Extraction of Rare Earth Elements from Coal Waste

Dr. Wencai Zhang

Assistant Professor

Department of Mining & Minerals Engineering, Virginia Tech

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VIRGINIA TECH

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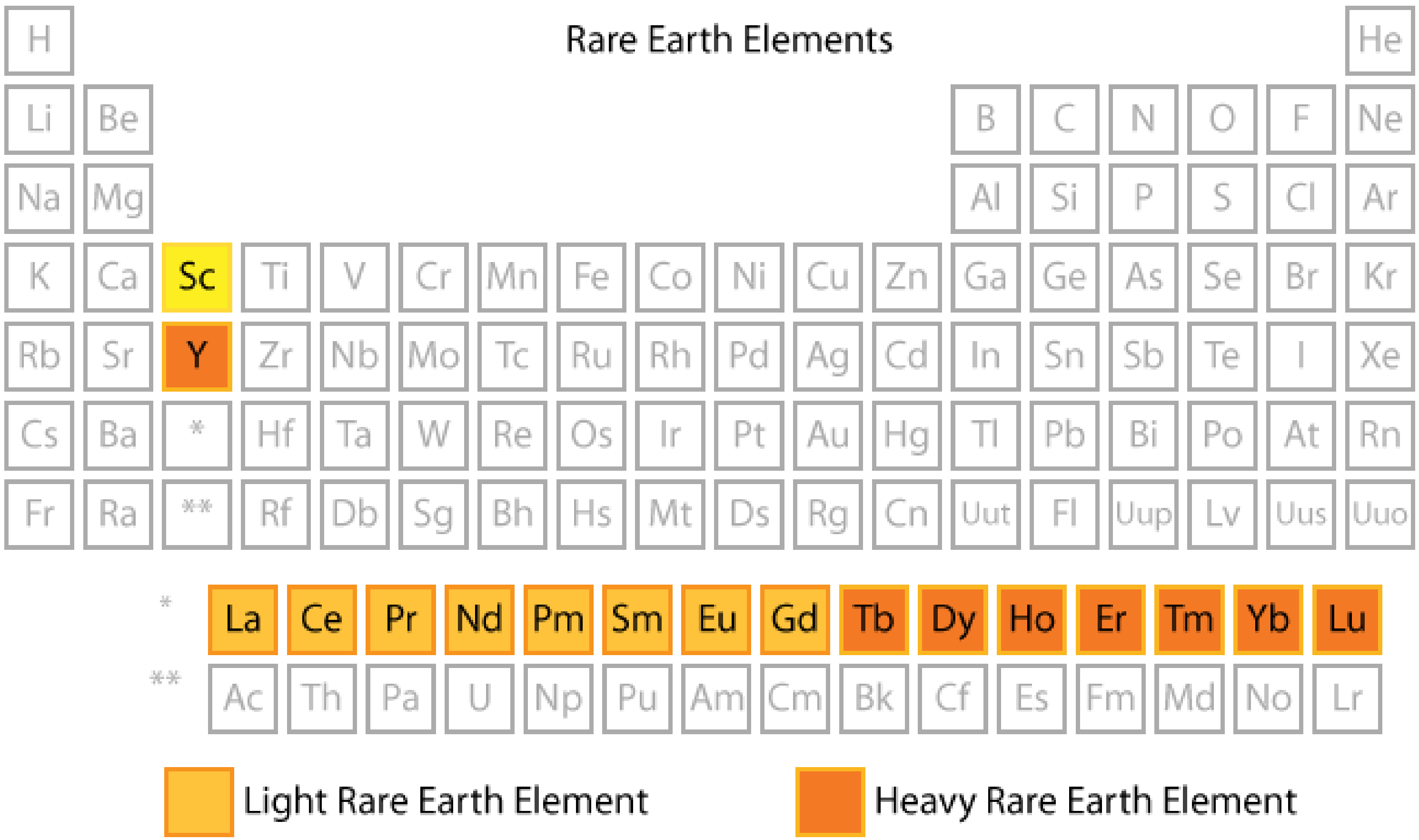
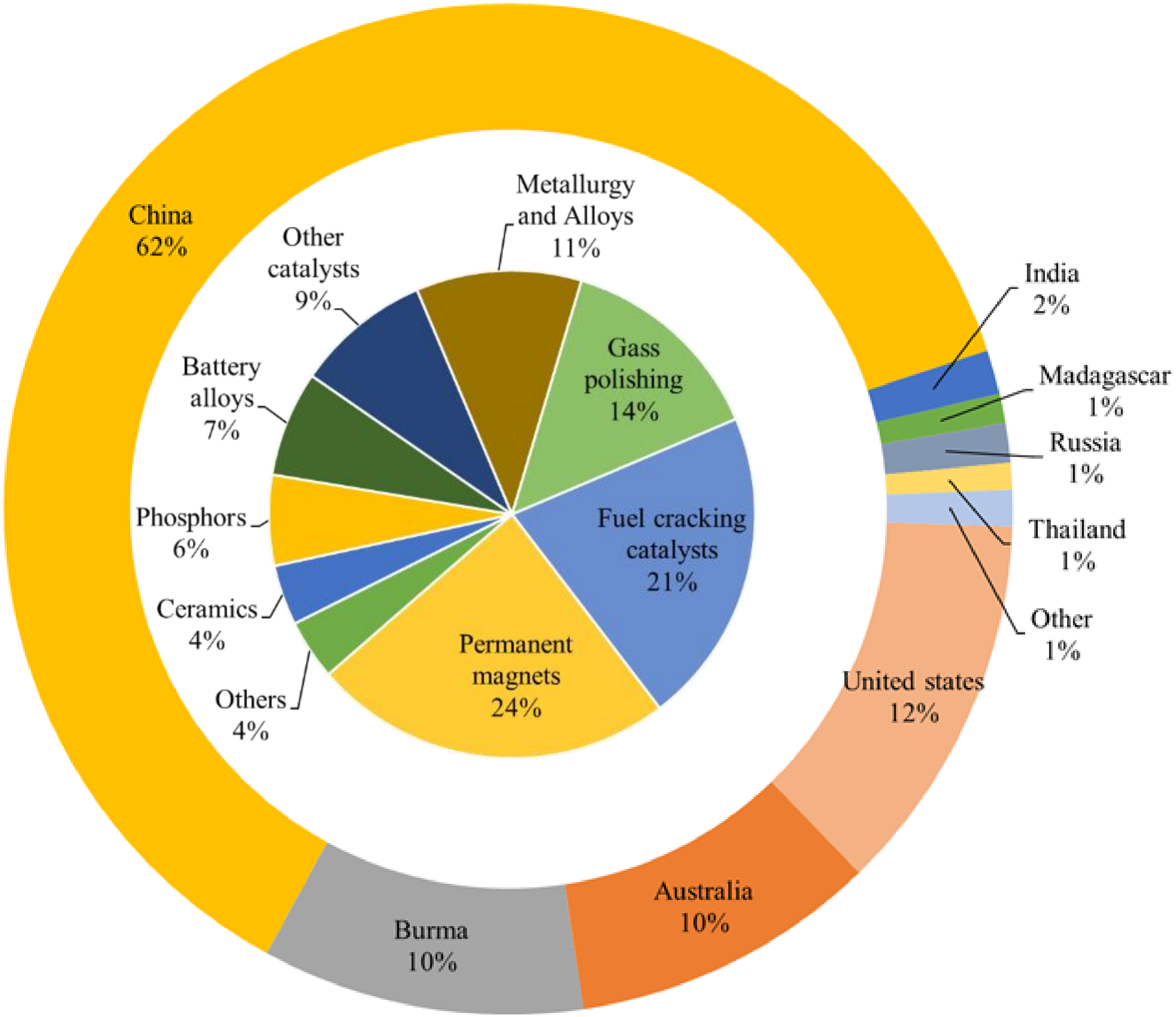
Rare Earth Elements



Rare Earth Elements



Rare Earth Elements

Rare Earth – Key Applications

Magnetics

Nd | Tb, Dy | Pr

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

Phosphors

Nd, Eu, Tb, Y | Er, Gd | Ce, Pr

Display phosphors - CRT, LPD, LCD
Fluorescent Lighting
Medical Imaging
Lasers
Fibre Optics

Metal Alloys

Nd, Y | La, Ce, Pr

NimH Batteries
Fuel Cells
Steel
Super Alloys
Aluminium / Magnesium

Catalysts

Nd | La, Ce, Pr

Petroleum Refining
Catalytic Converter
Fuel Additives
Chemical Processing
Air Pollution Controls

Ceramics

Nd, Y, Eu | Gd, Lu, Dy | La, Ce, Pr

Capacitors
Sensors
Colorants
Scintillators
Refractories

Glass & Polishing

Nd | Gd, Er, Ho | La, Ce, Pr

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

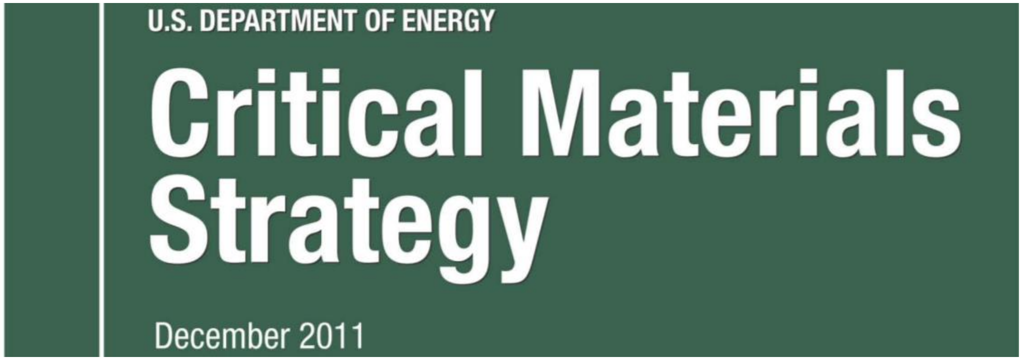
Defense

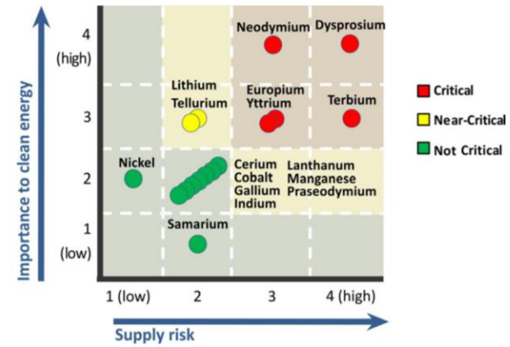
Nd, Eu, Tb, Dy, Y | Lu, Sm | Pr, La

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

CREOs
HREOs
LREOs

Criticality of REEs in the U.S.





Critical Material List (Executive Order 13817)

Aluminum (bauxite), antimony, arsenic, barite, beryllium, bismuth, cesium, chromium, cobalt, fluorspar, gallium, germanium, graphite (natural), hafnium, helium, indium, lithium, magnesium, manganese, niobium, platinum group metals, potash, rare earth elements group, rhenium, rubidium, scandium, strontium, tantalum, tellurium, tin, titanium, tungsten, uranium, vanadium, and zirconium.

