Extraction of Rare Earth Elements from Coal Waste



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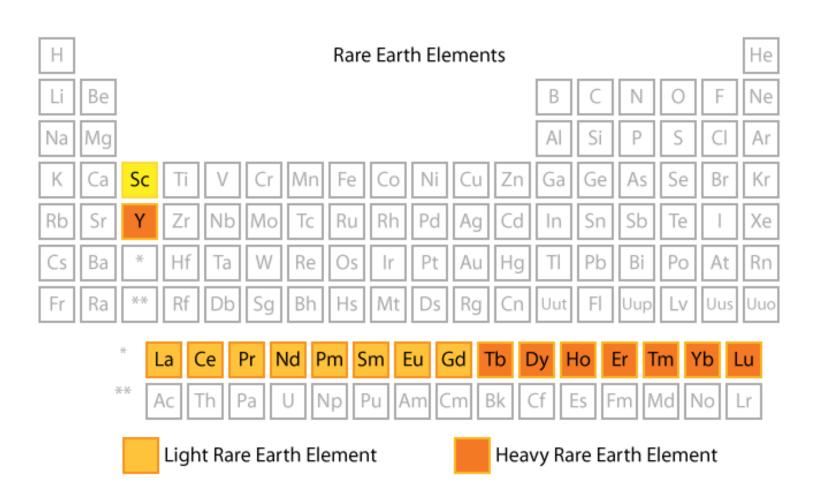
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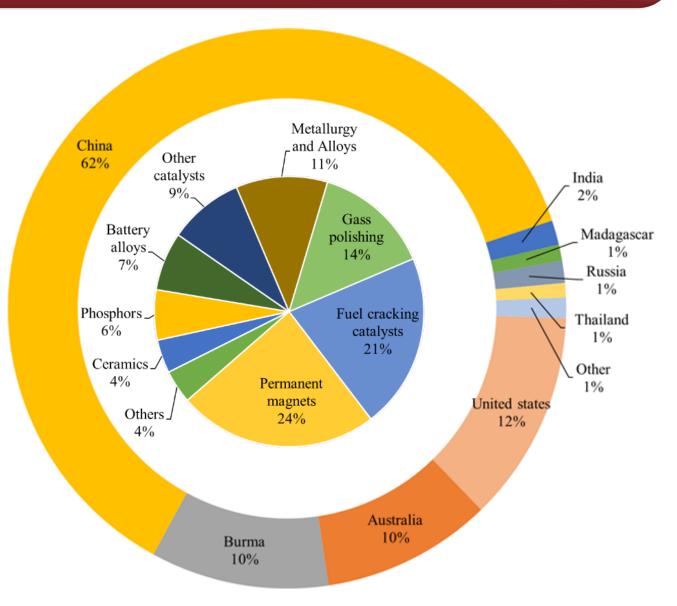
Rare Earth Elements





Rare Earth Elements





Rare Earth Elements



Rare Earth – Key Applications



Magnetics





To, Dy

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





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







Capacitors Sensors Colorants Scintillators

Refractories



Metal Alloys



NimH Batteries Fuel Cells Steel Super Alloys Aluminium / Magnesium



Catalysts



Petroleum Refining Catalytic Converter Fuel Additives Chemical Processing Air Pollution Controls



Glass & Polishing

Gd, Er, Ho



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



Defense

Nd, Eu, Tb, Dy, Y



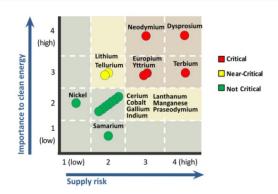


Satellite Communications Guidance Systems Aircraft Structures Fly-by-Wire Smart Missiles

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]

	Produc	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

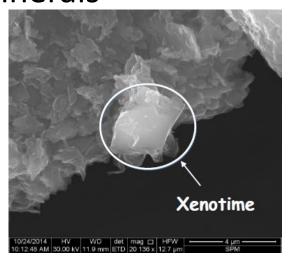
	RU^1	MO^2	WEC ³
CURR (Gt)	680	700.1	847.5
TLREE $(t)^4$	37,175,600	38,274,467	46,332,825
THREE $(t)^4$	12,036,000	12,391,770	15,000,750
TREE $(t)^{4}$	49,211,600	50,666,237	61,333,575

