

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



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Solutions for Today | Options for Tomorrow



What Are Rare Earth Elements (REE)

Periodic Table of the Elements

1 IA 1A	2 IIA 2A											13 IIIA 3A	14 IVA 4A	15 VA 5A	16 VIA 6A	17 VIIA 7A	18 VIIIA 8A
1 H Hydrogen 1.008	4 Be Beryllium 9.012											5 B Boron 10.811	6 C Carbon 12.011	7 N Nitrogen 14.007	8 O Oxygen 15.999	9 F Fluorine 18.998	10 Ne Neon 20.180
11 Na Sodium 22.990	12 Mg Magnesium 24.305	21 Sc Scandium 44.956	22 Ti Titanium 47.867	23 V Vanadium 50.942	24 Cr Chromium 51.996	25 Mn Manganese 54.938	26 Fe Iron 55.845	27 Co Cobalt 58.933	28 Ni Nickel 58.693	29 Cu Copper 63.546	30 Zn Zinc 65.38	31 Ga Gallium 69.723	32 Ge Germanium 72.631	33 As Arsenic 74.922	34 Se Selenium 78.971	35 Br Bromine 79.904	36 Kr Krypton 84.798
37 Rb Rubidium 84.468	38 Sr Strontium 87.62	39 Y Yttrium 88.906	40 Zr Zirconium 91.224	41 Nb Niobium 92.906	42 Mo Molybdenum 95.95	43 Tc Technetium 98.907	44 Ru Ruthenium 101.07	45 Rh Rhodium 102.906	46 Pd Palladium 106.42	47 Ag Silver 107.868	48 Cd Cadmium 112.411	49 In Indium 114.818	50 Sn Tin 118.711	51 Sb Antimony 121.760	52 Te Tellurium 127.6	53 I Iodine 126.904	54 Xe Xenon 131.294
55 Cs Cesium 132.905	56 Ba Barium 137.328	57-71 Lanthanide Series	72 Hf Hafnium 178.49	73 Ta Tantalum 180.948	74 W Tungsten 183.84	75 Re Rhenium 186.207	76 Os Osmium 190.23	77 Ir Iridium 192.227	78 Pt Platinum 195.085	79 Au Gold 196.967	80 Hg Mercury 200.592	81 Tl Thallium 204.383	82 Pb Lead 207.2	83 Bi Bismuth 208.980	84 Po Polonium [209]	85 At Astatine 209.987	86 Rn Radon 222.018
87 Fr Francium 223.020	88 Ra Radium 226.025	89-103 Actinide Series	104 Rf Rutherfordium [261]	105 Db Dubnium [262]	106 Sg Seaborgium [266]	107 Bh Bohrium [264]	108 Hs Hassium [269]	109 Mt Meitnerium [268]	110 Ds Darmstadtium [269]	111 Rg Roentgenium [272]	112 Cn Copernicium [277]	113 Uut Ununtrium unknown	114 Fl Flerovium [289]	115 Uup Ununpentium unknown	116 Lv Livermorium [293]	117 Uus Ununseptium unknown	118 Uuo Ununoctium unknown
Lanthanide Series			57 La Lanthanum 138.905	58 Ce Cerium 140.116	59 Pr Praseodymium 140.908	60 Nd Neodymium 144.243	61 Pm Promethium 144.913	62 Sm Samarium 150.36	63 Eu Europium 151.964	64 Gd Gadolinium 157.25	65 Tb Terbium 158.925	66 Dy Dysprosium 162.500	67 Ho Holmium 164.930	68 Er Erbium 167.259	69 Tm Thulium 168.934	70 Yb Ytterbium 173.055	71 Lu Lutetium 174.967
Actinide Series			89 Ac Actinium 227.028	90 Th Thorium 232.038	91 Pa Protactinium 231.036	92 U Uranium 238.029	93 Np Neptunium 237.048	94 Pu Plutonium 244.064	95 Am Americium 243.061	96 Cm Curium 247.070	97 Bk Berkelium 247.070	98 Cf Californium 251.080	99 Es Einsteinium [254]	100 Fm Fermium 257.095	101 Md Mendelevium 258.1	102 No Nobelium 259.101	103 Lr Lawrencium [262]

Light REE (LREE)
Heavy REE (HREE)