Trump Signs Executive Order To Protect, Build U.S. Rare Earths Industry

https://www.forbes.com/sites/kenrapoza/2020/10/01/trump-signs-executive-order-to-protect-build-us-rare-earths-industry/#26bcefe65b71

REEs in Coal

Table 3. Reserve and production of REE in worldwide countries [38]

	Production (t)		
Country	2011	2012	Resreve (t)
United States	ND	7,000	13,000,000
Australia	2,200	4,000	16,000,000
Brazil	250	300	36,000
China	105,000	95,000	55,000,000
India	2,800	2,800	3,100,000
Malaysia	280	350	30,000
Other countries	ND	ND	41,000,000
Total	111,000	111,000	110,000,000

Note. ND = no data.

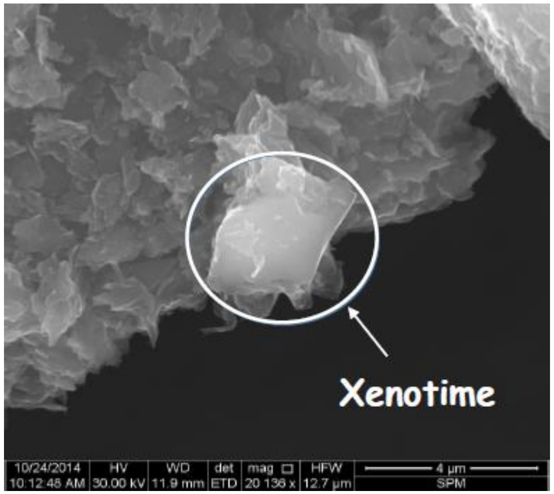
Table 4. The coal ultimate recoverable reserve (CURR), total REE reserve (TREE), total LREE reserve (TLREE), and total HREE reserve (THREE) in coal for different scenarios

	RU[1]	MO[2]	WEC[3]
CURR (Gt)	680	700.1	847.5
TLREE (t)[4]	37,175,600	38,274,467	46,332,825
THREE (t)[4]	12,036,000	12,391,770	15,000,750
TREE (t)[4]	49,211,600	50,666,237	61,333,575

[1]From Rutledge [39]. [2]From Mohr and Evans [40] estimated using Hubbert Linearization method. [3]From World Energy Council [41]. [4]The concentration of rare earth in coal used for calculation was cited from Ketris and Yudovich [36], shown in Table 2.

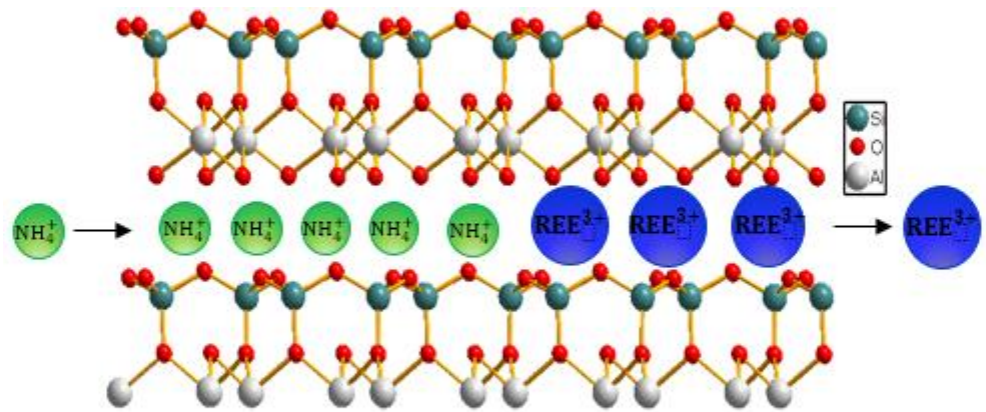
REEs in Coal

- Minerals



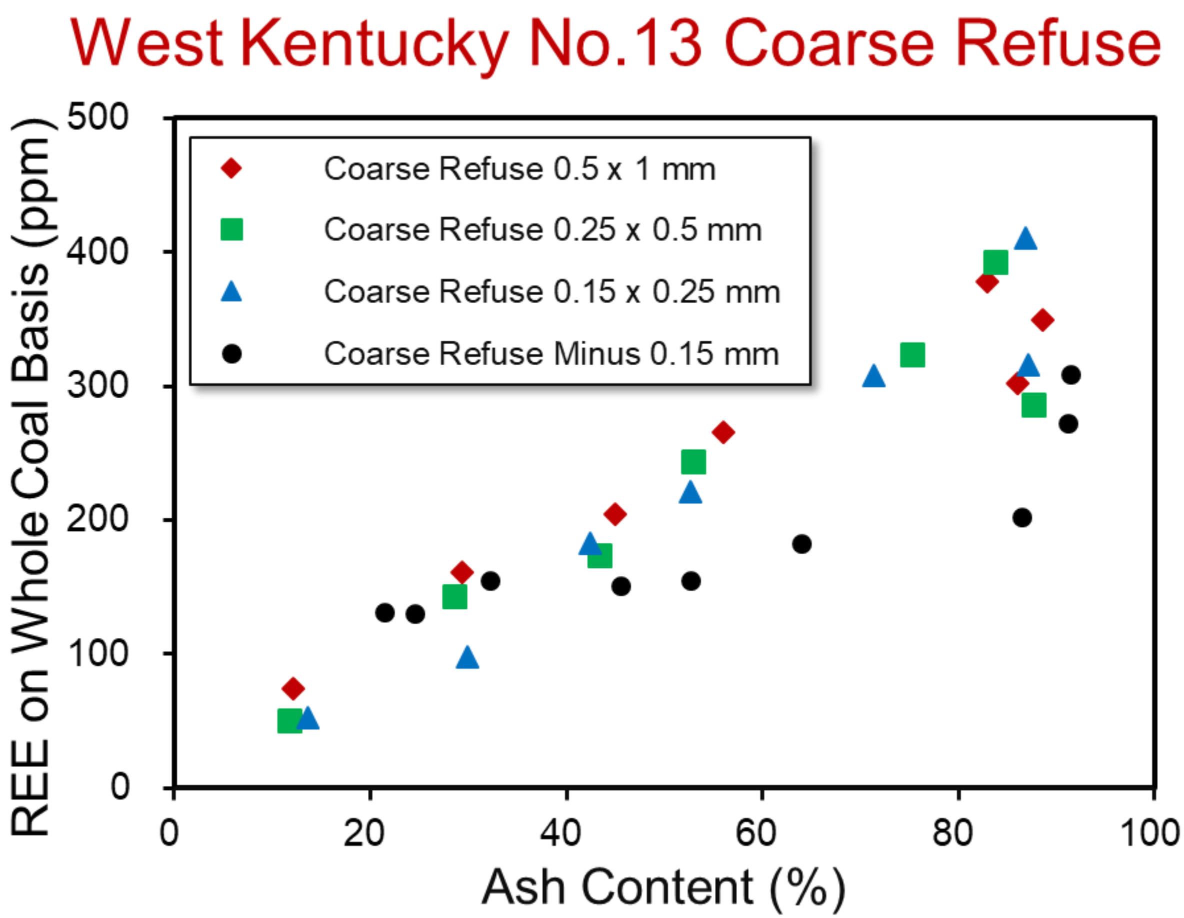
Xenotime-YPO_4
Monazite-(Ce, La, Nd, Sm, Th)PO_4

- Ion-Substitution in Clays



- Organic Associations

REE Recovery from Coal



- REEs tend to associate with density fractions with higher ash contents, which indicates the feasibility of REE recovery from coal coarse refuse

Recovery through Physical Methods

Separation Method	Sample	Sources	Separation Method	REE (ppm)	*ER*	*Re* (%)	Reference
Gravity Separation	Coarse refuse (28 × 100 mesh fraction)	Fire Clay	Riffle table	252 [w]	1.1	16.8	[35]
	Coarse refuse (28 × 100 mesh fraction)	Eagle Seam	Riffle table	213 [w]	1.1	16.1	
	Coarse refuse (28 × 100 mesh fraction)	Fire Clay Rider	Riffle table	234 [w]	1.1	24.75	
	Coarse refuse (<100 mesh fraction)	Eagle Seam	Multi-gravity separation	257 [a]	1.2	90	
	Coarse refuse (<100 mesh fraction)	Fire Clay	Multi-gravity separation	290 [a]	1.2	85	
	Coarse refuse (<100 mesh fraction)	Fire Clay Rider	Multi-gravity separation	254 [a]	1.1	87	
Flotation	Decarbonized thickener underflow	Fire Clay	Multi-stage flotation using a conventional cell with sodium oleate as the collector	2300 [a]	5.3	<5	[33]
	Decarbonized thickener underflow	Fire Clay	Multi-stage flotation using a column with sodium oleate as the collector	4700 [a]	10.9	<5	
	Decarbonized thickener underflow	Fire Clay	Single-stage conventional cell flotation using oleic acid as the collector	386 [w]	1.4	23	[35]
	Decarbonized thickener underflow	Eagle Seam	Single-stage flotation using a conventional cell with oleic acid as the collector	367 [w]	1.8	31	
	Decarbonized thickener underflow	Fire Clay Rider	Single-stage conventional cell flotation using oleic acid as the collector	377 [w]	1.3	13	
HHS	Decarbonized thickener underflow	Fire Clay	Potassium octylhydroxamate and sorbitan monooleate were used as the hydrophobizing agent	17,428 [a]	53	5.9	[11]
Magnetic Separation	Decarbonized middling	Fire Clay	Three-stage wet high intensity magnetic separation (1.4 T)	7000 [w]	14	<5	[20]