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

REEs in Coal



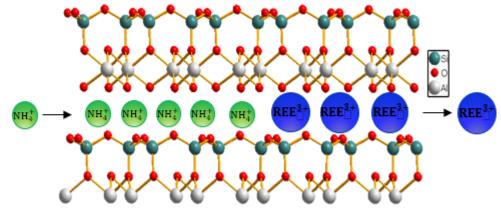
Minerals





Xenotime-YPO₄
Monazite-(Ce, La, Nd, Sm, Th)PO₄

Ion-Substitution in Clays

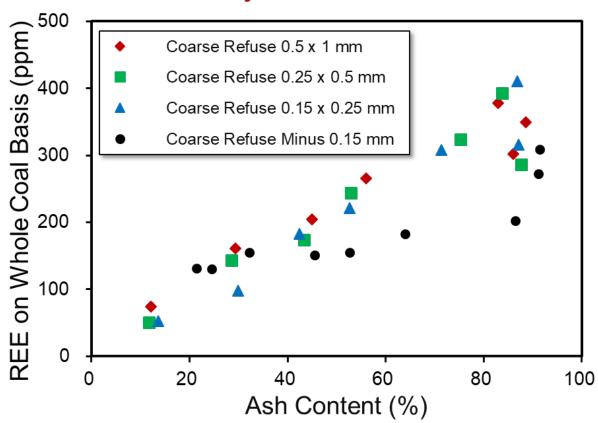


Organic Associations

REE Recovery from Coal



West Kentucky No.13 Coarse Refuse



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

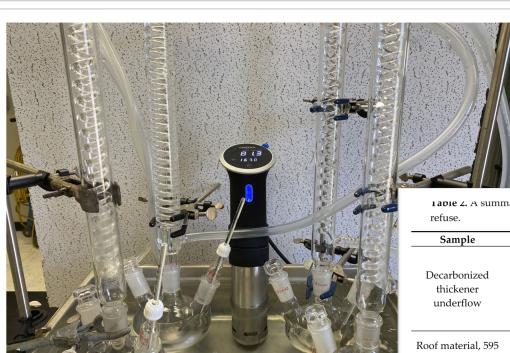
Recovery through Physical Methods



Separation Method	Sample	Sources	Separation Method	REE (ppm)	ER	Re (%)	Refere nce
Memod	Coarse refuse (28 × 100 mesh fraction)	Fire Clay	Riffle table	252 w	1.1	16.8	
	Coarse refuse (28 × 100 mesh fraction)	Eagle Seam	Riffle table	213 w	1.1	16.1	=
Gravity	Coarse refuse (28 × 100 mesh fraction)	Fire Clay Rider	Riffle table	234 w	1.1	24.75	-
Separation	Coarse refuse (<100 mesh fraction)	Eagle Seam	Multi-gravity separation	257ª	1.2	90	– [35 <u>]</u>
	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	_
	Decarbonized thickener underflow	Fire Clay	Multi-stage flotation using a conventional cell with sodium oleate as the collector	2300 a	5.3	<5	1001
	Decarbonized thickener underflow	Fire Clay	Multi-stage flotation using a column with sodium oleate as the collector	4700 a	10.9	<5	— [33 <u>]</u>
Flotation	Decarbonized thickener underflow	Fire Clay	Single-stage conventional cell flotation using oleic acid as the collector	386 w	1.4	23	
	Decarbonized thickener underflow	Eagle Seam	Single-stage flotation using a conventional cell with oleic acid as the collector	367 w	1.8	31	 [35]
	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