Alkali Metal

Alkaline Earth

Transition Metal

Basic Metal

Semimetal

Nonmetal

Halogen





Noble Gas

Lanthanide

Actinide

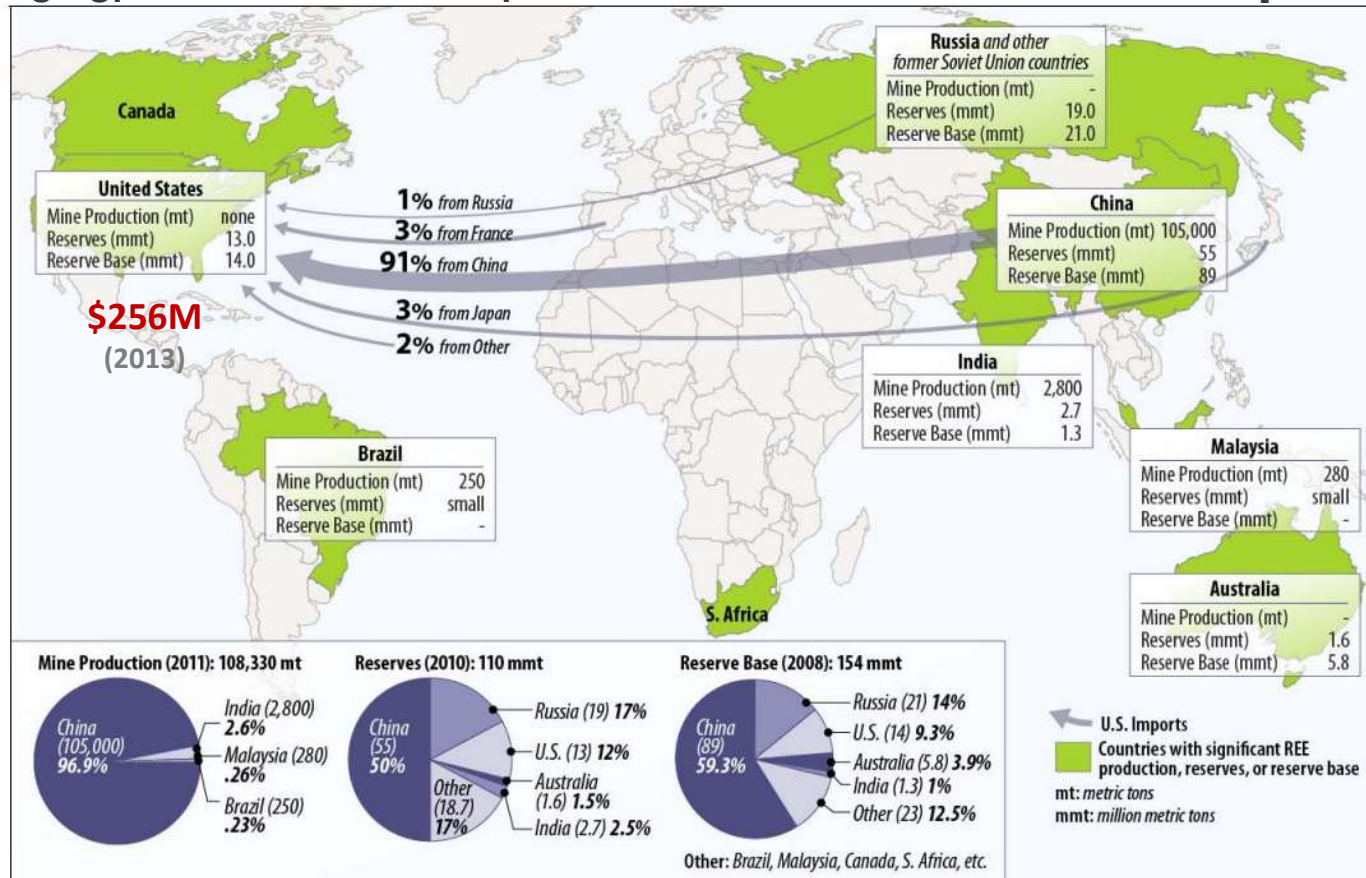
REE applications

ENERGY PRODUCTION	ENERGY REDUCTION	ENERGY EFFICIENCY	LIFESTYLE
			
Petroleum Refining La	UV Filters in Glass Ce	New Generation Vehicles Nd Sm	Colour Screen LCDs/PDPs Eu Tb Y
High-Powered Electric Motors Nd Dy Tb	Reducing Fuel Consumption Nd	Rechargeable Batteries La	Components to Hardware Nd
New Generation Vehicles La	Lighter Vehicles - Improved performance Dy	Energy-Efficient Lighting Pr Eu	Medical Services Nd Gd
La (Lanthanum) Nd (Neodymium) Dy (Dysprosium) Tb (Terbium) Ce (Cerium) Sm (Samarium) Pr (Praseodymium) Eu (Europium) Y (Yttrium) Gd (Gadolinium)			
			Medical Services Ce

		
Predator Drone Neodymium, Samarium Electric Motors and Guidance	Smart Bomb Neodymium, Samarium Electric Motors and Guidance	Tomahawk Cruise Missile Neodymium, Samarium Electric Motors and Guidance
		
Night Vision Goggles Terbium, Erbium, Gadolinium Optical Lenses	F-22 Fighter Jet Europium, Yttrium Terbium, Erbium Optical Systems, Visuals and Fiber Optics	Bullet Proof Vest Yttrium Hardened Ceramics
		
Bradley Tank Yttrium Hardened Ceramics	Radar Detection Europium, Lutetium Signal Amplification	Nuclear Submarine Europium, Lutetium Sonar Detection

U.S. 100% Depends On REE Imports

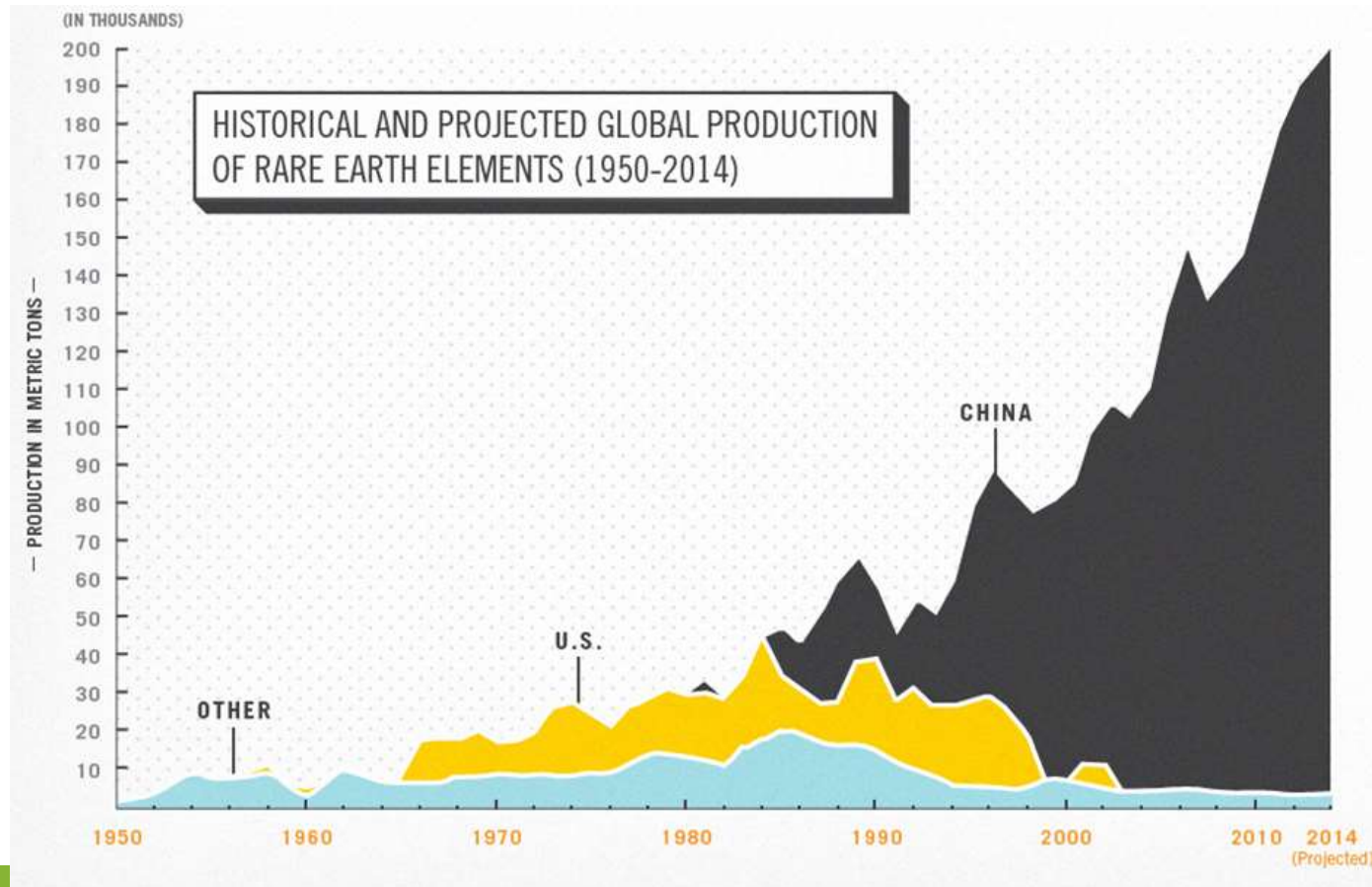
<https://www.fas.org/sgp/crs/natsec/R41347.pdf>