REE Recovery through Hydrometallurgy

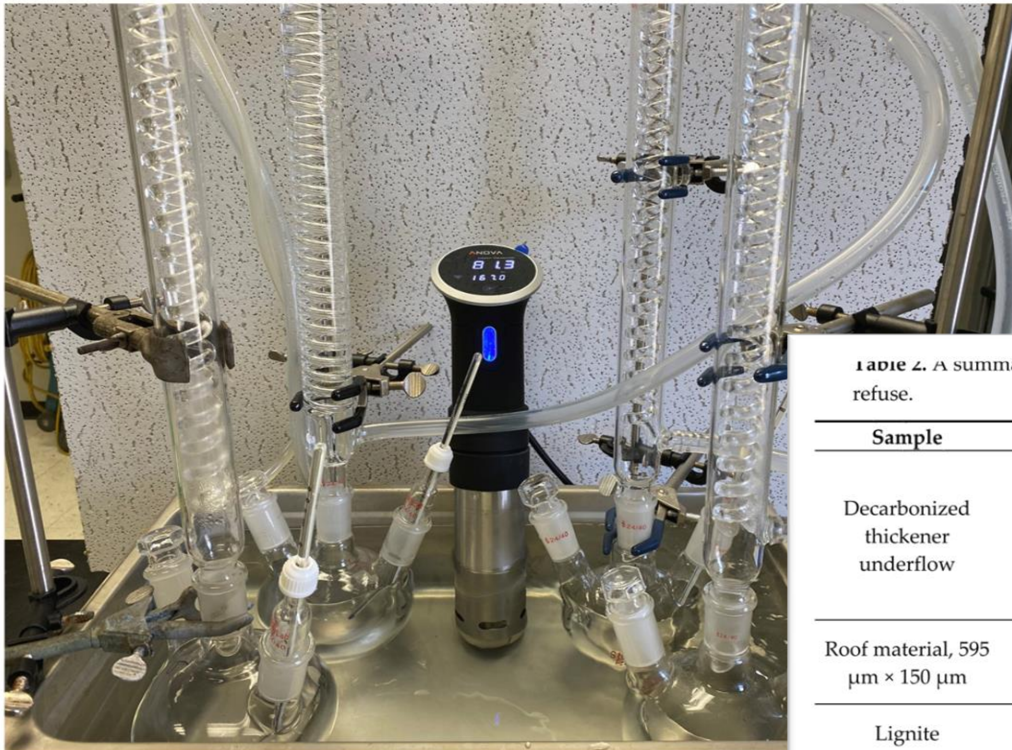
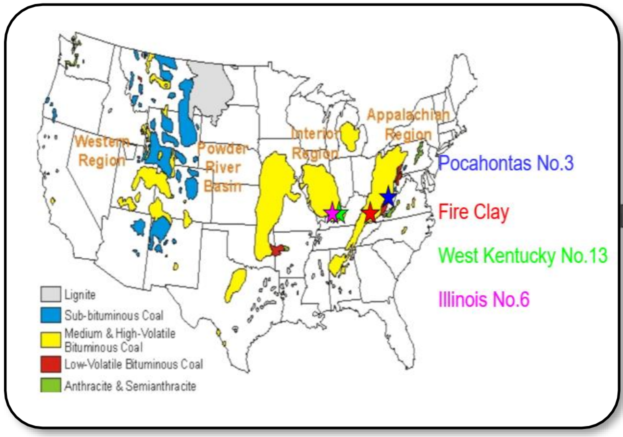
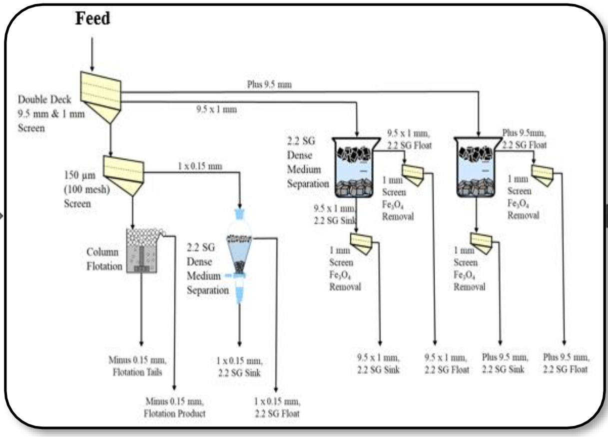


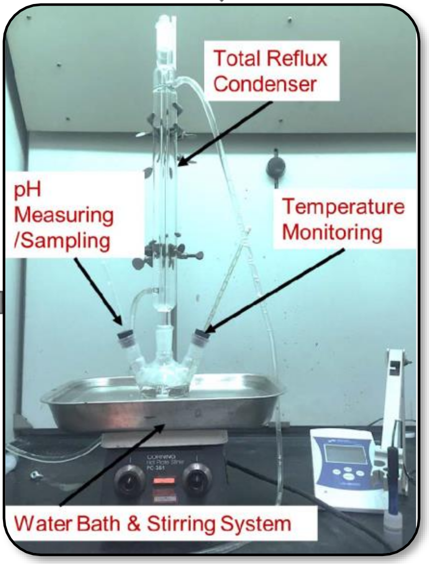
Table 2. A summary of salt and acid leaching of rare earth elements (REEs) from coal and coal refuse.

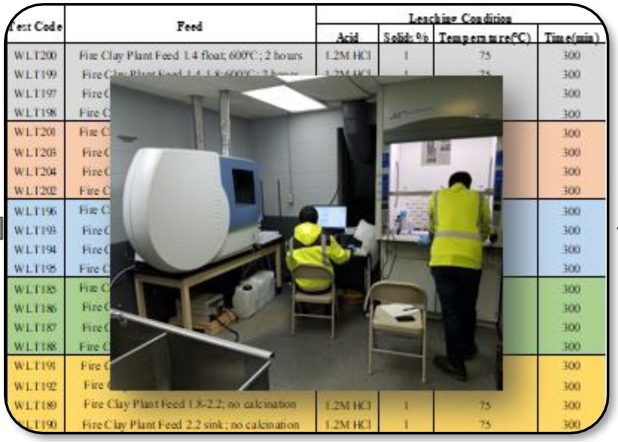
Sample	Coal Seam	Extraction Condition	Leaching Recovery	Reference
Decarbonized thickener underflow	West Kentucky No. 13	0.1 M $(NH_4)_2SO_4$, pH 5	Around 10% of total REEs, 7% of LREEs, and 18% of HREEs	[41]
		0.1 M $(NH_4)_2SO_4$, pH 3	Around 12% of total REEs, 10% of LREEs, and 21% of HREEs	
Roof material, 595 μm × 150 μm	Upper Kittanning	1 M $(NH_4)_2SO_4$, 1/2 solid/solution mass ratio, room temperature	Nearly 90% of the total REEs were extracted after 1 h of reaction	[48]
Lignite	Fort Union	0.5 M H_2SO_4, 40 °C, 48 h	Nearly 90% of the total REEs	[25]
Decarbonized middlings	Fire Clay	Nitric acid solution of pH 0 at 75 °C	83% of total REEs, 86% of LREEs, and 69% of HREEs	[11]
	West Kentucky No. 13	Nitric acid solution of pH 0 at 75 °C	15% of La, 21% of Ce, 31% of Nd, 45% of Y	
	Lower Kittanning	Nitric acid solution of pH 0 at 75 °C	41% of total REEs	
Decarbonized thickener underflow	Fire Clay	Nitric acid solution of pH 0 at 75 °C	31% of La, 26% of Ce, 40% of Nd, 36% of Y	
	West Kentucky No. 13	Nitric acid solution of pH 0 at 75 °C	6% of La, 5% of Ce, 16% of Nd, 34% of Y	
	Lower Kittanning	Nitric acid solution of pH 0 at 75 °C	2% of La, 5% of Ce, 8% of Nd, 25% of Y	

REE Recovery through Pyrometallurgy



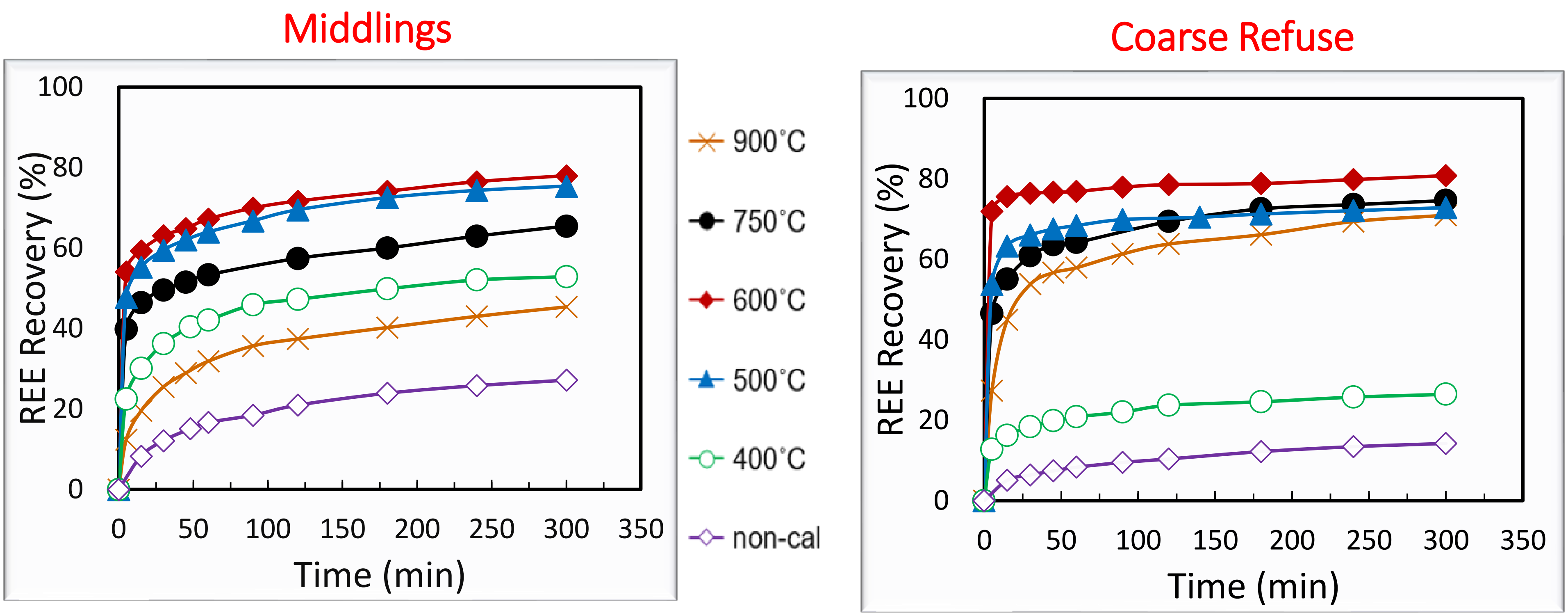






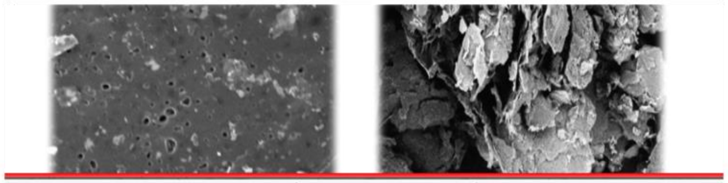
1.2 M HCl; 75°C; 1 g/L solid concentration

Enhanced REE Recovery through Calcination



- REE leaching recovery was increased significantly
- Optimum temperature lied between 500-750℃
- Quick leaching kinetics at the beginning
- The middlings and coarse refuse showed different leaching characteristics

Mechanisms



Sample	S_{BET} (m²/g)	V (cm³/g)	D (nm)
M400			5.9
M600			19.8
M750			23.1
M900	3.7	0.022	27.2

Note: S_{BET}, surface area; V, pore volume; D, average pore diameter.