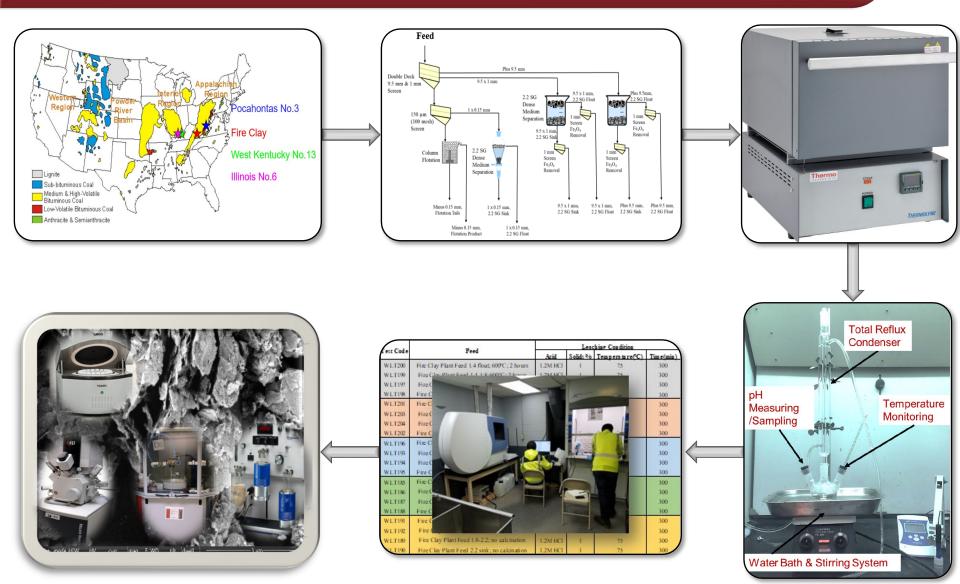


1 арые 2. A summary of sait and acid leacning of rare earth elements (КЕЕS) from coal and coal refuse

Sample	Coal Seam	Extraction Condition	Leaching Recovery	Reference
Decarbonized	West	0.1 M (NH4)2SO4, pH 5	Around 10% of total REEs, 7% of LREEs, and 18% of HREEs	
thickener underflow	Kentucky No. 13	0.1 M (NH ₄) ₂ SO ₄ , pH 3	Around 12% of total REEs, 10% of LREEs, and 21% of HREEs	- [41]
Roof material, 595 μm × 150 μm	Upper Kittanning	1 M (NH ₄) ₂ SO 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 ₂ SO ₄ , 40 °C, 48 h	Nearly 90% of the total REEs	[25]
	Fire Clay	Nitric acid solution of pH 0 at 75 °C	83% of total REEs, 86% of LREEs, and 69% of HREEs	
Decarbonized middlings	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	[11]
	Fire Clay	Nitric acid solution of pH 0 at 75 °C	31% of La, 26% of Ce, 40% of Nd, 36% of Y	
Decarbonized thickener underflow	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