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

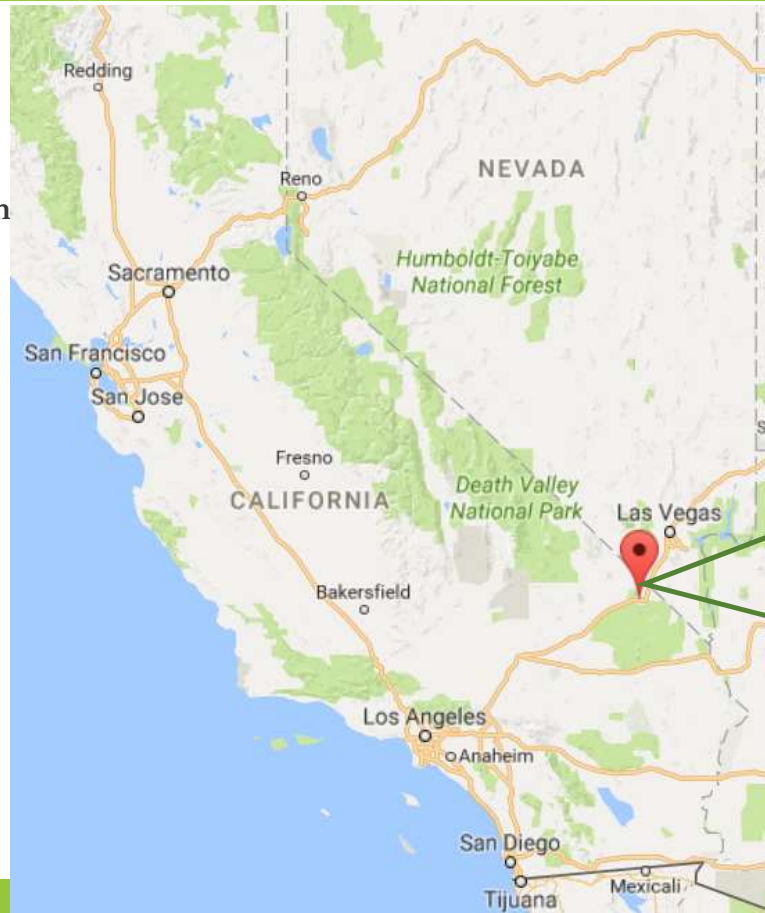
Top REE Suppliers In The World: Then and Now

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



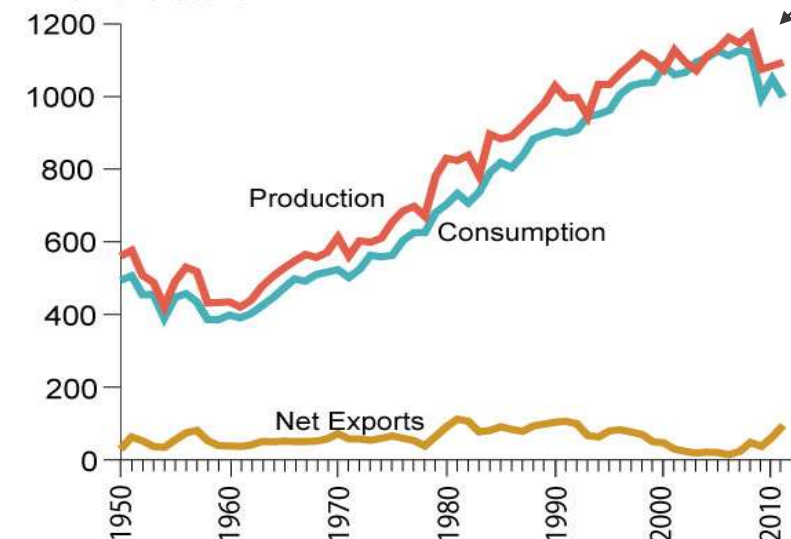
- ❖ 10% REO
- ❖ Bastnasite
- ❖ Cerium
- ❖ Lanthanum
- ❖ Neodymium
- ❖ Europium
- ❖ Estimated Reserve: 1.5 M tons

REE from Coal and Coal By-Products: Opportunities



U.S. Coal Production, Consumption, and Exports, 1950-2011

million short tons

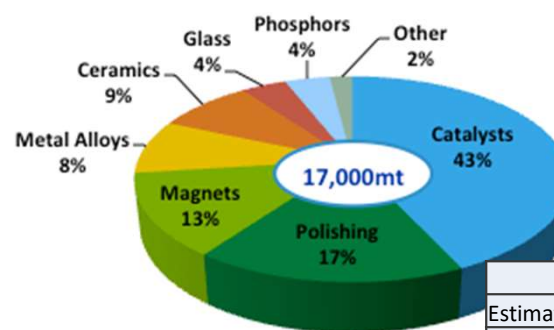


Source: U.S. Energy Information Administration, *Annual Energy Review and Quarterly Coal Report (June 2012)*, preliminary 2011 data.

~ 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

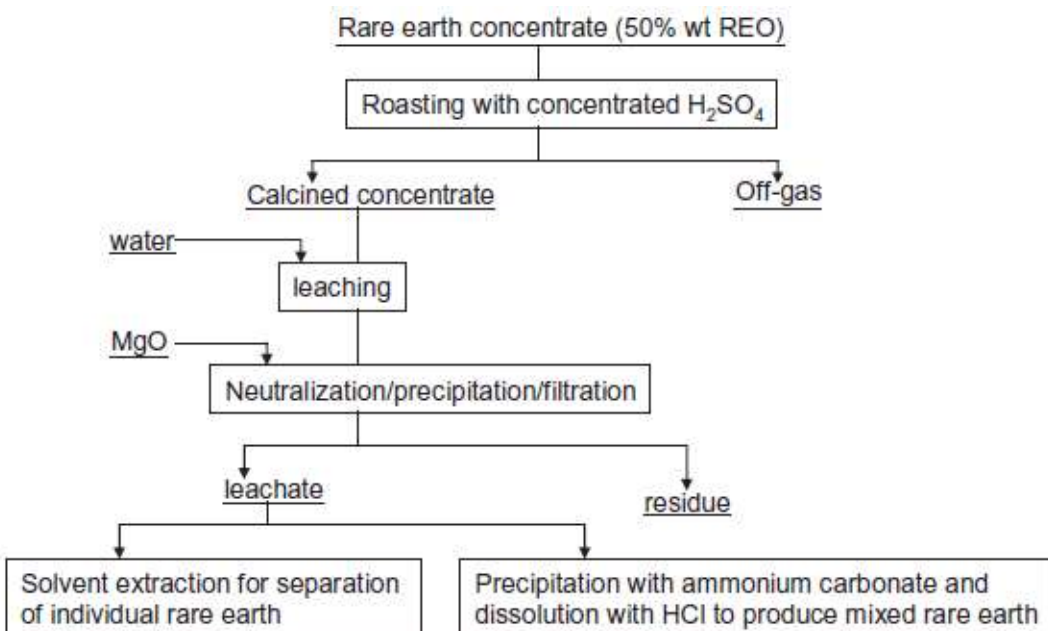


Fig. 1. Schematic leaching process used for Baotou rare earth concentrates (after Huang et al., 2006).