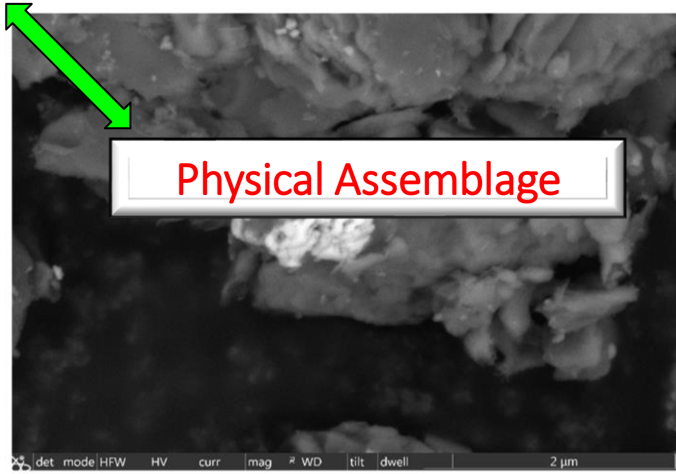
Dehydration

The increase in surface area after calci
contributed to the mass transfer rate d
the leaching process

Materia	Spectrum	P	Ce	Nd	La	Pr	Sm	Gd	REEs	REEs/P	Al	Si	Al/Si
Calcined	1	6.9	11.1	5.5	3.6	1.5	1.2	0.9	23.8	0.75	9.6	13.0	0.77
		6.8	12.7	5.1	5.1	0	0.5	0	23.4	0.76	10.7	11.6	0.96
	3	5.9	2.3	5.6	0	0	2.7	2.6	13.2	0.47	11.6	15.5	0.78
	4	7.7	15.0	6.5	5.0	0	0	0	26.5	0.76	9.9	13.0	0.79
												12.7	0.94
												12.5	0.96
												Si	Al/Si
												7.8	0.88
	8	7.7	15.8	4.6	2.7	2.0	1.9	1.0	28.0	[illegible]	9.6	11.9	0.84
	Spectrum	P	Ce	Nd	La	Pr	Sm	Gd	REEs	REEs/P	Al	Si	Al/Si
Non-Calcined	9	8.8	7.6	3.2	4.3	0	0.3	0	15.4	0.38	14.3	5.0	2.98
	10	9.9	9.1	3.1	5.3	0	0	0	17.5	0.39	16.6	2.8	6.17
	11	3.3	5.2	2.5	2.2	0	0.3	0	10.2				
	12	4.2	6.0	3.7	2.0	0	0	0	11.7				
	13	1.5	1.0	0	0	0	0	0	1.0				

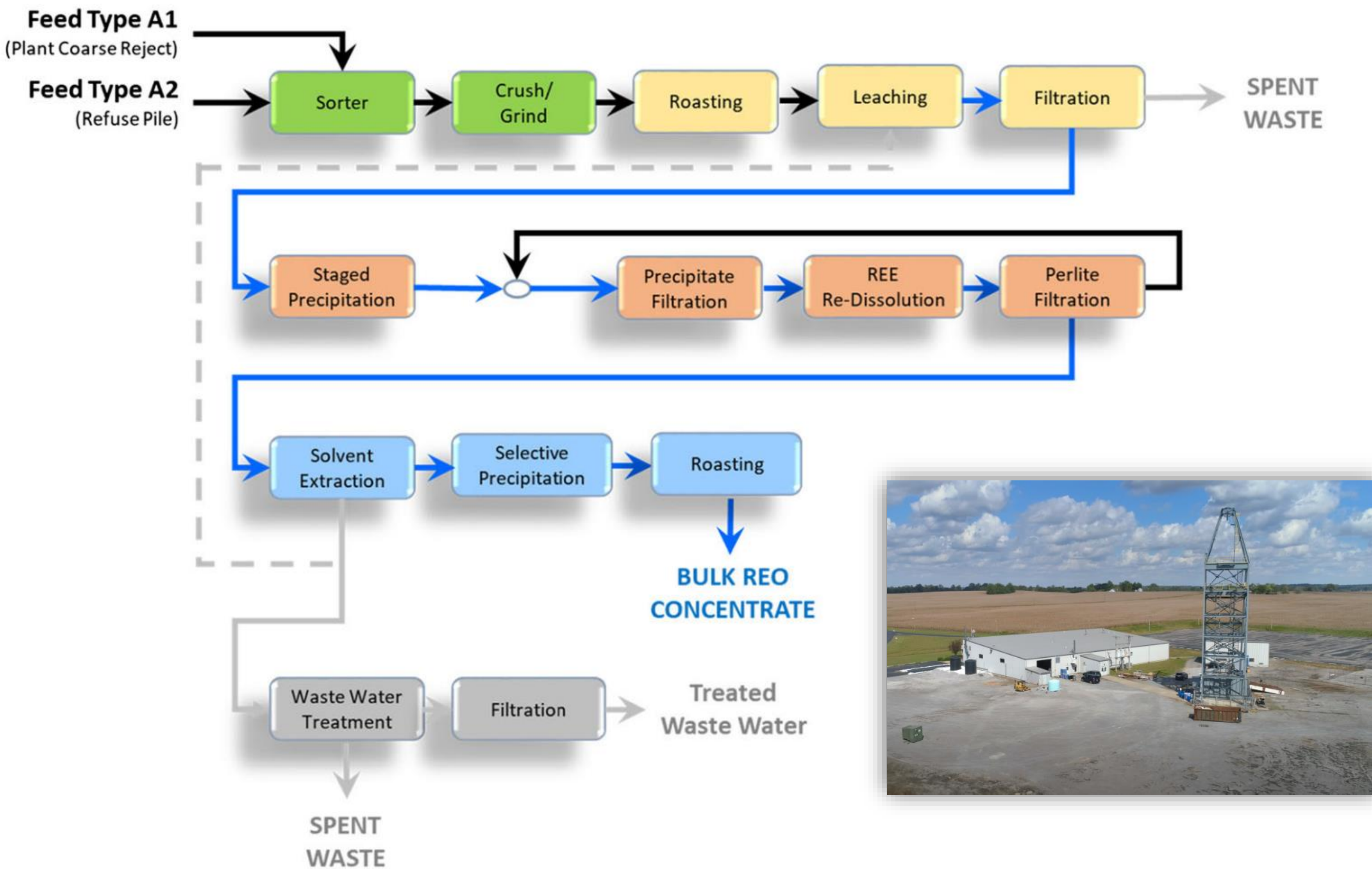
Thermal Decomposition

- The REE contents were increased after c
  relative to P



Physical Assemblage

Pilot-Scale Testing



Recovery of Other Critical Materials from Coal

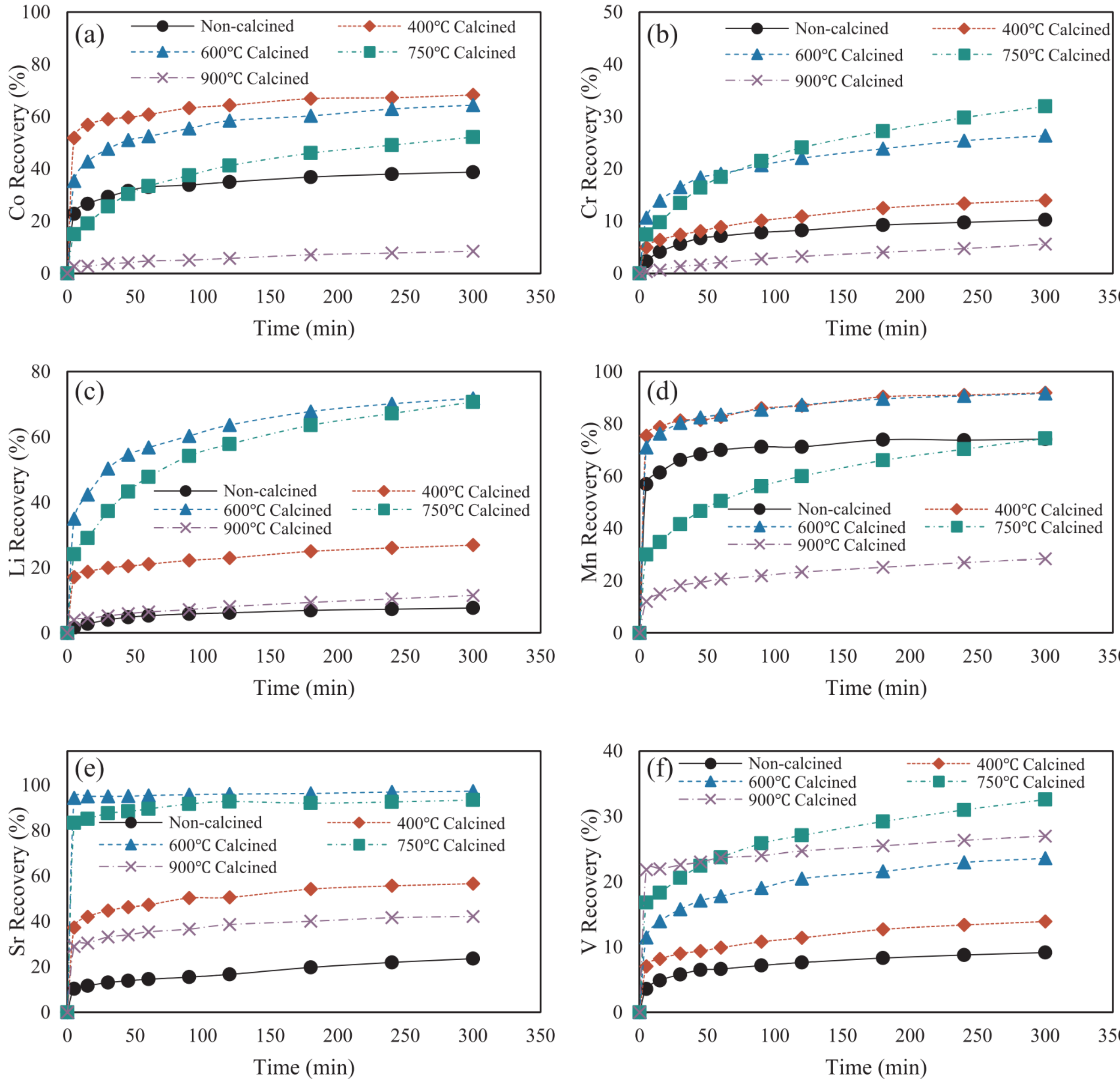


Fig. 6. The effects of calcination temperature on the leaching recoveries of other critical metals from the Baker materials.

REE Recovery from Coal

minerals MDPI

Review

A Comprehensive Review of Rare Earth Elements Recovery from Coal-Related Materials

Wencai Zhang [1,*], Aaron Noble [1], Xinbo Yang [2] and Rick Honaker [2]

Contents lists available at ScienceDirect
Fuel
journal homepage: www.elsevier.com/locate/fuel

Full Length Article

Lithium leaching recovery and mechanisms from density fractions of an Illinois Basin bituminous coal

Wencai Zhang[a,*], Aaron Noble[a], Xinbo Yang[b], Rick Honaker[b]

Contents lists available at ScienceDirect
Fuel
journal homepage: www.elsevier.com/locate/fuel

Full Length Article

Characterization and recovery of rare earth elements and other critical metals (Co, Cr, Li, Mn, Sr, and V) from the calcination products of a coal refuse sample

Wencai Zhang[a,*], Rick Honaker[b]

Contents lists available at ScienceDirect
Fuel
journal homepage: www.elsevier.com/locate/fuel

Full Length Article

Mineralogy characterization and recovery of rare earth elements from the roof and floor materials of the Guxu coalfield

Wencai Zhang[*], Aaron Noble

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Enhanced leachability of rare earth elements from calcined products of bituminous coals

Wencai Zhang, Rick Honaker[*]

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Calcination pretreatment effects on acid leaching characteristics of rare earth elements from middlings and coarse refuse material associated with a bituminous coal source

Wencai Zhang, Rick Honaker[*]

(19) **United States**
(12) **Patent Application Publication**
Honaker et al.
(10) **Pub. No.: US 2020/0308667 A1**
(43) **Pub. Date: Oct. 1, 2020**

(54) **METHOD FOR RECOVERING VALUABLE ELEMENTS FROM PRECOMBUSTION COAL-BASED MATERIALS**

(71) Applicant: **University of Kentucky Research Foundation**, Lexington, KY (US)

(72) Inventors: **Rick Honaker**, Lexington, KY (US); **Wencai Zhang**, Lexington, KY (US)

(21) Appl. No.: **16/832,157**

(22) Filed: **Mar. 27, 2020**

Related U.S. Application Data

(60) Provisional application No. 62/827,361, filed on Apr. 1, 2019.