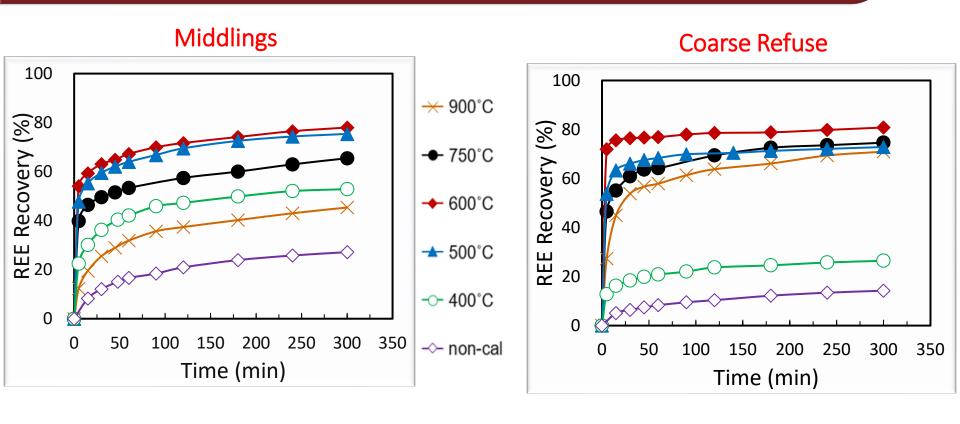




1.2 M HCl; 75°C; 1 g/L solid concentration

Enhanced REE Recovery through Calcination

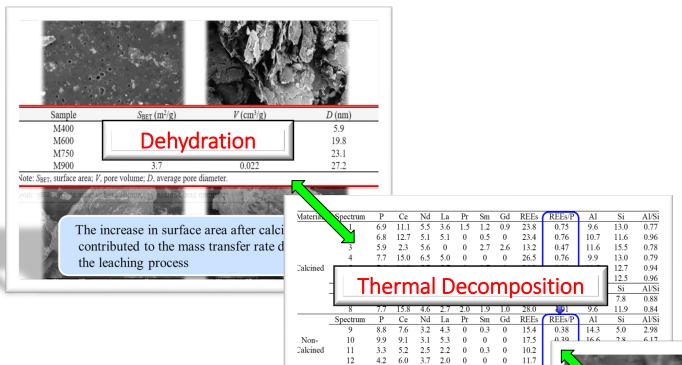




- REE leaching recovery was increased significantly
- Optimum temperature lied between 500-750°C
- Quick leaching kinetics at the beginning
- ☐ The middlings and coarse refuse showed different leaching characteristics