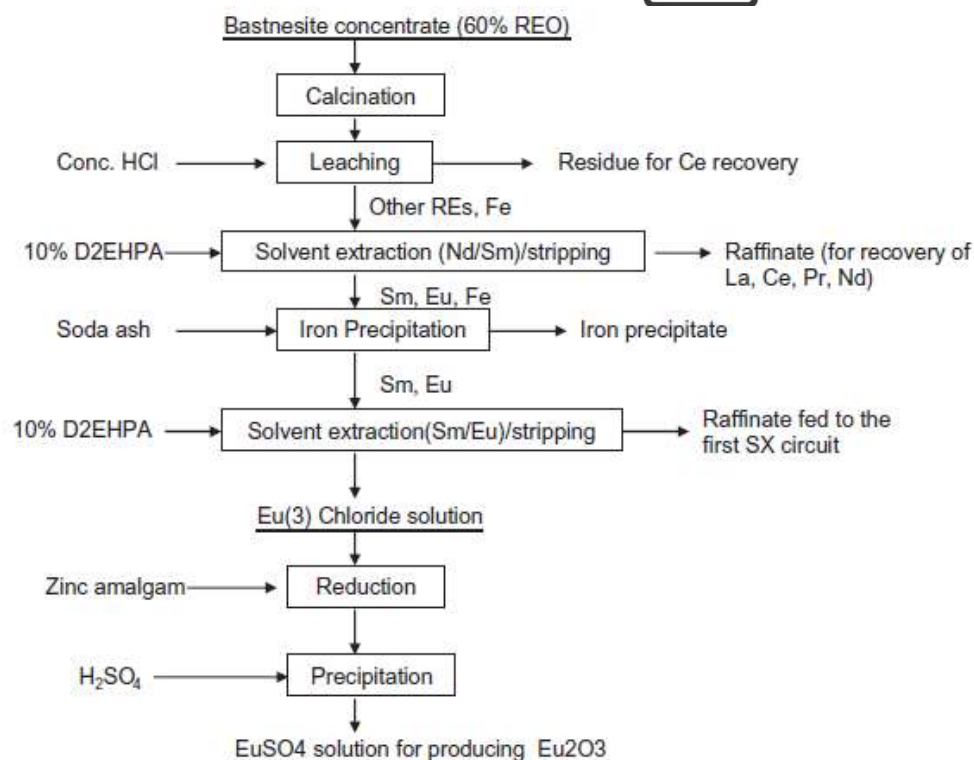


Fig. 2. Molycorp process for producing europium oxide from the bastnesite concentrate (after Gupta and Krishnamurthy, 2005).

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 ₂ O ₂	10:1	10	1.0	25/85	1 + 1	2-3
		2) 30% H ₂ O 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	-	-	-

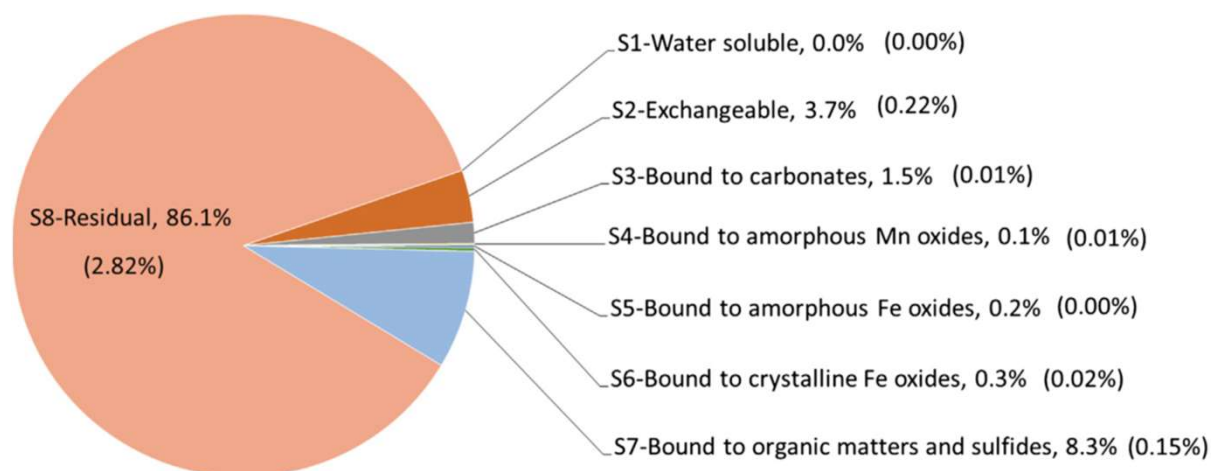
Follow Taggart et al ., 7- step sequential process to recover REE from fly ash



• Material Fly ash 345

- Dry fly ash from a pulverized coal power plant in Ohio.
- Coal seams unidentified.
- Class F fly ash (>70%)
 - $\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$: ~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



- 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 ?

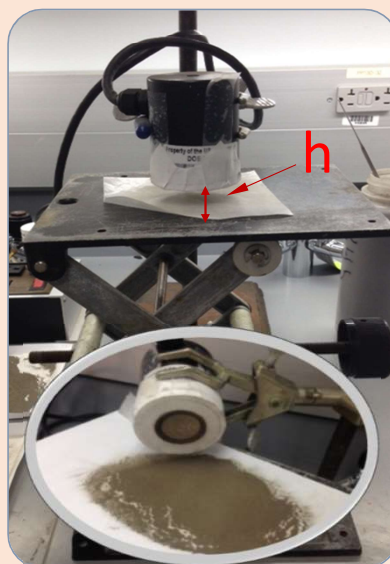
Prior study via size, density and magnetic separation of REE from fly ash 345

Size Separation



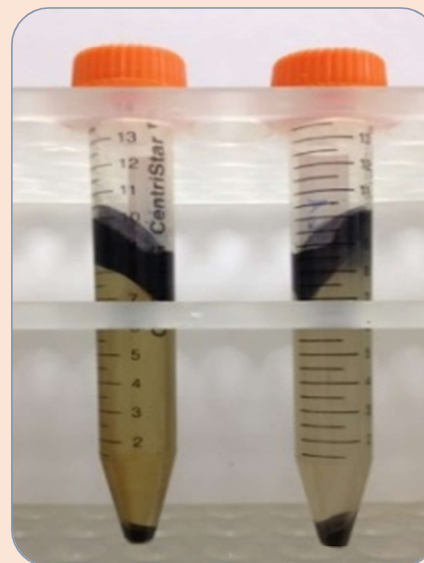
100 - 635 mesh

Magnetic Separation



$h = 0.3, 0.5, 1.0, 1.5, 2.0 \text{ cm}$

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:

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

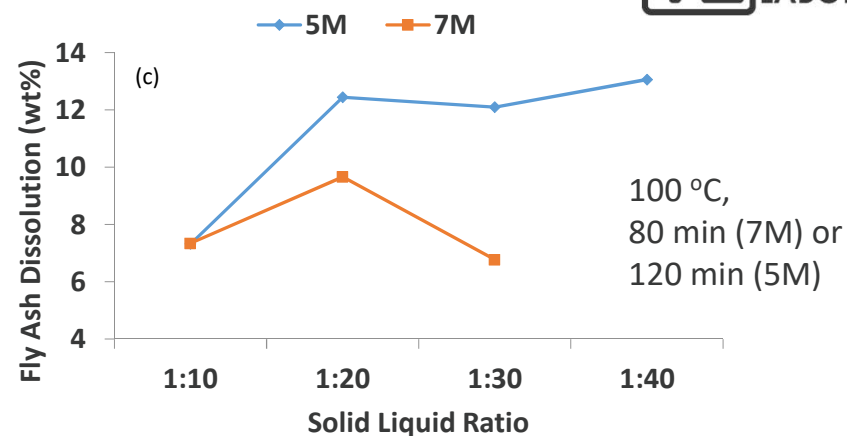
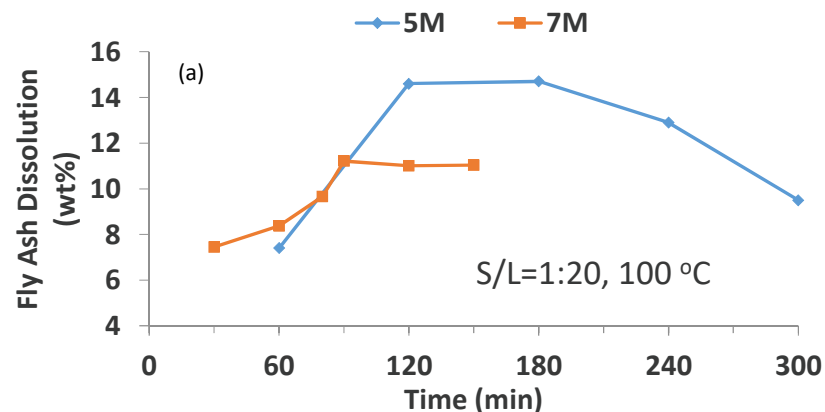
Recovery:

