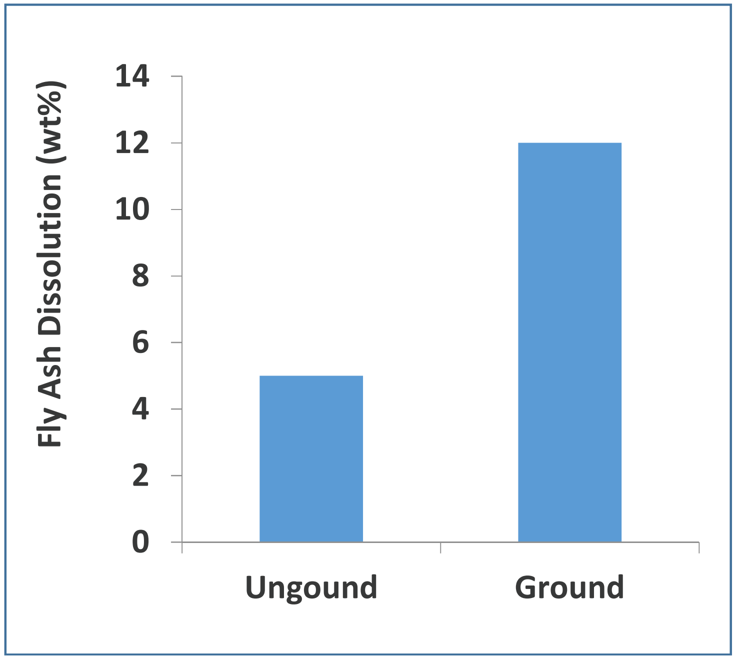


Composition of Major Oxides after 10 cycles of NaOH HT treatment

Oxides	Before NaOH HT (%)	After NaOH HT (%)	Dissolved (%)
Na_2O	0.6	3.5	0
MgO	0.7	2.2	0
Al_2O_3	22	19	70
SiO_2	58	26	85
K_2O	2	0	100
CaO	60	17	0
TiO_2	1.1	3.2	0
Fe_2O_3	9.8	29	0

Grinding Promotes Ash Dissolution





Impact of HCl Pretreatment

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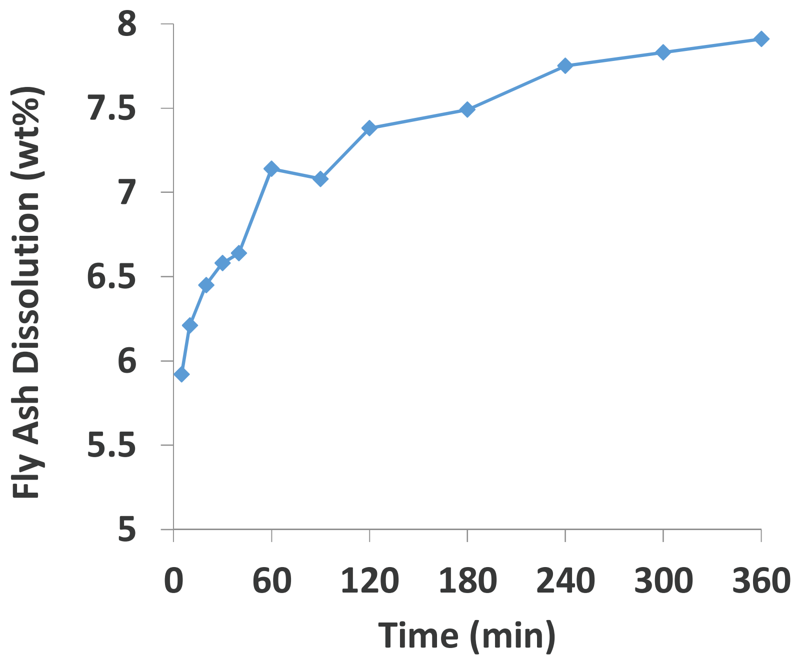
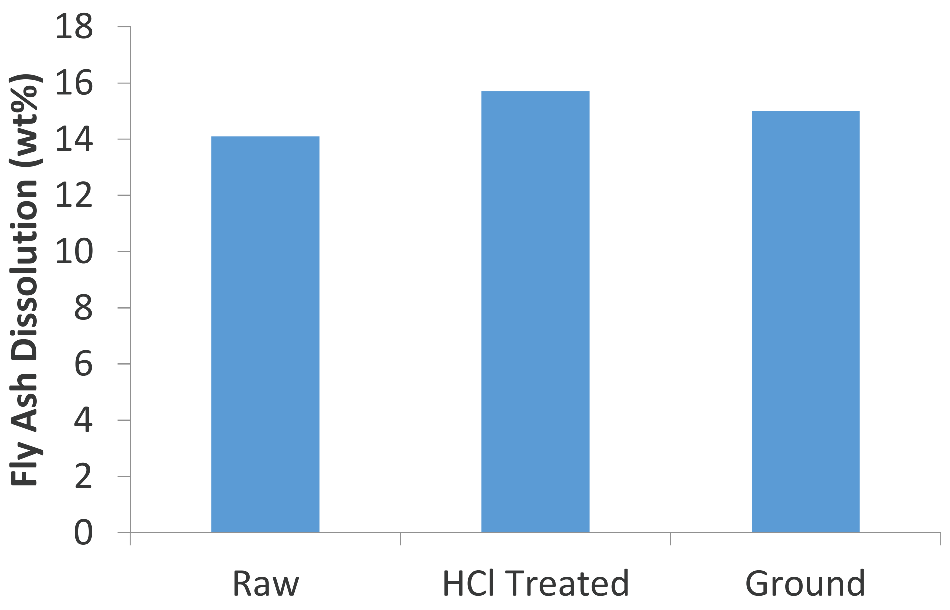
HCl pretreatment showed a negligible effect on fly ash dissolution by NaOH HT.





