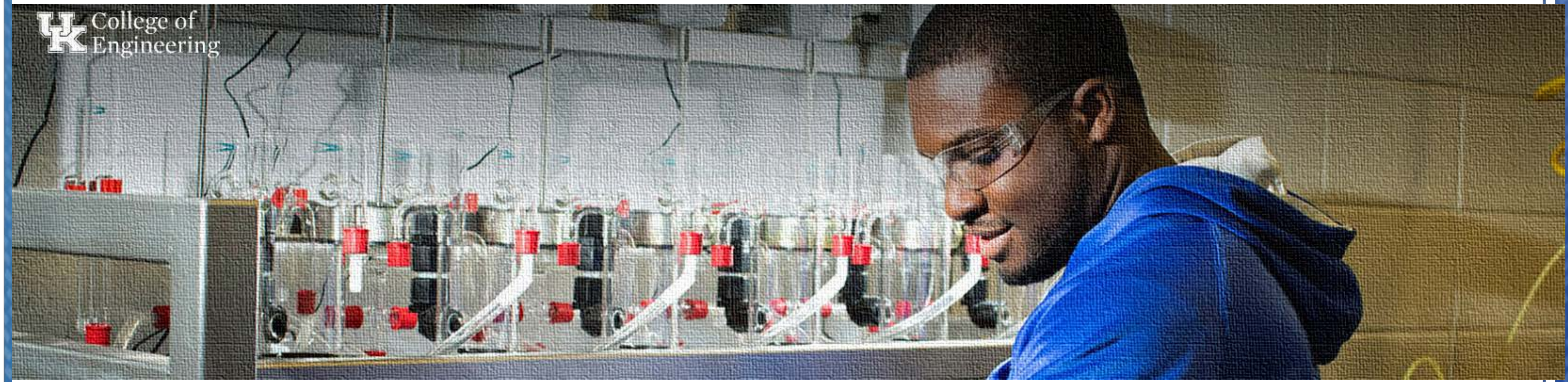


Low-Temperature Plasma Treatment for Enhanced Recovery of Highly Valued Critical Rees from Coal

PRINCIPAL INVESTIGATOR:
Dr. Rick Honaker
University of Kentucky

DOE Award Number: FE0031525
Period of Performance: 11/15/2017 – 5/15/2019
NETL Program Manager: Jason Hissam