Mechanisms



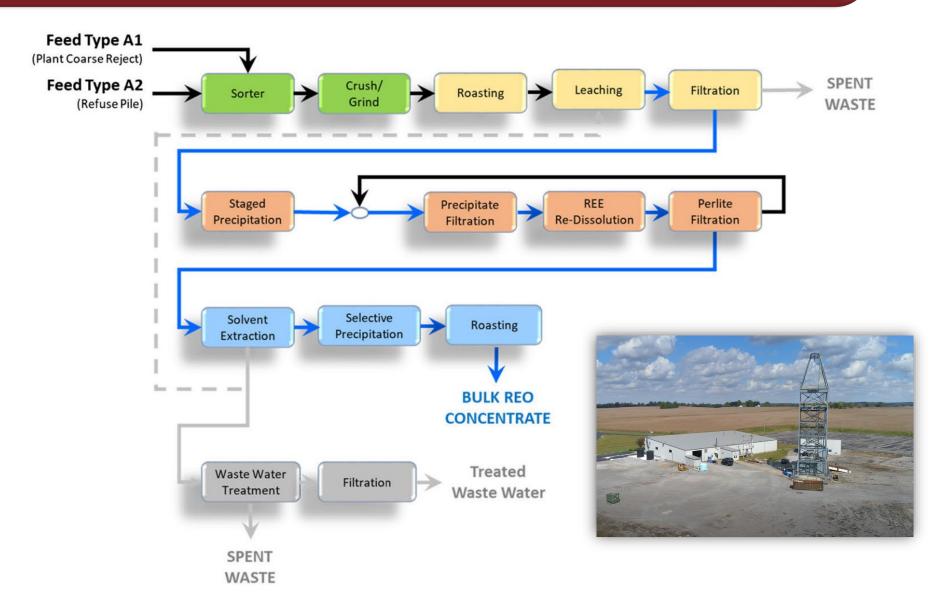


☐ The REE contents were increased after or relative to P



Pilot-Scale Testing





Recovery of Other Critical Materials from Coal



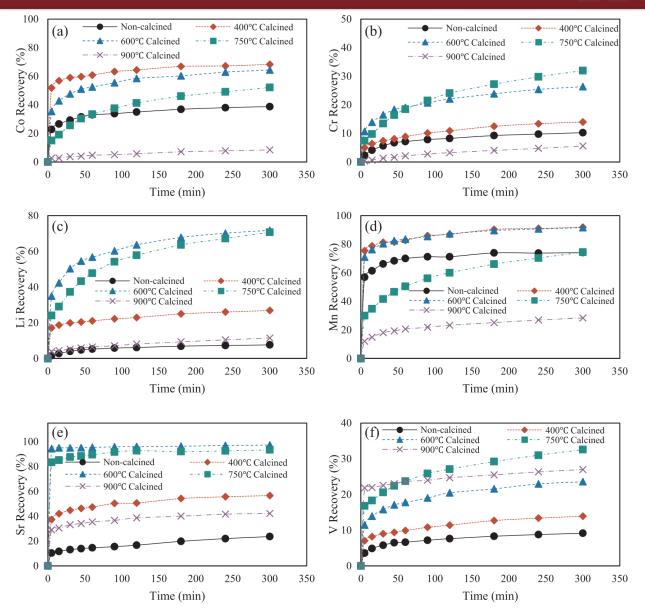


Fig. 6. The effects of calcination temperature on the leaching recoveries of other critical metals from the Baker materials.

REE Recovery from Coal







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



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

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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



Contents lists available at ScienceDirect

Minerals Engineering

journal homepage: www.elsevier.com/locate/mineng



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



Wencai Zhang, Rick Honaker



Contents lists available at ScienceDirect

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journal homepage: www.elsevier.com/locate/fuel



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 (10) Pub. No.: US 2020/0308667 A1 Honaker et al.
- - (43) Pub. Date:

Oct. 1, 2020

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

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

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(2006.01)(2006.01)

- (2006.01)C22B 3/22 C22B 3/04 (2006.01)
- C22B 59/00 (2006.01) C22B 3/44 (2006.01)(52) U.S. Cl.

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

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



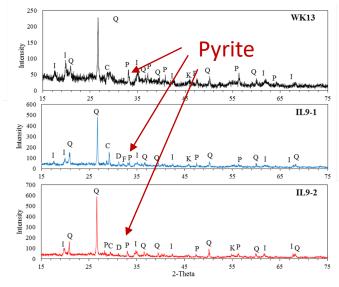
☐ Both oxygen and ferric ions can oxidize pyrite

$$FeS_{2(s)} + 14Fe_{(aq)}^{3+} + 18H_2O_{(l)} = 15Fe_{(aq)}^{2+} + 2SO_{4(aq)}^{2-} + 16H_{(aq)}^{+}$$

$$FeS_{2(s)} + 7/2 O_{2(aq)} + H_2 O_{(l)} = Fe_{(aq)}^{2+} + 2SO_{4(aq)}^{2-} + 2H_{(aq)}^{+}$$

$$Fe_{(aq)}^{2+} + 1/4 O_{2(aq)} + H_{(aq)}^{+} = Fe_{(aq)}^{3+} + 1/2 H_2 O_{(l)}$$

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





REEs in Acid Coal Mine Drainage

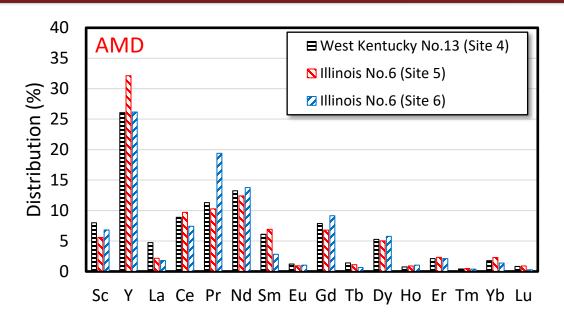


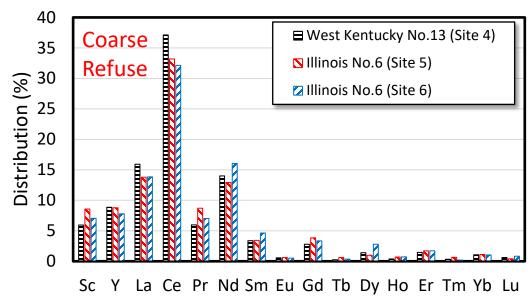
Leachate samples were collected from the coarse refuse piles of six different coal preparation plants