Concentrations of elements in the post-treatment solution after each cycle

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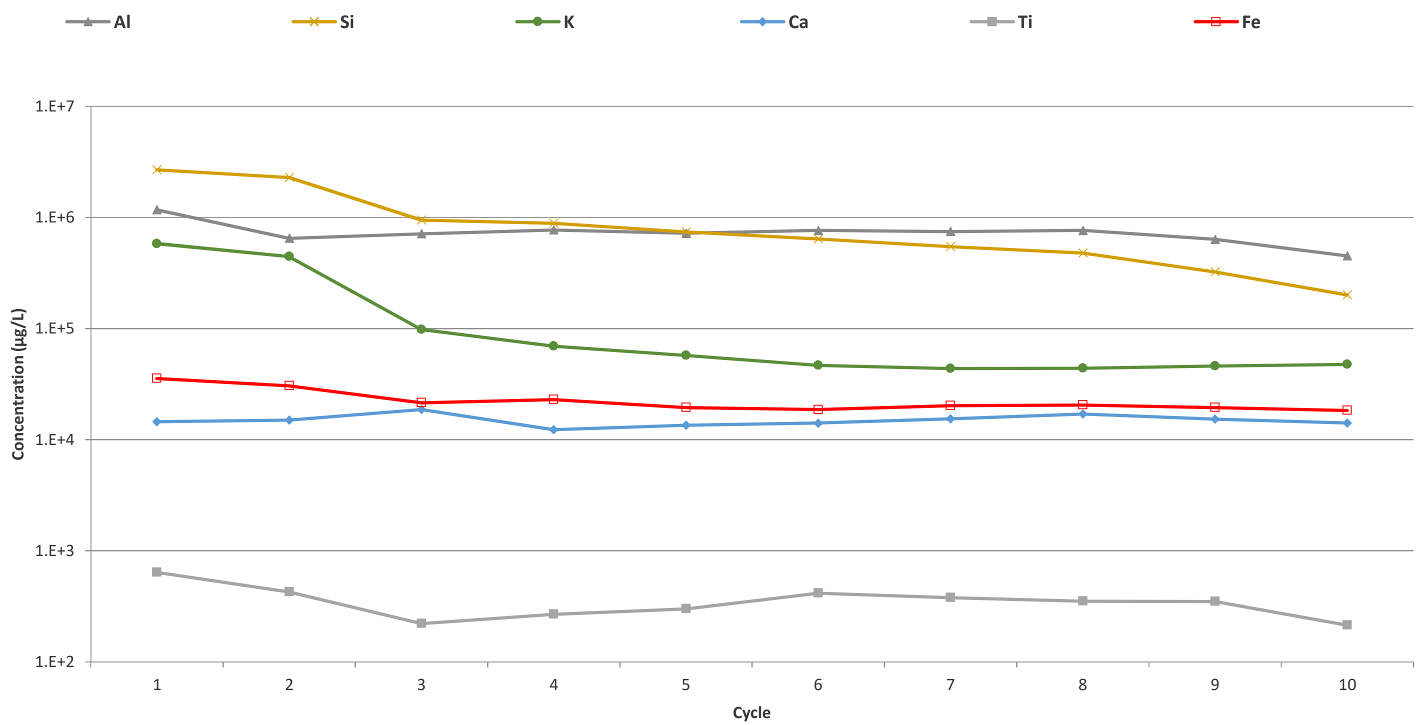
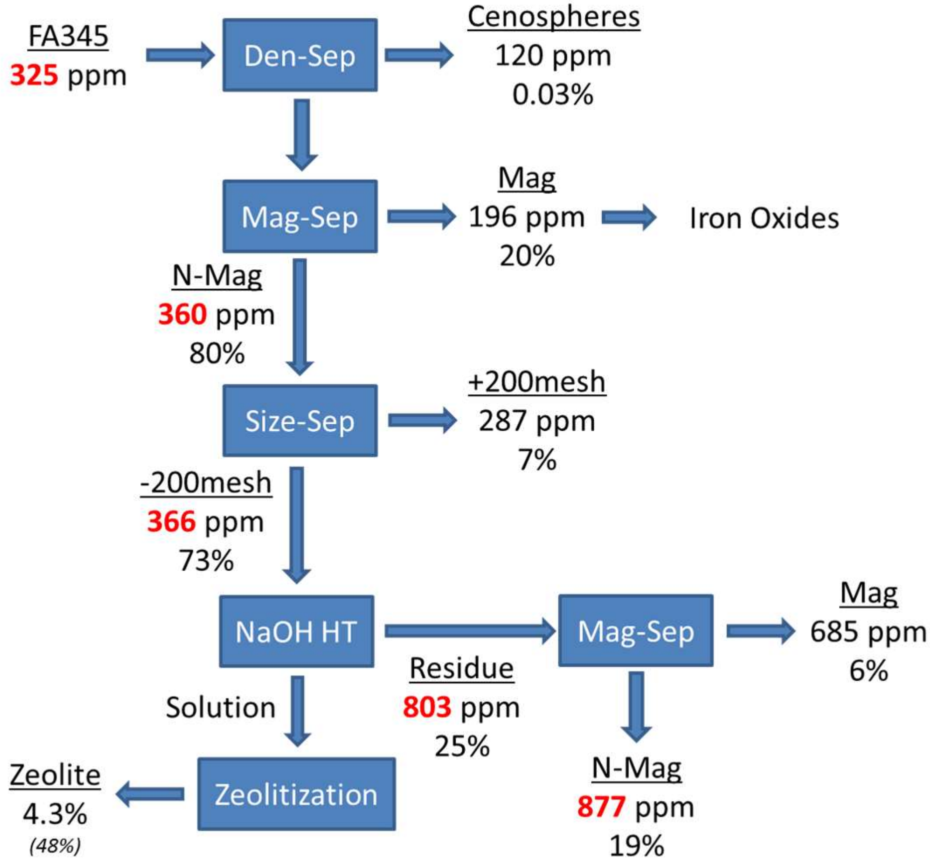