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

Approaches in current study

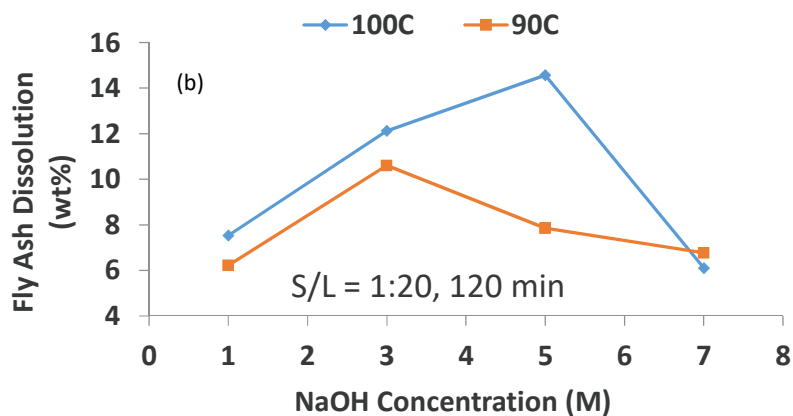
- The combination of physical separation (size, density, and magnetic) with alkaline treatment (NaOH) to dissolve glassy phases of separated fly ash
- Goal : to determine the optimum conditions of alkaline treatment such as concentrations, temperature, treatment time and solid to liquid ratios
 - NaOH concentration: 1-7M
 - S/L ratio: 1:10 – 1:40
 - Temperature: 90 and 100 °C
 - Time of treatment : 30-300 min

Optimal NaOH HT Conditions

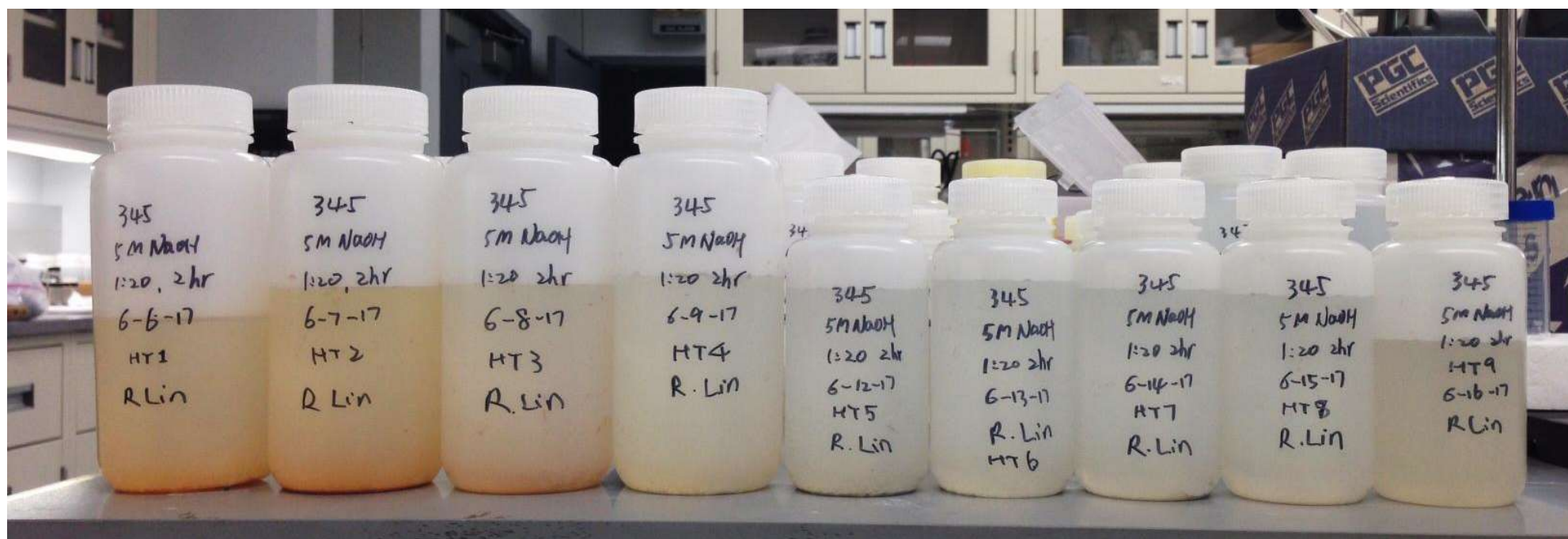


Key findings:

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

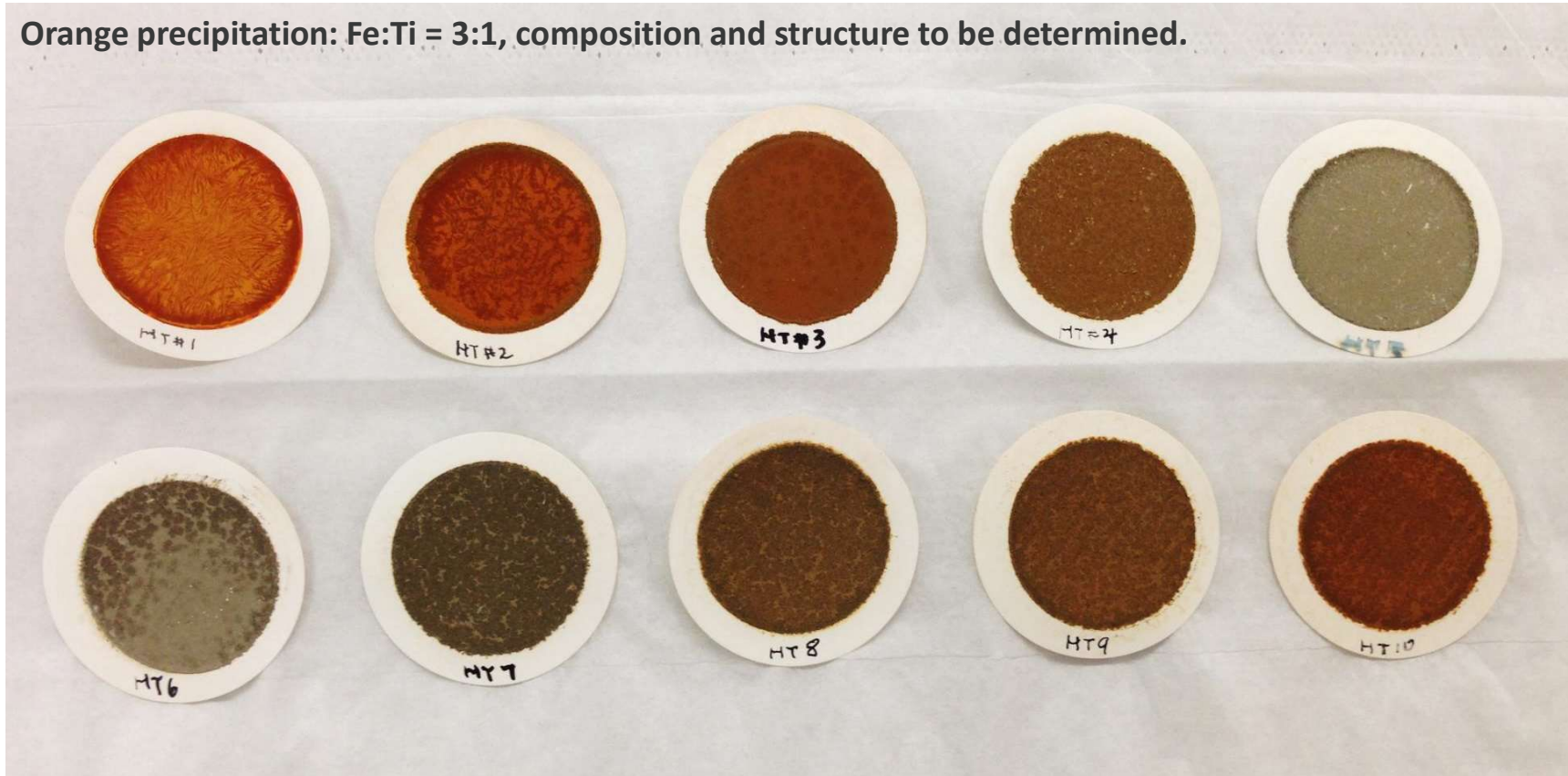


Precipitation In NaOH solution with conditions of 5M NaOH, 120 min, 100 °C, S/L=1:20



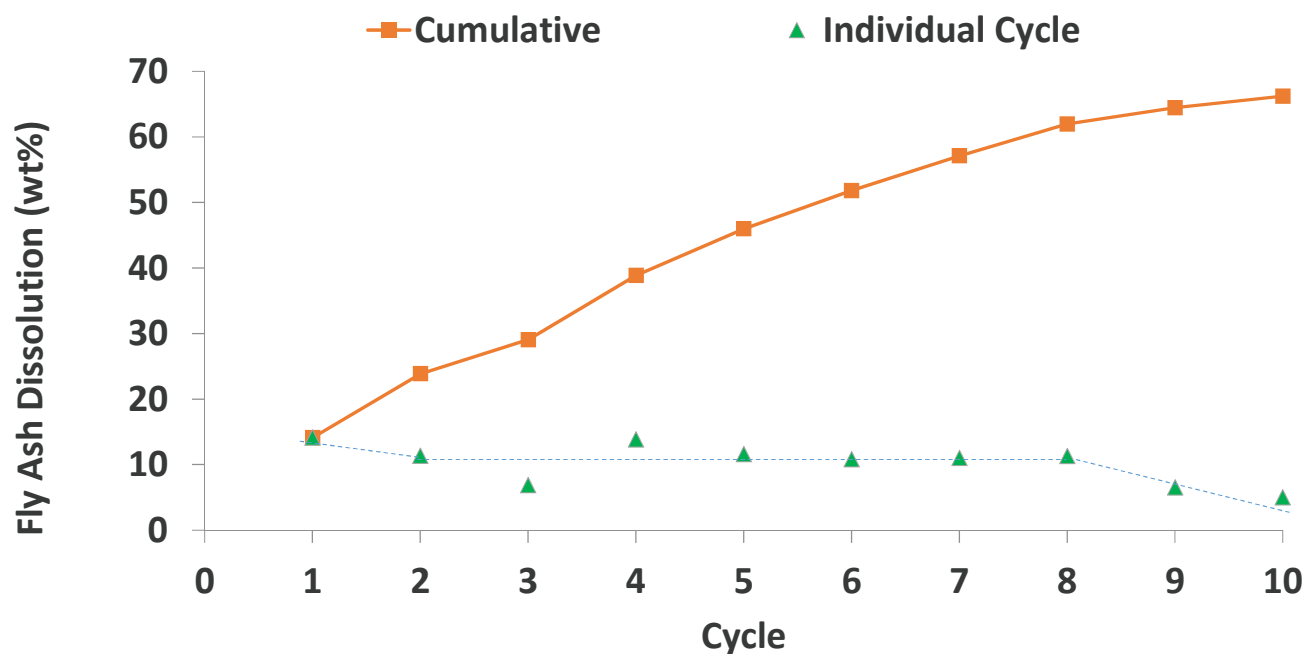
Precipitation and Ash from NaOH Solution after each treatment

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



Fly ash dissolution vs. cycle of NaOH HT

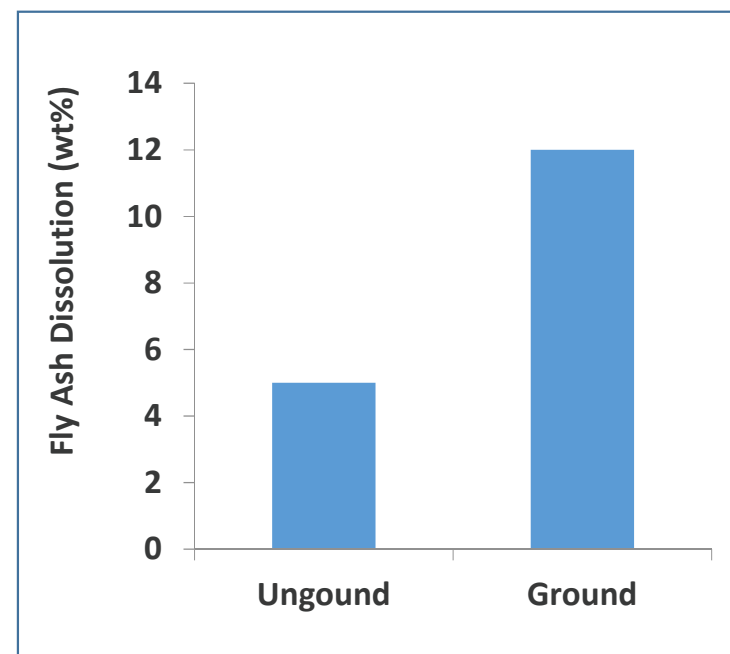
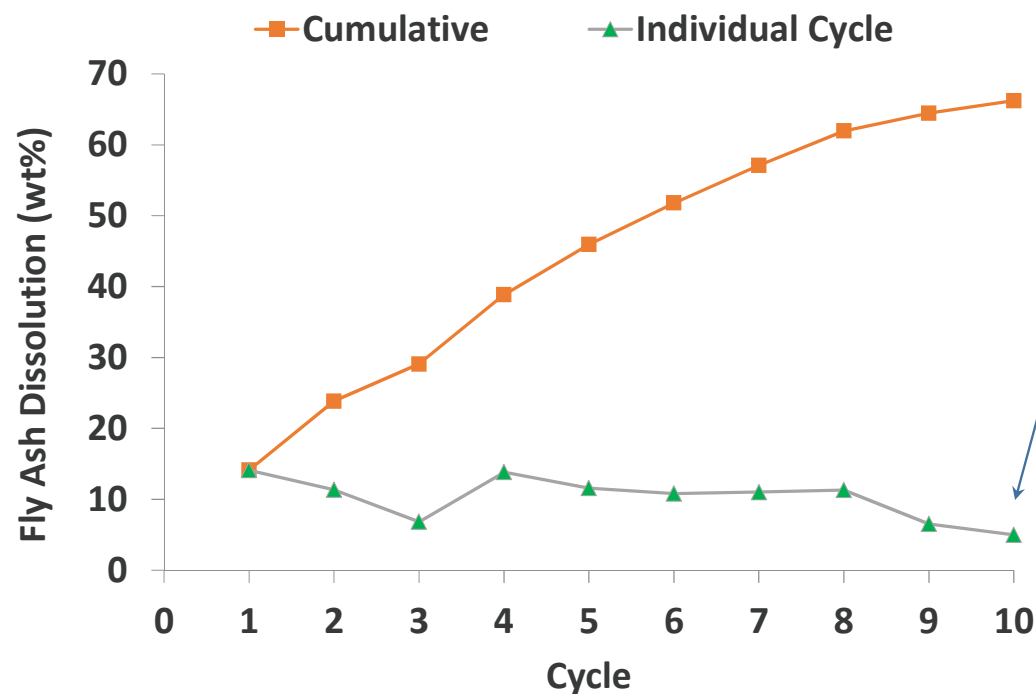
After 10 cycles, **66 wt.%** of the ash was dissolved.