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C22B 3/04 (2006.01)
C22B 59/00 (2006.01)
C22B 3/44 (2006.01)

(52) **U.S. Cl.**

CPC *C22B 1/02* (2013.01); *C22B 1/24* (2013.01); *C22B 3/44* (2013.01); *C22B 3/04* (2013.01); *C22B 59/00* (2013.01); *C22B 3/22* (2013.01)

(57) **ABSTRACT**

A method for recovering valuable elements from pre-combustion coal-based materials includes the steps of grinding the materials to a predetermined size, roasting the ground materials at a temperature of 600° C.-700° C. for a predetermined residence time needed for mineral decomposition, submerging the roasted, ground materials in a solution of lixiviant, filtering the lixiviant solution to separate residual solids from a pregnant leach solution including the valuable elements and recovering and concentrating the valuable elements from the pregnant leach solution.

REEs in Acid Coal Mine Drainage

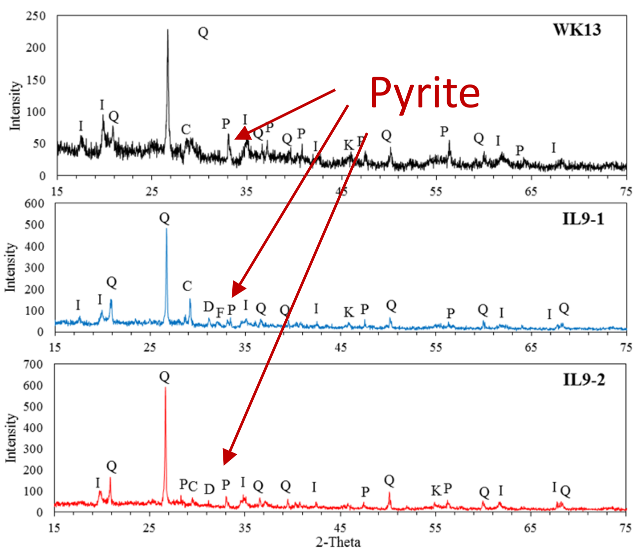
- Both oxygen and ferric ions can oxidize pyrite

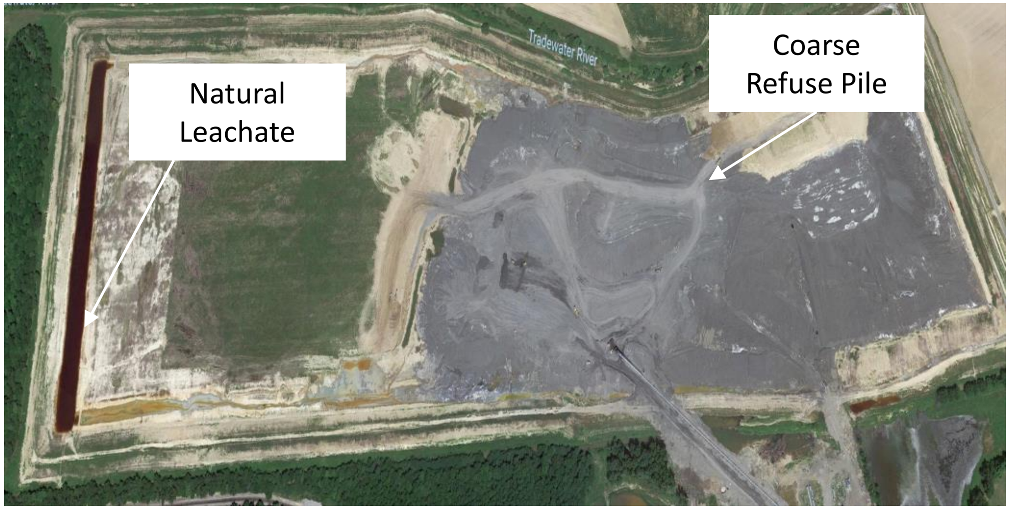
$$FeS_{2(s)} + 14Fe^{3+}_{(aq)} + 18H_2O_{(l)} = 15Fe^{2+}_{(aq)} + 2SO^{2-}_{4(aq)} + 16H^{+}_{(aq)}$$

$$FeS_{2(s)} + 7/2\,O_{2(aq)} + H_2O_{(l)} = Fe^{2+}_{(aq)} + 2SO^{2-}_{4(aq)} + 2H^{+}_{(aq)}$$

$$Fe^{2+}_{(aq)} + 1/4\,O_{2(aq)} + H^{+}_{(aq)} = Fe^{3+}_{(aq)} + 1/2\,H_2O_{(l)}$$

- Acidity was generated through pyrite oxidization, which transfers REEs from solid into solution through dissolution.



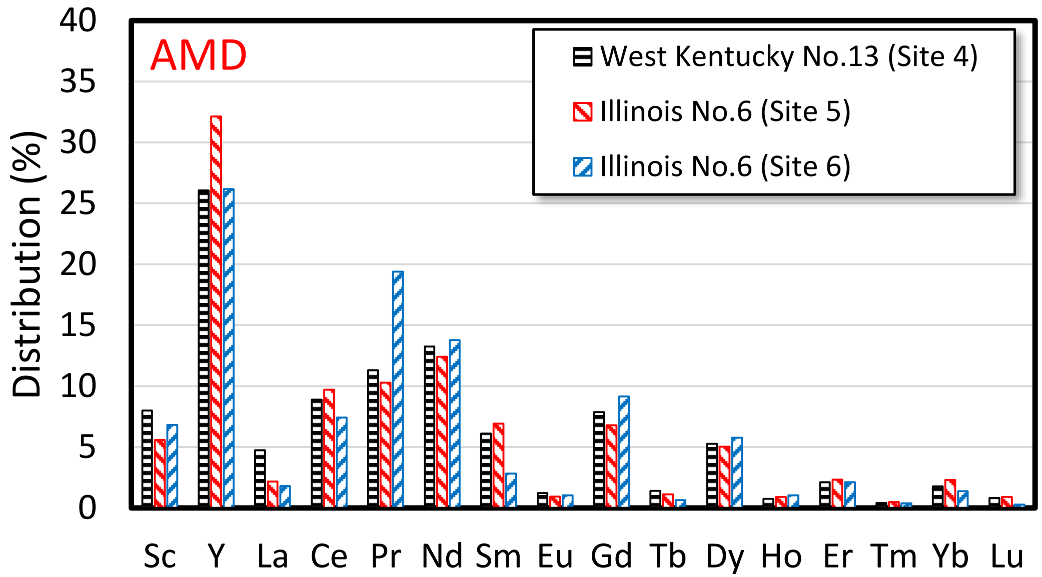


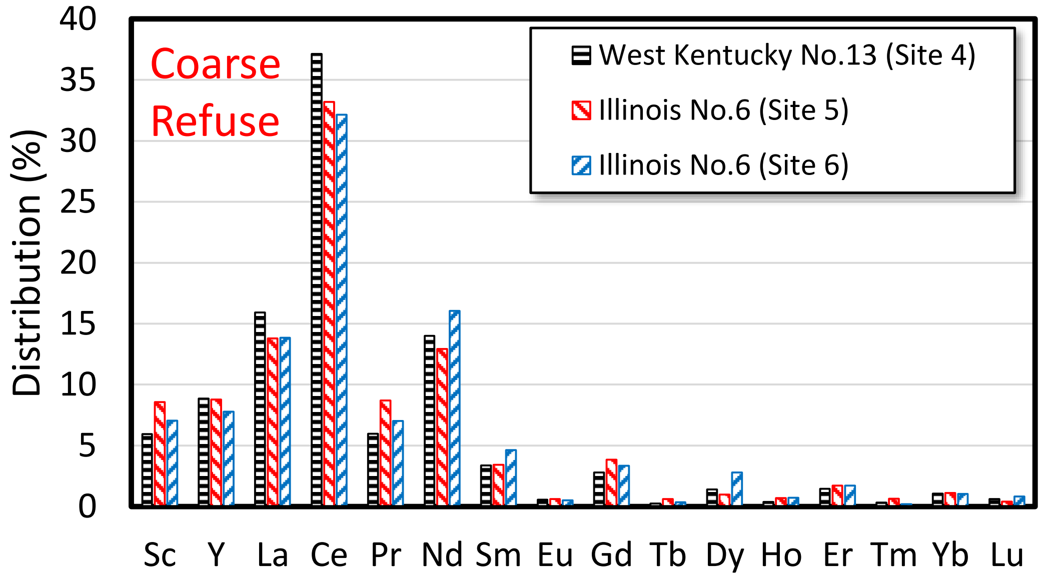
REEs in Acid Coal Mine Drainage

- Leachate samples were collected from the coarse refuse piles of six different coal preparation plants