Coal Seam	West Kent	tucky No.9	West Kentucky No.9 and 11	West Kentucky No.13	Illinoi	s No.6
Processing Plant	Site 1	Site 2	Site 3	Site 4	Site 5	Site 6
pН	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
$Sm (\mu g/L)$	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

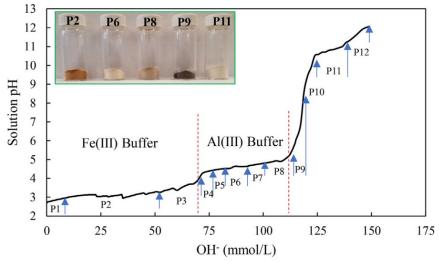




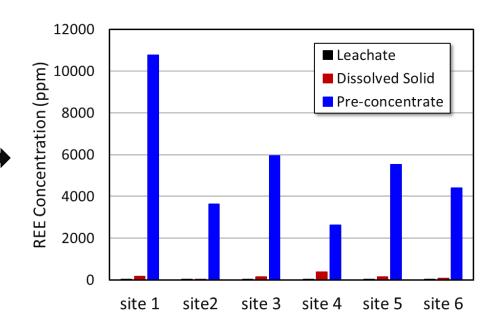


REE Recovery from AMD – Staged Precipitation



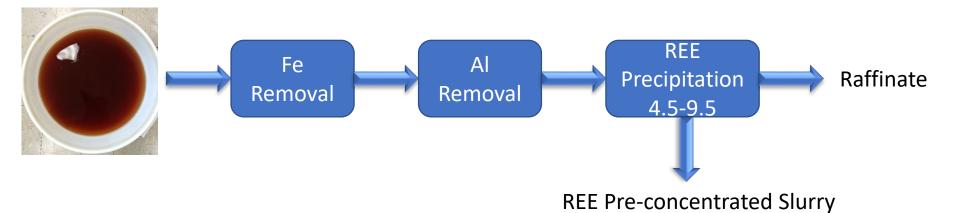


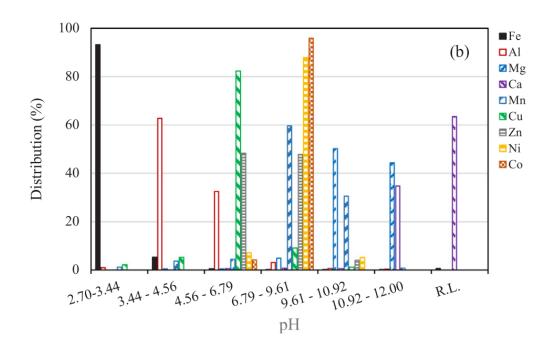
Feed	pH Range
Site 1	4.85-6.11
Site 2	5.11-6.32
Site 3	4.66-6.32
Site 4	5.01-6.36
Site 5	4.94-8.29
Site 6	3.25-8.10