Composition of Major Oxides after 10 cycles of NaOH HT treatment

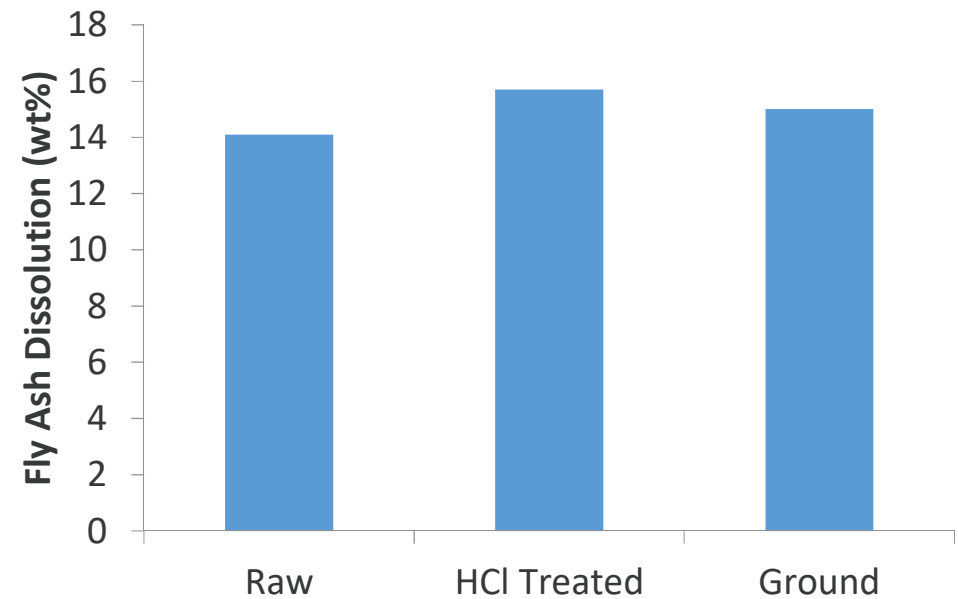
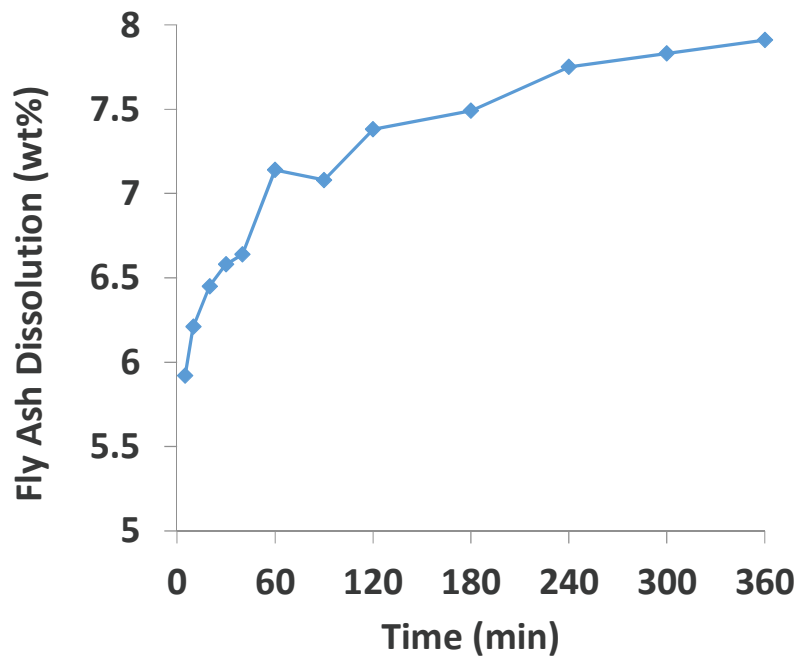
Oxides	Before NaOH HT (%)	After NaOH HT (%)	Dissolved (%)
Na ₂ O	0.6	3.5	0
MgO	0.7	2.2	0
Al ₂ O ₃	22	19	70
SiO ₂	58	26	85
K ₂ O	2	0	100
CaO	60	17	0
TiO ₂	1.1	3.2	0
Fe ₂ O ₃	9.8	29	0