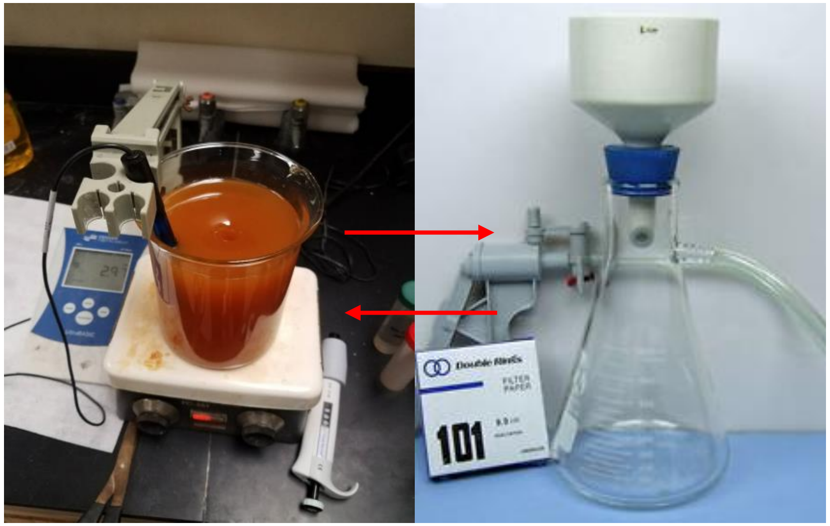
Coal Seam	**West Kentucky No.9**		**West Kentucky No.9 and 11**	**West Kentucky No.13**	**Illinois No.6**	
Processing Plant	Site 1	Site 2	Site 3	Site 4	Site 5	Site 6
pH	2.86	3.25	2.99	2.70	2.51	3.14
D.S. (g/L)	7.78	14.19	6.00	17.69	20.38	7.08
SO_4^{2-} (mg/L)	5340	3705	3600	12800	15170	3365
Cl^- (mg/L)	300	460	370	-	708	1300
F^- (mg/L)	-	-	20	-	155	-
Sc (μg/L)	147.5	55.6	115.7	536.5	172.5	39.1
Y (μg/L)	300.1	98.8	230	1750	990.2	150
La (μg/L)	57.5	8.1	19.1	318.4	66.7	10.4
Ce (μg/L)	190.3	24.9	69.2	597.3	299.3	42.5
Pr (μg/L)	195.2	137.4	172.1	758.9	317.1	111.1
Nd (μg/L)	202.2	39.9	117.5	889.6	382.4	78.9
Sm (μg/L)	72.9	6.7	22.5	409.9	213.6	16.2
Eu (μg/L)	13.7	3.3	8	81.7	28.7	5.9
Gd (μg/L)	98.3	42.8	73.2	528.7	209.7	52.5
Tb (μg/L)	12.1	1.8	6	94.2	34.4	3.7
Dy (μg/L)	60	19.4	44.2	352.9	155.2	33
Ho (μg/L)	12.1	3.9	9.2	51	27.9	6
Er (μg/L)	23.9	7.2	18.7	142.1	71.6	12.2
Tm (μg/L)	4.8	0.8	2.7	27	14.8	2.2
Yb (μg/L)	21.6	4.1	12.2	119.4	70.7	7.9
Lu (μg/L)	8.4	1.2	3	56.6	28.4	1.6
TREE (μg/L)	**1420.6**	**455.9**	**923.3**	**6714.2**	**3083.2**	**573.2**
TREE in DS (ppm)	182.6	32.1	153.9	379.5	151.3	81.0
HREEs/LREEs	0.64	0.67	0.79	0.91	1.12	0.92
Critical/Uncritical	0.71	0.56	0.78	0.89	1.07	0.90

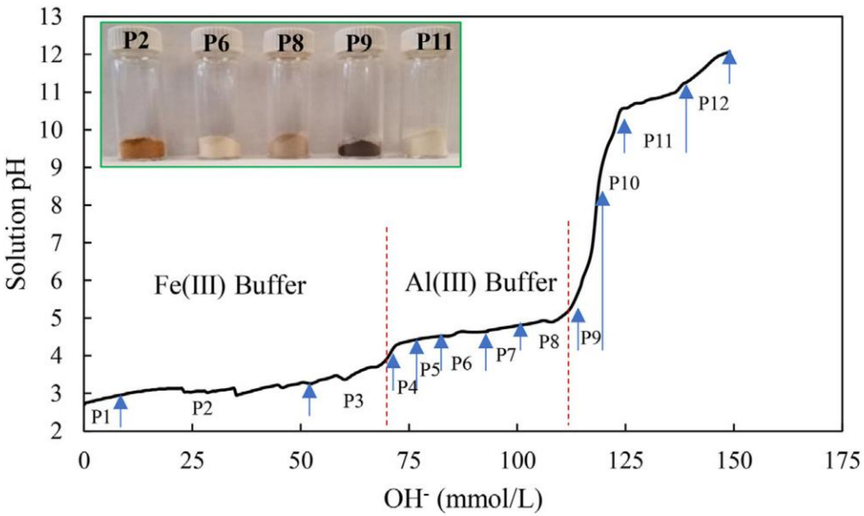
REEs in AMD versus Coarse Refuse



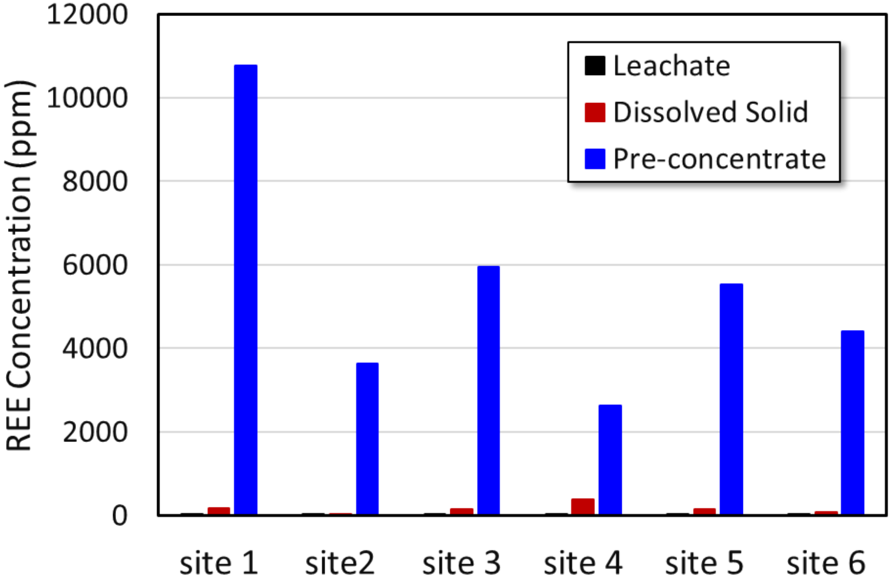


REE Recovery from AMD – Staged Precipitation

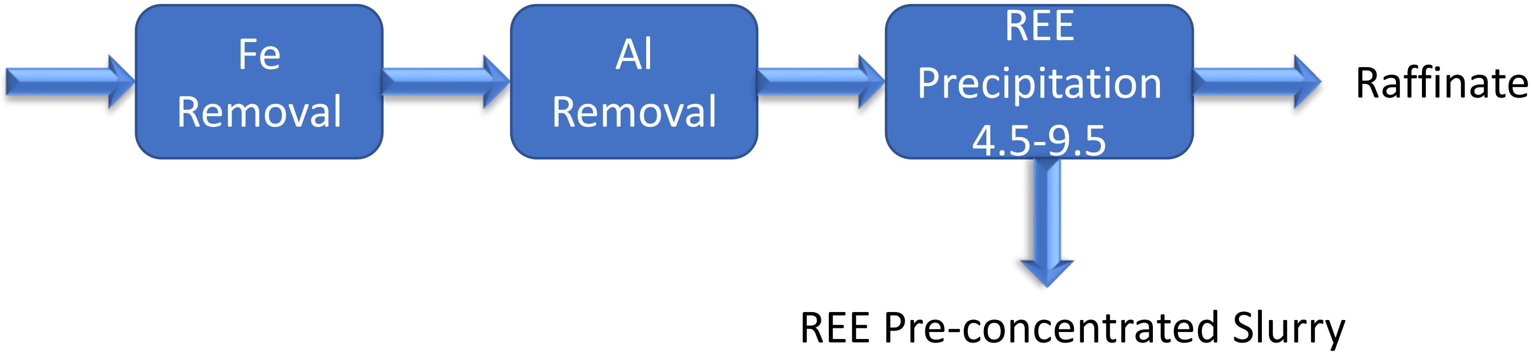


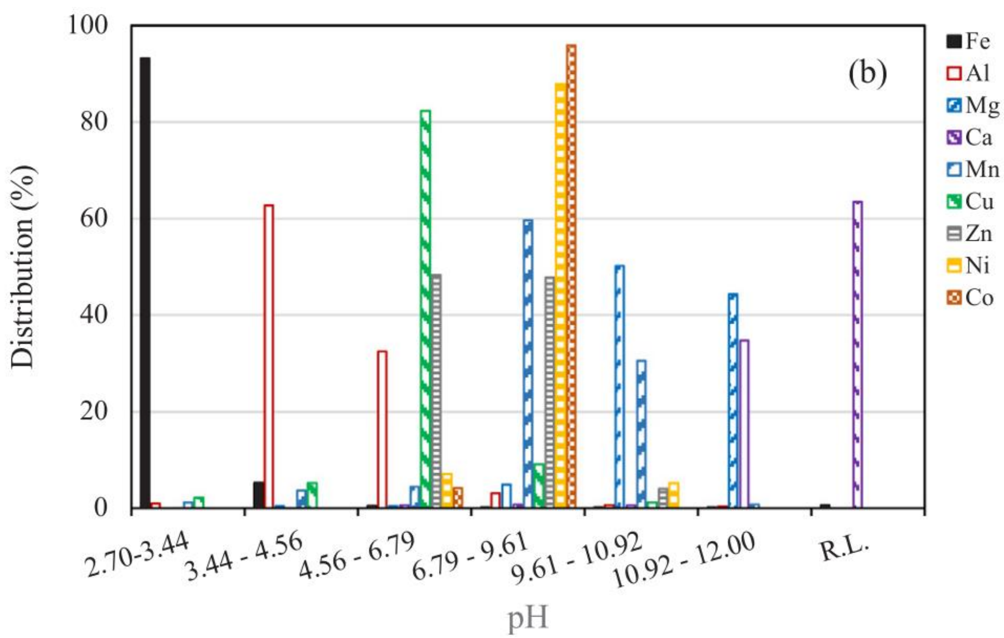


Feed	pH Range
Site 1	4.85-6.11
Site 2	5.11-6.32
Site 3	4.66-6.32
Site 4	5.01-6.36
Site 5	4.94-8.29
Site 6	3.25-8.10