REE Recovery from AMD - Staged Precipitation

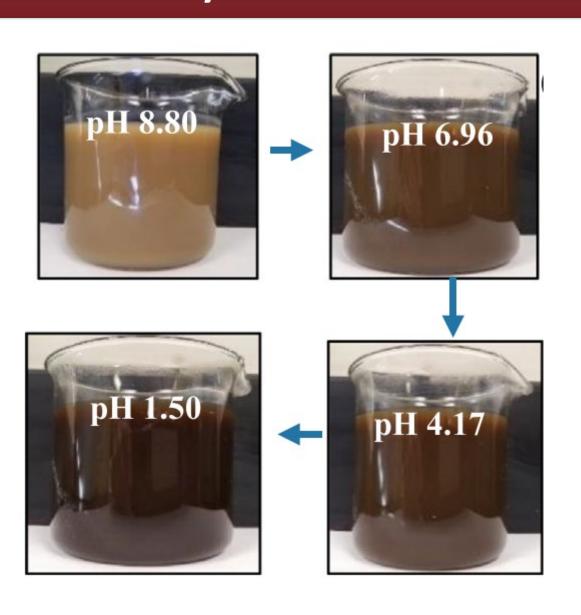


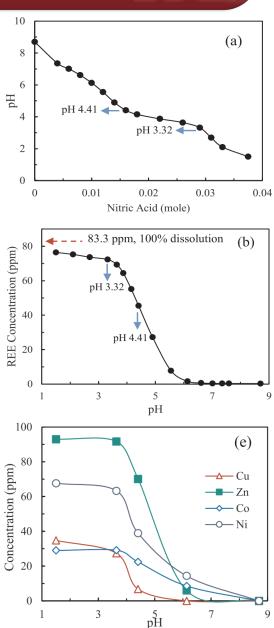




REE Recovery from AMD – Re-dissolution



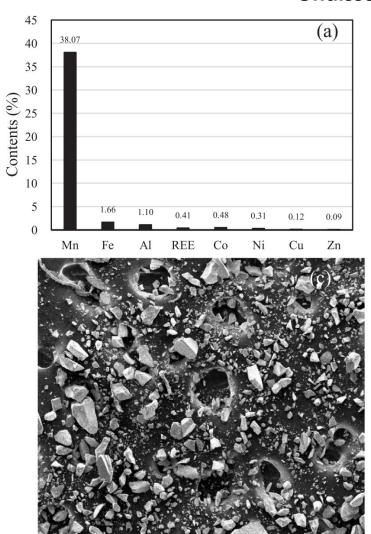


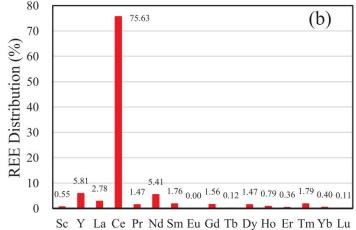


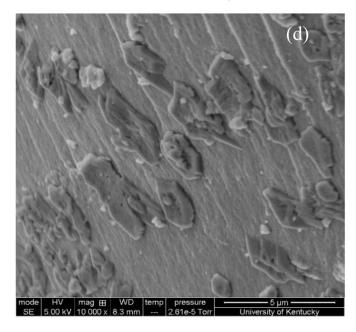
REE Recovery from AMD – Re-dissolution



Undissolved Material







REE Recovery from AMD – Re-dissolution



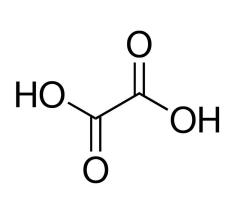
Dissolved Solution (Pre-concentrated Solution)

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

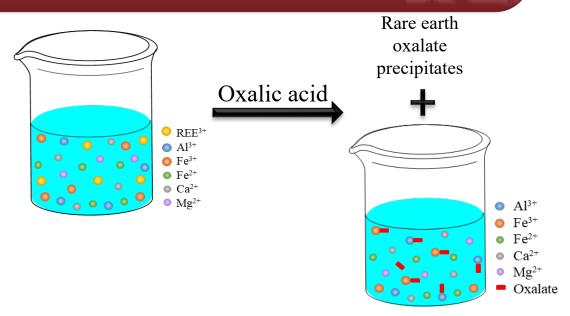
Elements	Sc	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy
ppm	0.66	19.24	8.15	13.34	2.87	11.40	3.45	0.75	4.40	0.61	3.86
Elements	Но	Er	Tm	Yb	Lu	HREEs	LREEs	REEs	Ca	Mg	Al
ppm	0.64	1.36	0.47	1.00	0.17	22.40	20.06	70.07	270	700	1355
F F	0.01	1.50	0.47	1.00	0.17	32.49	39.86	72.37	370	700	1333
Elements	Mn	Zn	Cu	Co	0.17	32.49	39.86	/2.3/	370	700	

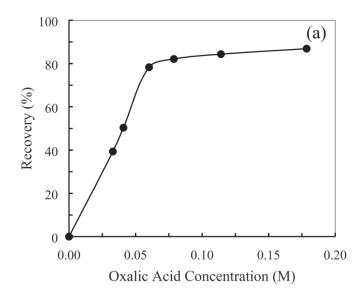
REE Recovery from Pre-concentrated Solution