Grinding Promotes Ash Dissolution

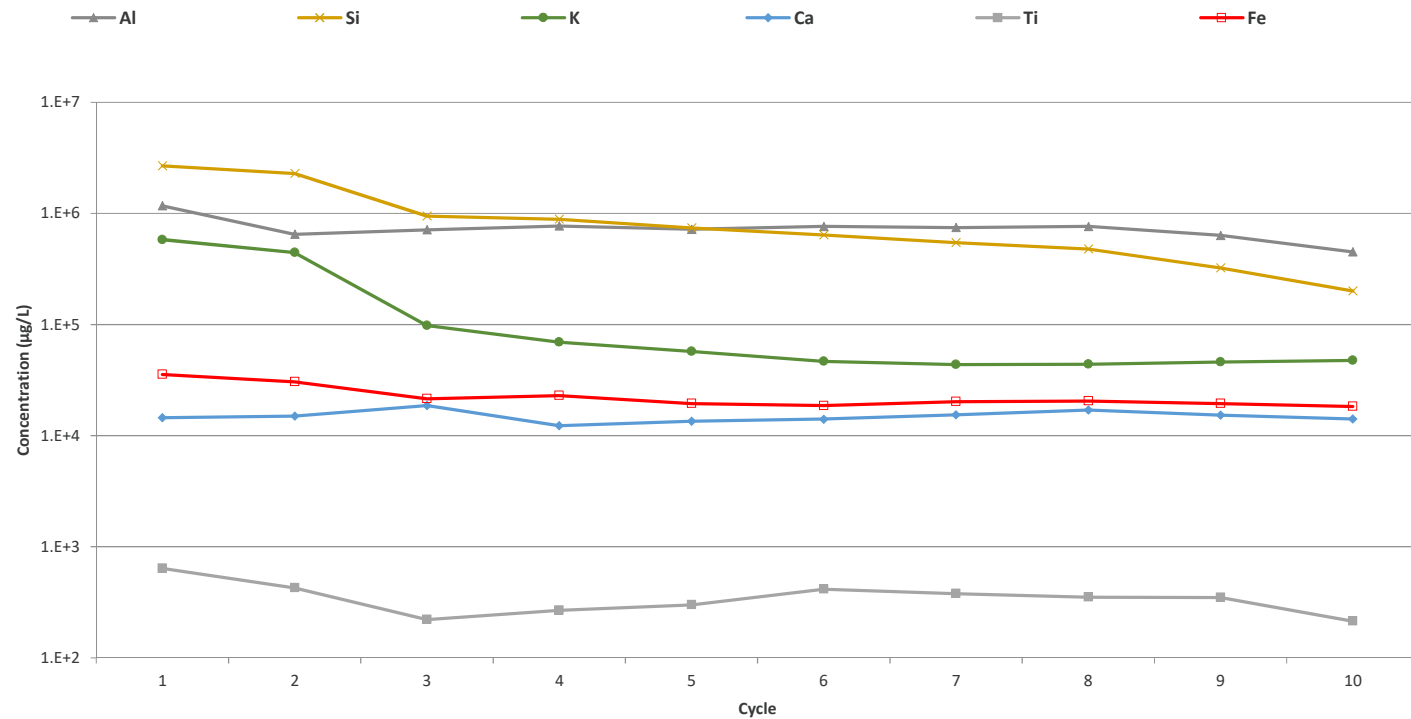


Impact of HCl Pretreatment

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

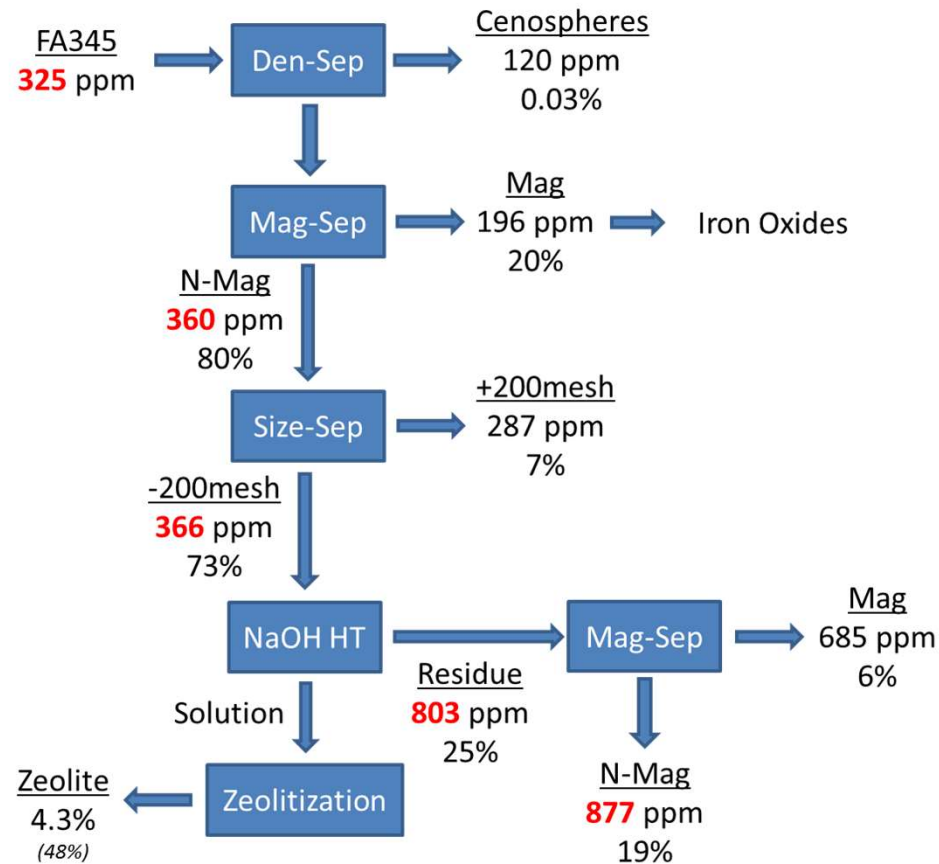


Concentrations of elements in the post-treatment solution after each cycle



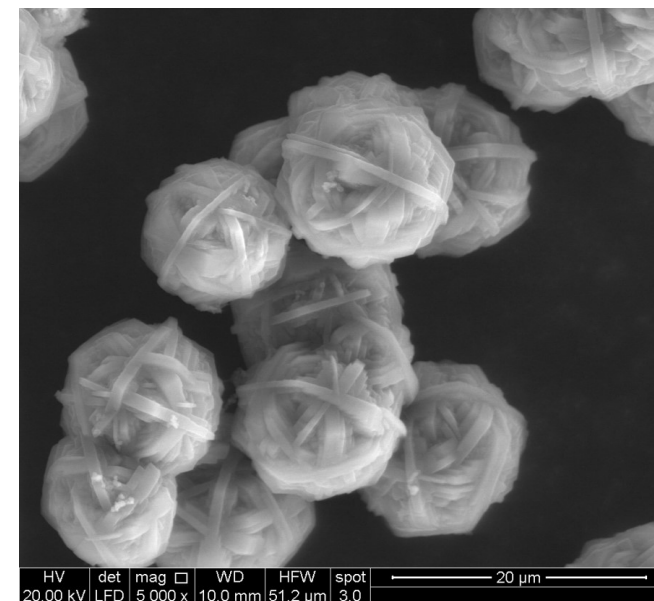
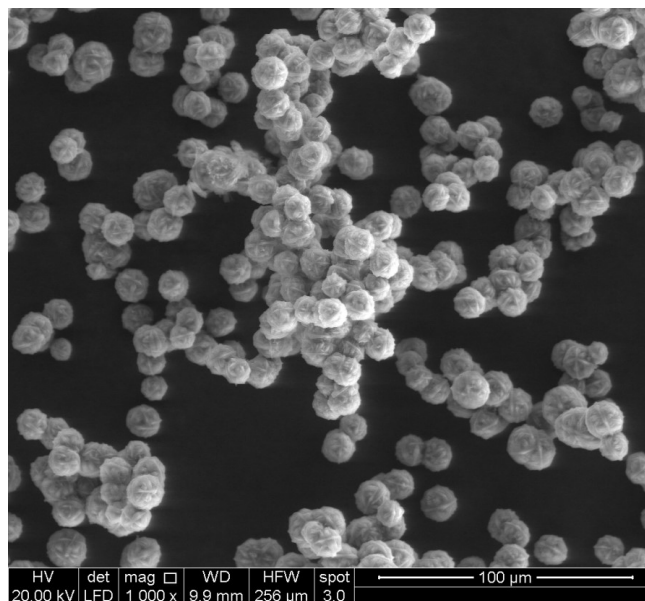
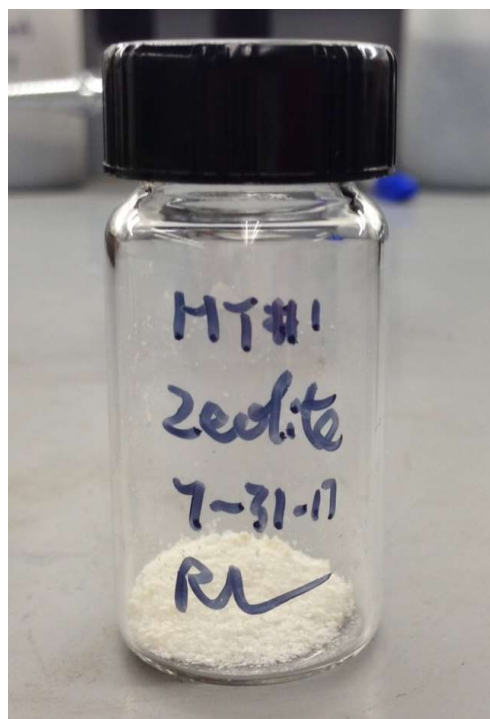
Final Results

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 °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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