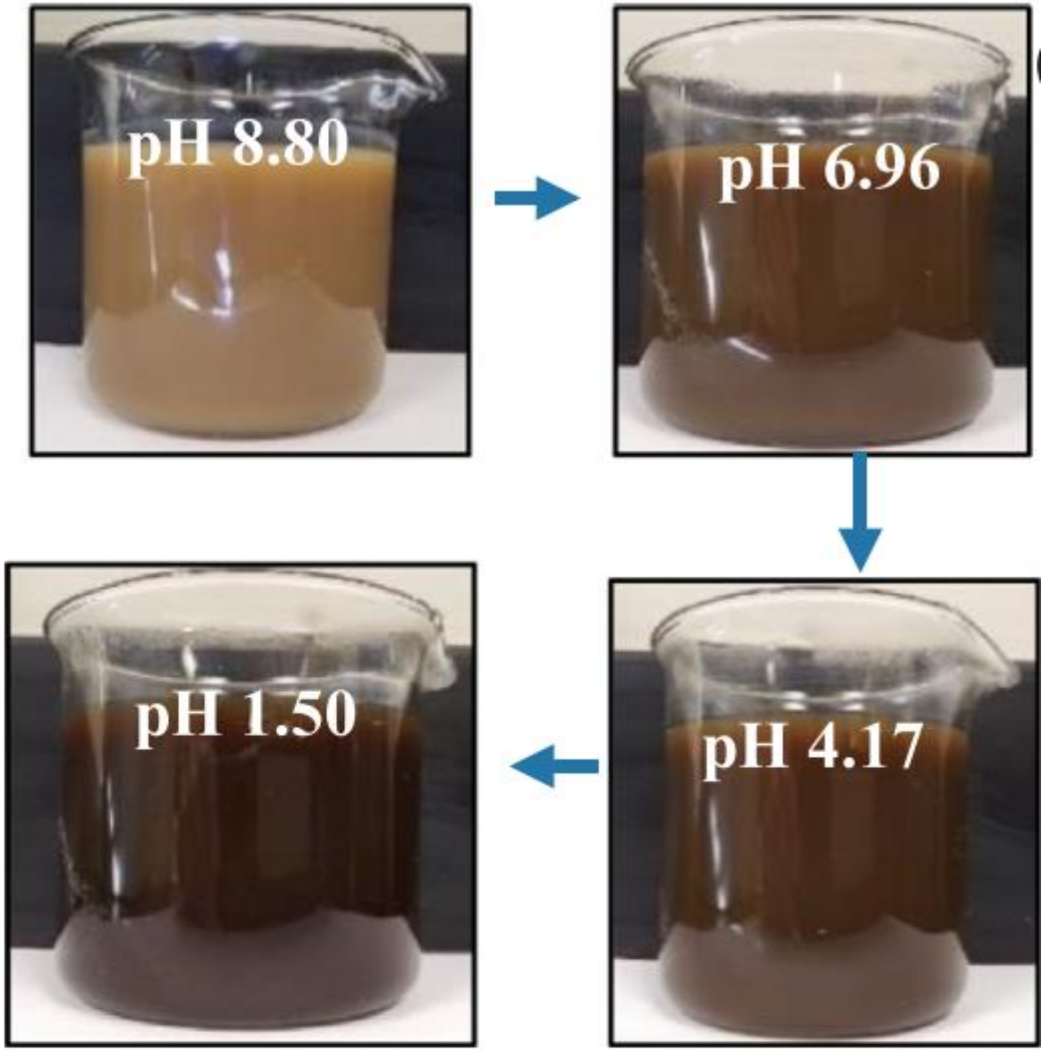


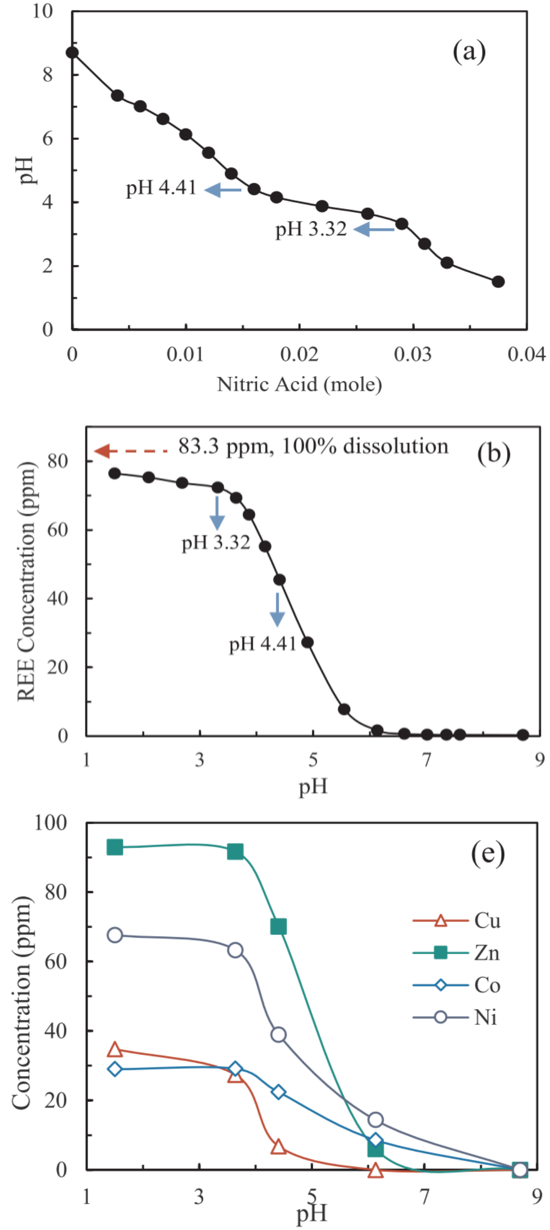
REE Recovery from AMD - Staged Precipitation





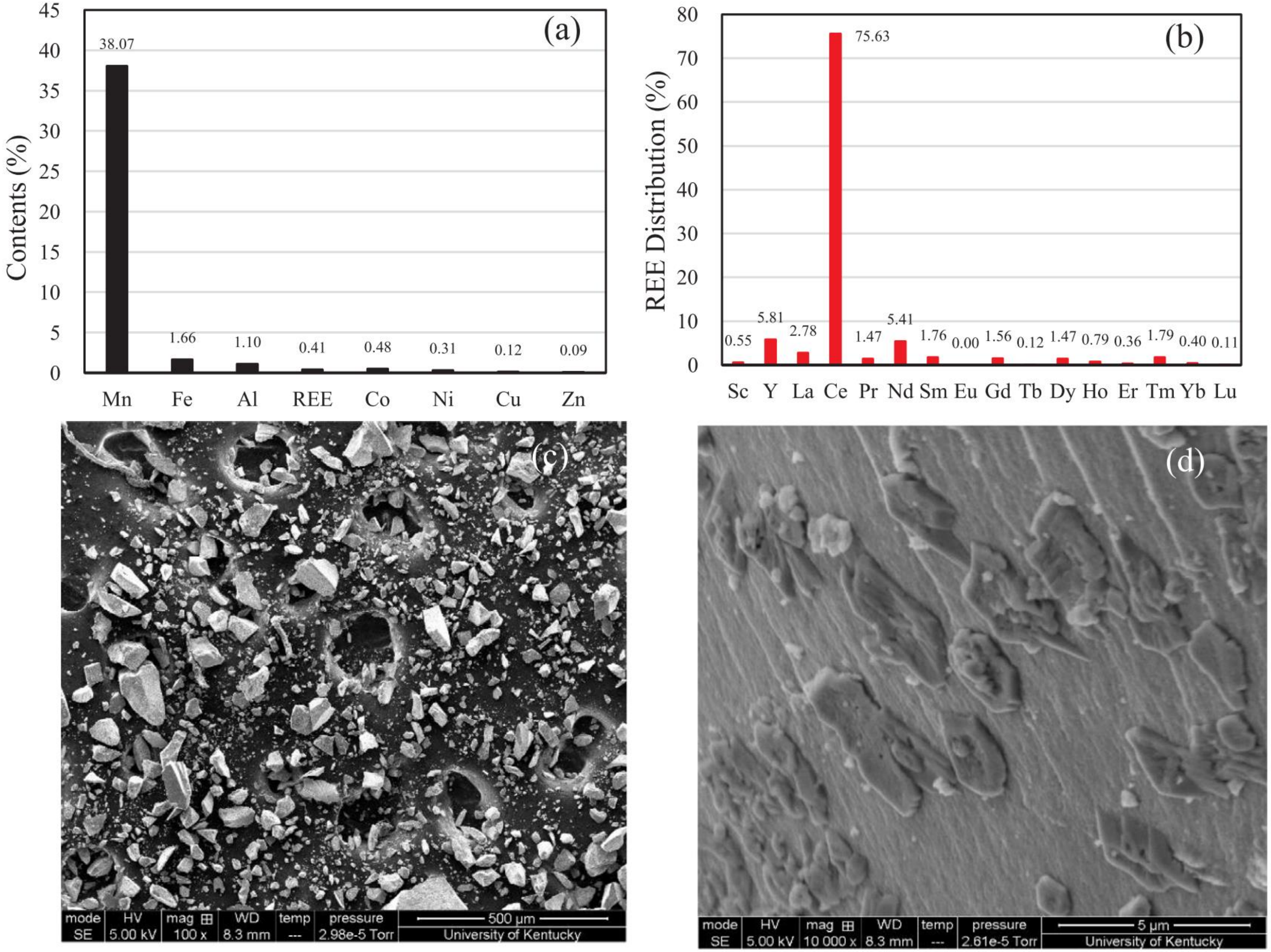
REE Recovery from AMD – Re-dissolution





REE Recovery from AMD – Re-dissolution

Undissolved Material



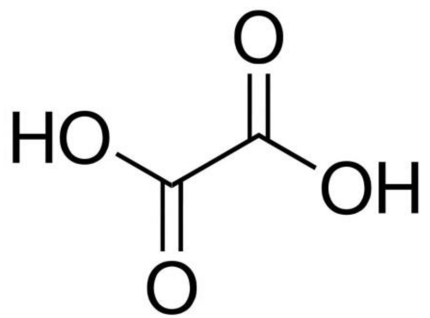
REE Recovery from AMD – Re-dissolution

Dissolved Solution (Pre-concentrated Solution)

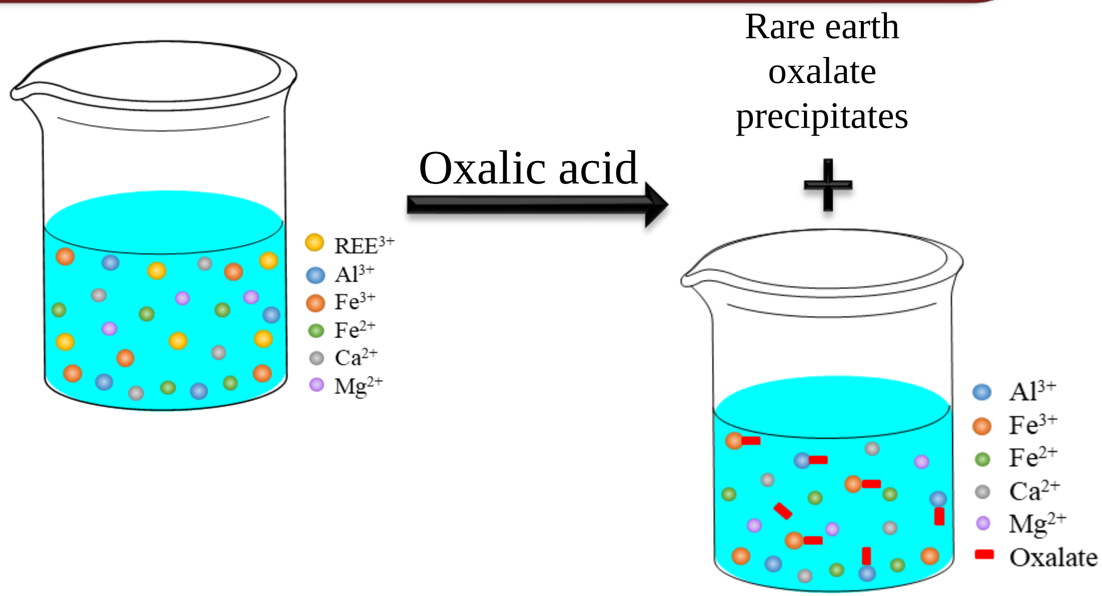
Concentration of rare earth and other elements in the pre-concentrated solution.