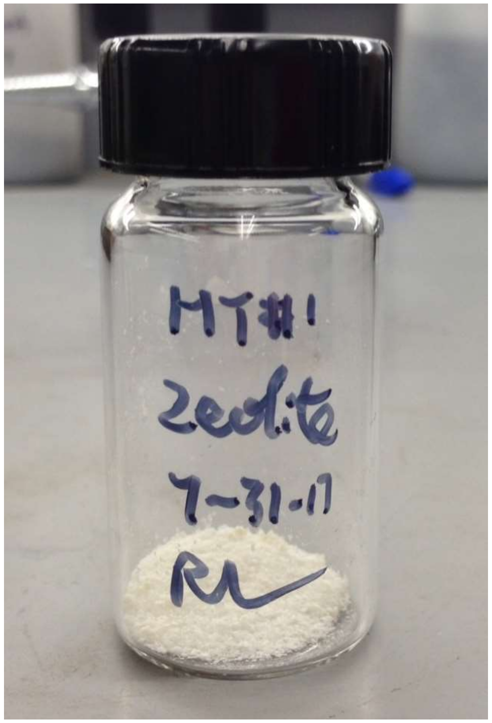
Final Results

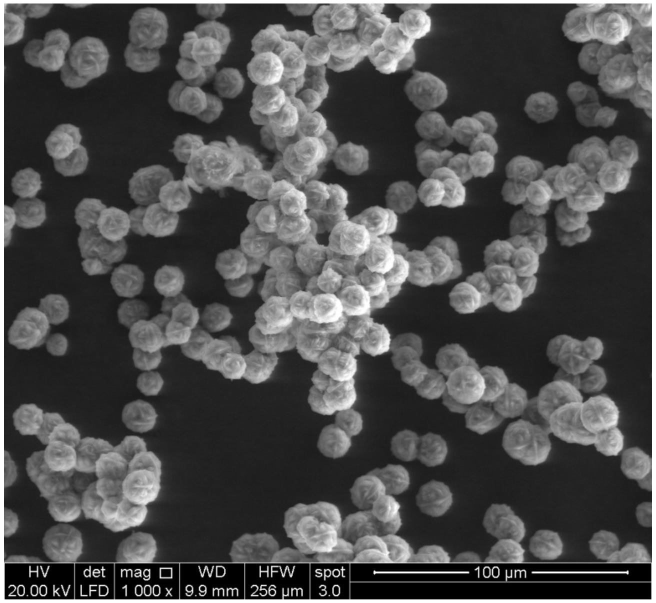
A combination of physical separations and NaOH HT resulted in REE enrichment by a factor of 2.7.

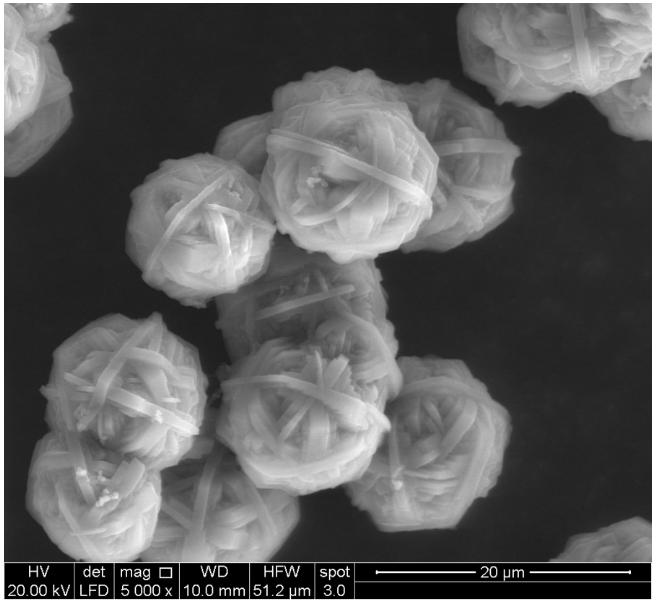


Zeolites from Coal Fly Ash

Zeolites formed only in the solution from the first cycle of NaOH HT.







Summary

- **Optimal NaOH HT conditions were determined.**
  - 5M NaOH, 120 min, 100 ^{o}C, S/L=1:20
- **Multi-cycle HT dissolved ~66% glassy phase.**
  - Al_2O_3 70%, SiO_2 85%, and K_2O 100%
- **A combination of physical separations and NaOH HT resulted in REE enrichment by a factor of 2.7.**
- **Grinding promotes ash dissolution.**
- **HCl pretreatment showed negligible effect on NaOH HT of fly ash.**

Future Work

- **Process development and optimization**
  - Recycle NaOH to minimize NaOH consumption
  - Add flotation to the process
- **Process scale-up to produce more samples for additional experiments**
  - e.g. flotation tests
- **Zeolites from fly ash**
  - Zeolitization process optimization
  - Zeolite characterization
  - Potential applications of zeolites

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