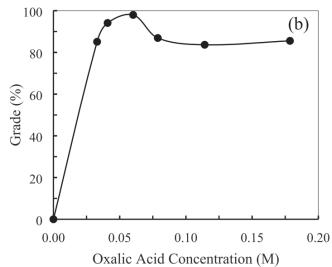




Oxalic acid (H₂C₂O₄)



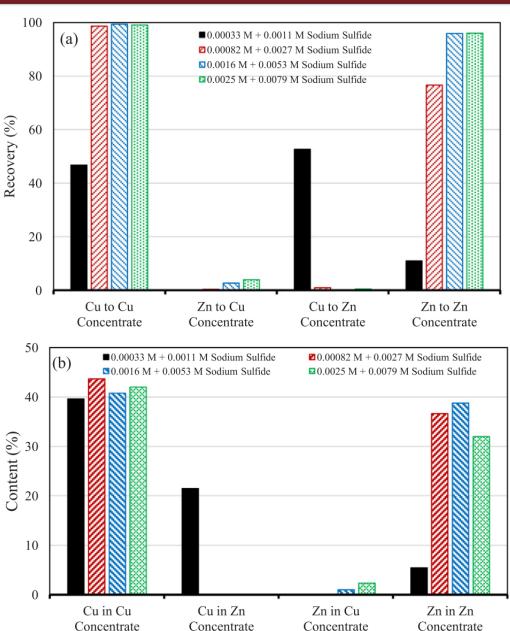




REEs	Content (%)
Sc2O3	0.05
Y2O3	21.05
La2O3	9.11
CeO2	23.32
Pr6O11	4.13
Nd2O3	17.67
Sm2O3	5.62
Eu2O3	1.24
Gd2O3	6.41
Tb2O3	0.89
Dy2O3	4.84
Ho2O3	0.81
Er2O3	1.55
Tm2O3	0.19
Yb2O3	0.92
Lu2O3	0.17
Total	97.97

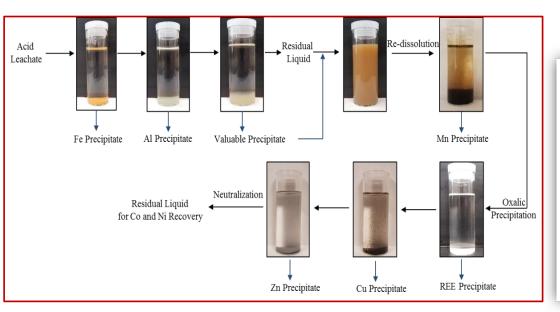
Cu and Zn Recovery from Pre-concentrated Solution





Process Summary





(19) United States

(12) Patent Application Publication (10) Pub. No.: US 2019/0136344 A1 Zhang et al.

May 9, 2019 (43) Pub. Date:

(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

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(60) Provisional application No. 62/583,644, filed on Nov.

Publication Classification

(51) Int. Cl. C22B 59/00 (2006.01)C22B 3/22 (2006.01)

US 20190136344A1

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

(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.

Minerals Engineering 153 (2020) 106382 Contents lists available at ScienceDirect ENGINEERING Minerals Engineering journal homepage: www.elsevier.com/locate/mineng Process development for the recovery of rare earth elements and critical metals from an acid mine leachate Wencai Zhang^{a,*}, Rick Honaker^b Department of Mining and Minerals Engineering, Virginia Polytechnic Institute and State University, Blacksburg, VA 24061, USA

Department of Mining Engineering, University of Kentucky, Lexington, KY 40506, USA

International Journal of Coal Geology 195 (2018) 189-199 Contents lists available at ScienceDirect

International Journal of Coal Geology

journal homepage: www.elsevier.com/locate/coal



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 the research in my group; ☐ Investment from industrial stakeholders is needed for the ultimate commercial deployment of the technologies.

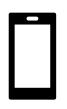
Thank you!







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