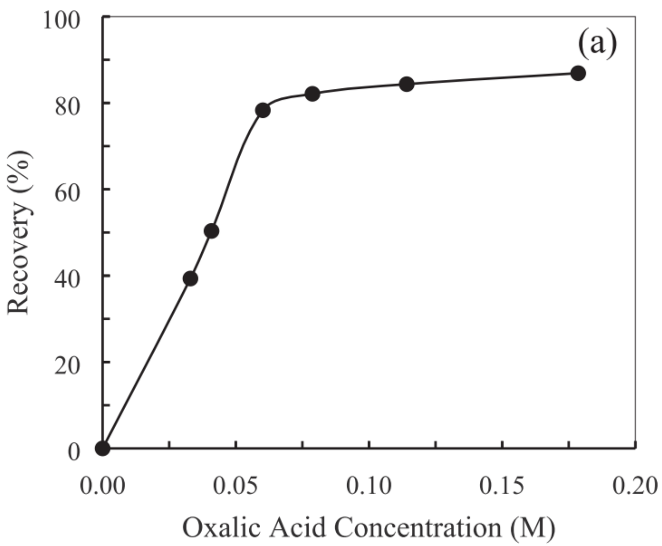
Elements	Sc	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy
ppm	0.66	19.24	8.15	13.34	2.87	11.40	3.45	0.75	4.40	0.61	3.86
Elements	Ho	Er	Tm	Yb	Lu	HREEs	LREEs	REEs	Ca	Mg	Al
ppm	0.64	1.36	0.47	1.00	0.17	32.49	39.86	72.37	370	700	1355
Elements	Mn	Zn	Cu	Co							
ppm	434	105	41	33							

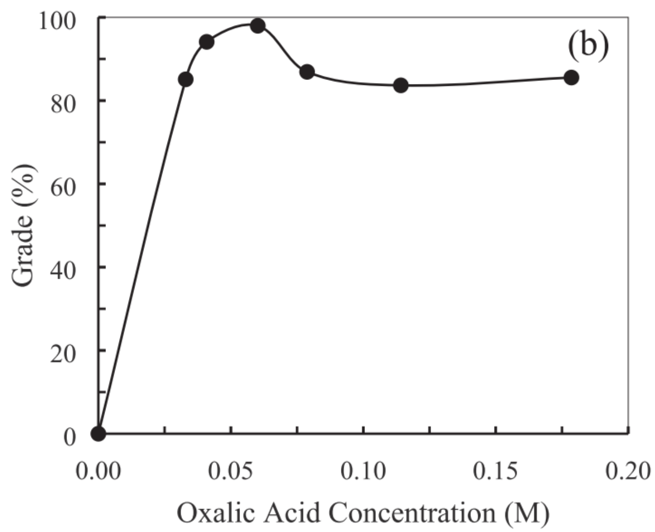
REE Recovery from Pre-concentrated Solution



Oxalic acid ($H_2C_2O_4$)

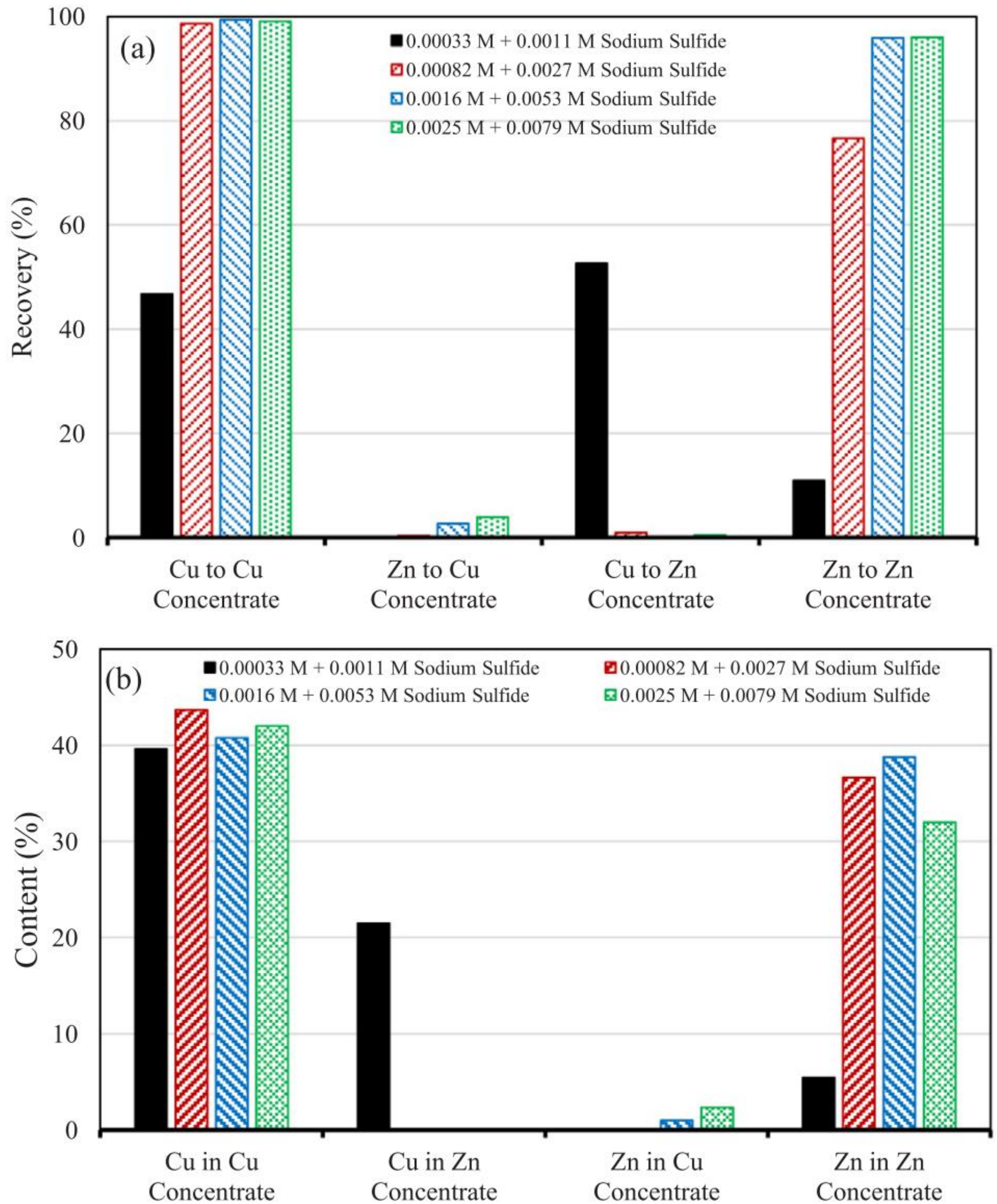




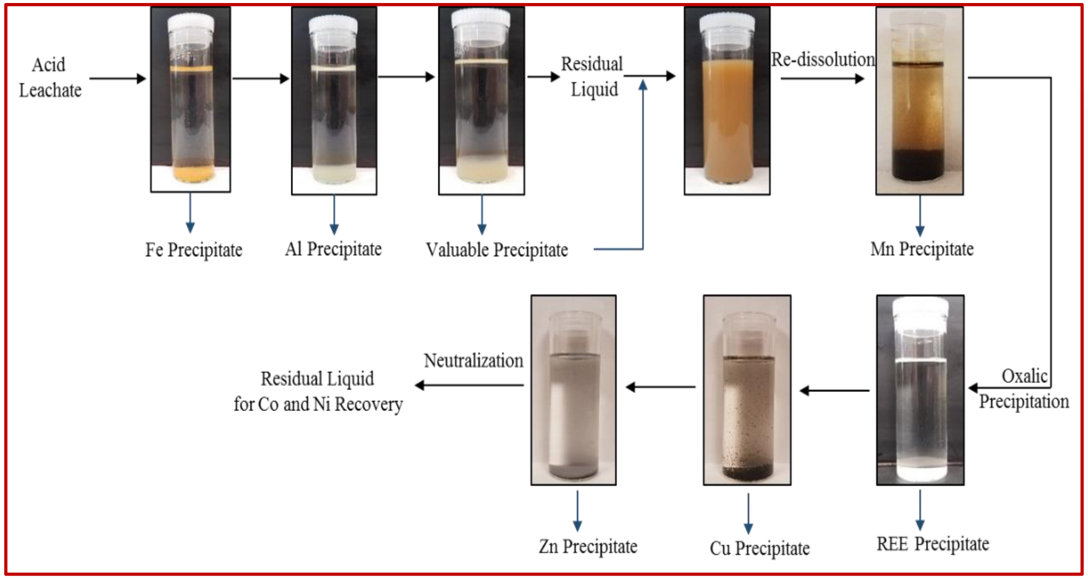


REEs	Content (%)
Sc2O3	0.05
Y2O3	21.05
La2O3	9.11
CeO2	23.32
Pr6O11	4.13
Nd2O3	17.67
Sm2O3	5.62
Eu2O3	1.24
Gd2O3	6.41
Tb2O3	0.89
Dy2O3	4.84
Ho2O3	0.81
Er2O3	1.55
Tm2O3	0.19
Yb2O3	0.92
Lu2O3	0.17
Total	**97.97**

Cu and Zn Recovery from Pre-concentrated Solution



Process Summary



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(43) **Pub. Date: May 9, 2019**

(54) **LOW-COST SELECTIVE PRECIPITATION CIRCUIT FOR RECOVERY OF RARE EARTH ELEMENTS FROM ACID LEACHATE OF COAL WASTE**

(71) Applicant: **University of Kentucky Research Foundation**, Lexington, KY (US)

(72) Inventors: **Wencai Zhang**, Lexington, KY (US); **Rick Q. Honaker**, Lexington, KY (US)

(21) Appl. No.: **16/185,120**

(22) Filed: **Nov. 9, 2018**

Related U.S. Application Data

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(52) **U.S. Cl.**
CPC *C22B 59/00* (2013.01); *C22B 3/22* (2013.01)

(57) **ABSTRACT**

The present invention concerns a process of selective precipitation for the purpose of recovering rare earth elements from acidic media derived from coal and coal byproducts via two main steps of sequential precipitation and selective precipitation. An intermediary step of re-precipitation can be included to further increase RRE concentrations, as well as improve contaminant metal removal.

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Process development for the recovery of rare earth elements and critical metals from an acid mine leachate

Wencai Zhang[a,*], Rick Honaker[b]

[a] Department of Mining and Minerals Engineering, Virginia Polytechnic Institute and State University, Blacksburg, VA 24061, USA
[b] Department of Mining Engineering, University of Kentucky, Lexington, KY 40506, USA

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Rare earth elements recovery using staged precipitation from a leachate generated from coarse coal refuse

Wencai Zhang, Rick Q. Honaker*

University of Kentucky, Lexington, Kentucky 40506-0107, USA

Summary

- Coal waste is a promising resource of REEs and other critical materials;
- REE and other critical material recovery from coal waste have been progressed to pilot-scale testing;
- Innovative processing technologies, such as thermal activation through calcination as well as staged precipitation, have been developed from my research;
- Investment from industrial stakeholders is needed for the ultimate commercial deployment of the technologies.

Thank you!

wencaizhang@vt.edu

(859) 351-6264

(540) 231-8110

https://www.mining.vt.edu/people/faculty/wencai-zhang.html