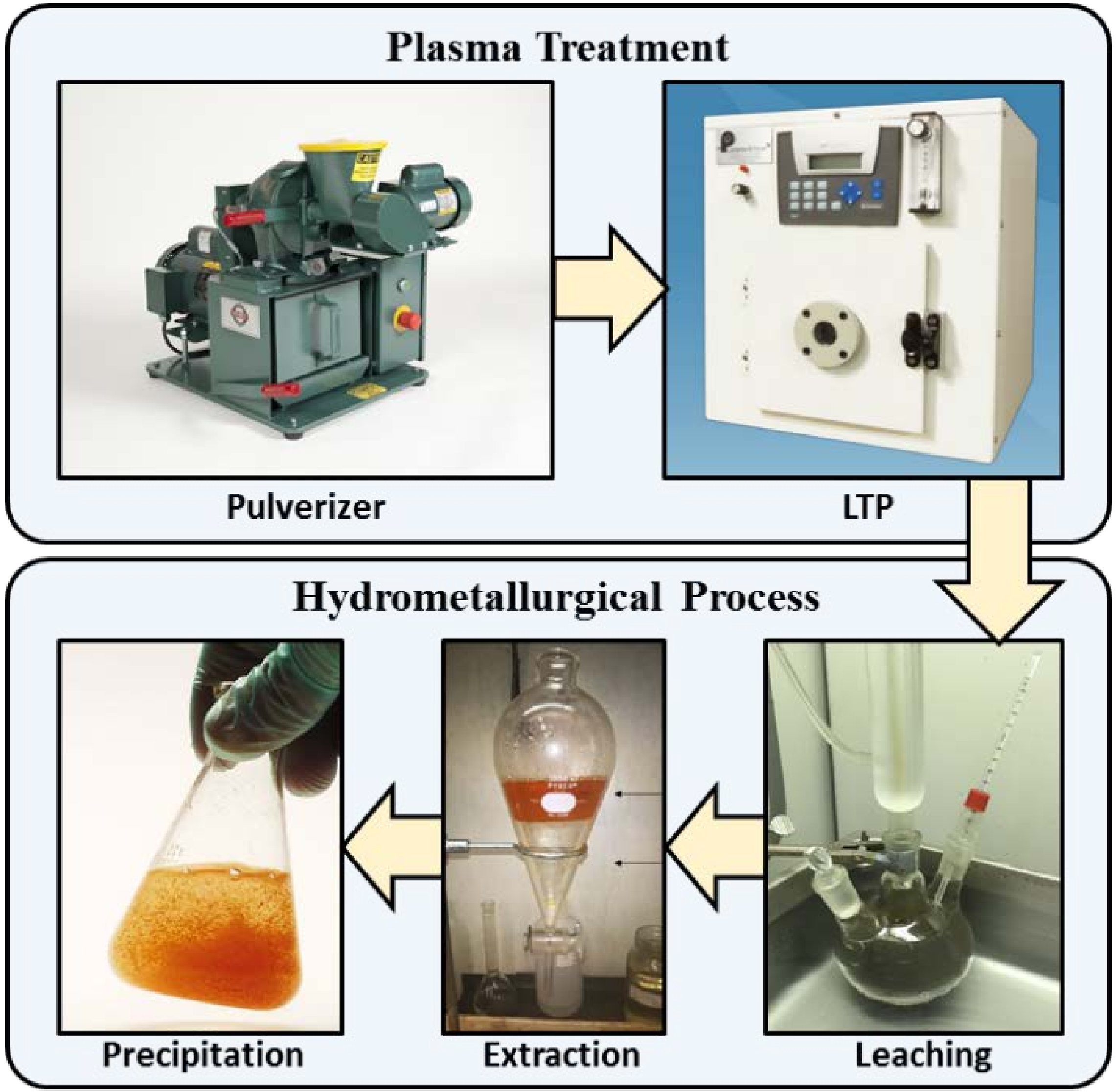
2019 Annual Project Review Meeting

Crosscutting Research, Rare Earth Elements, Gasification Systems, and Transformative Power Generation

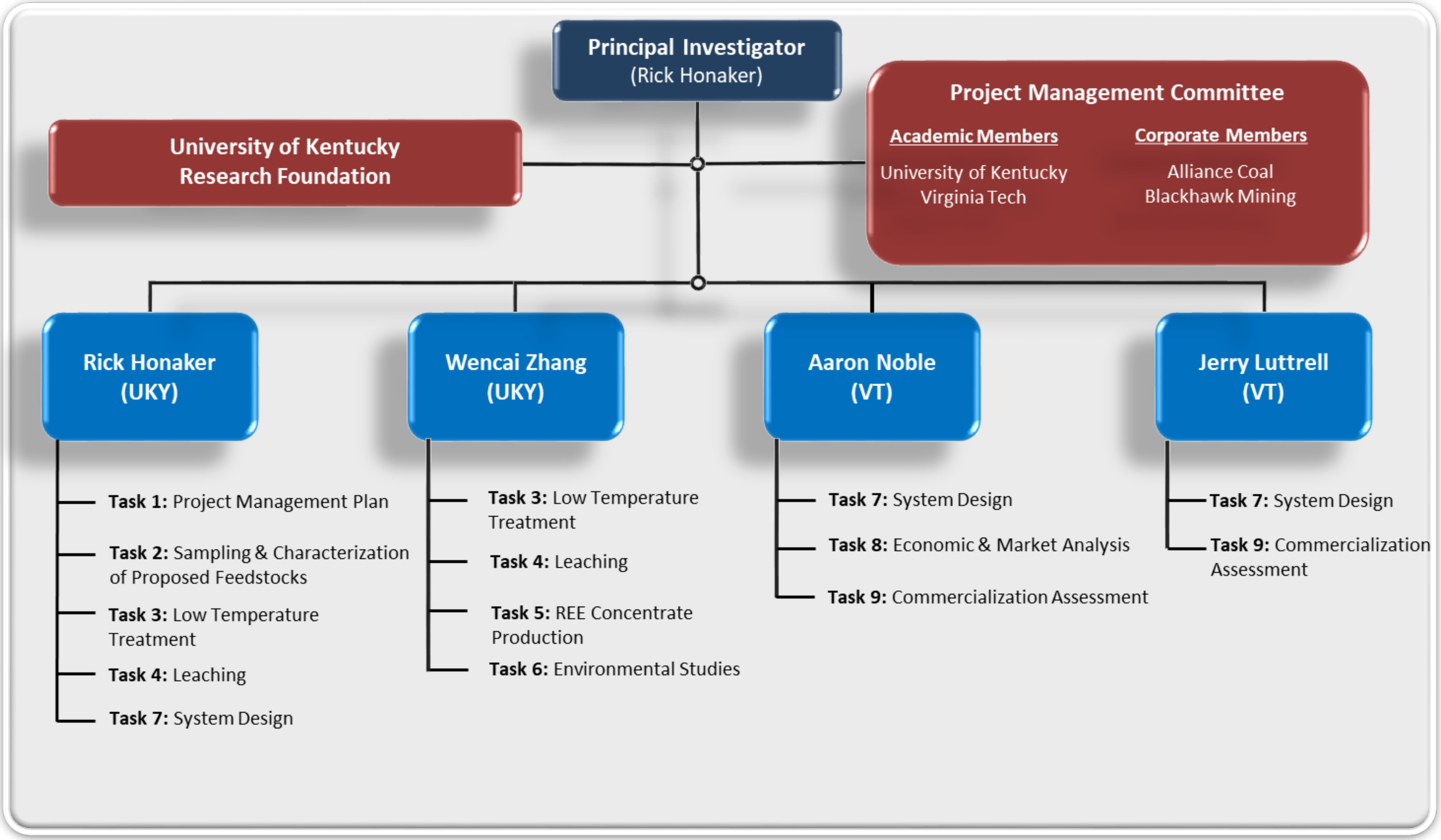
April 9 - 11, 2019

Objectives

- A novel process is to be developed using Low-Temperature Plasma (LTP) treatment integrated with hydrometallurgical processes to recover rare earth elements (REEs)
- LTP is utilized to pre-treat the feed to liberate, release, oxidize and/or activate the REEs embedded in coal or mineral matter
- LTP technique can enhance the leaching characteristics of the REEs and a product containing ≥ 90% of total REEs (TREE) on a dry whole mass basis can be produced.



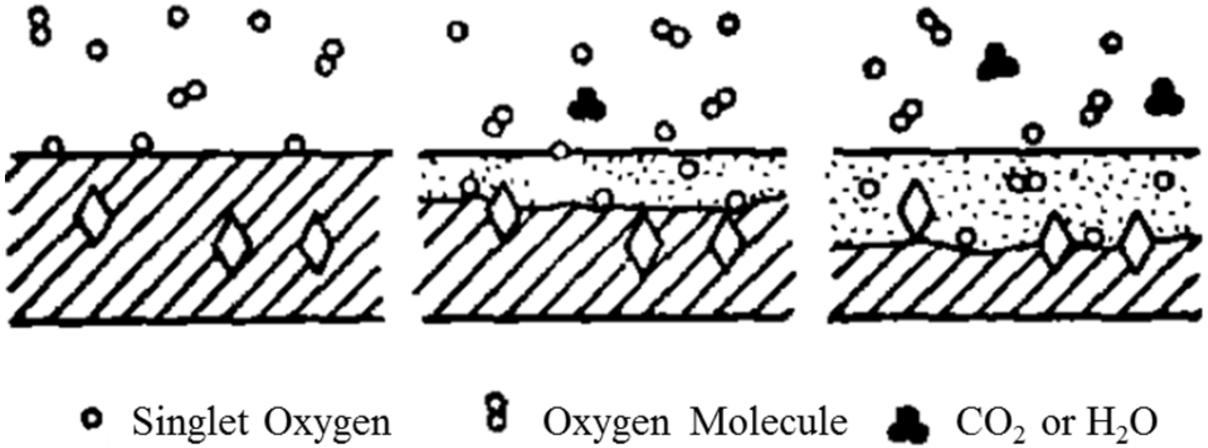
Project Team

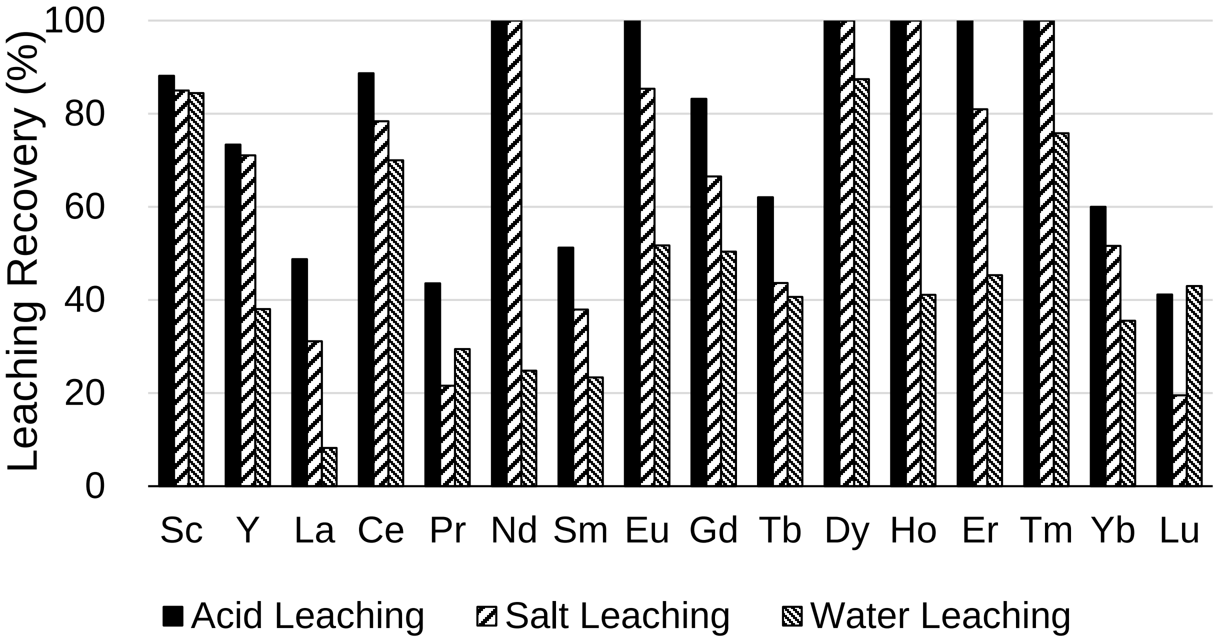


Low Temperature Plasma Treatment

Electron Ionization

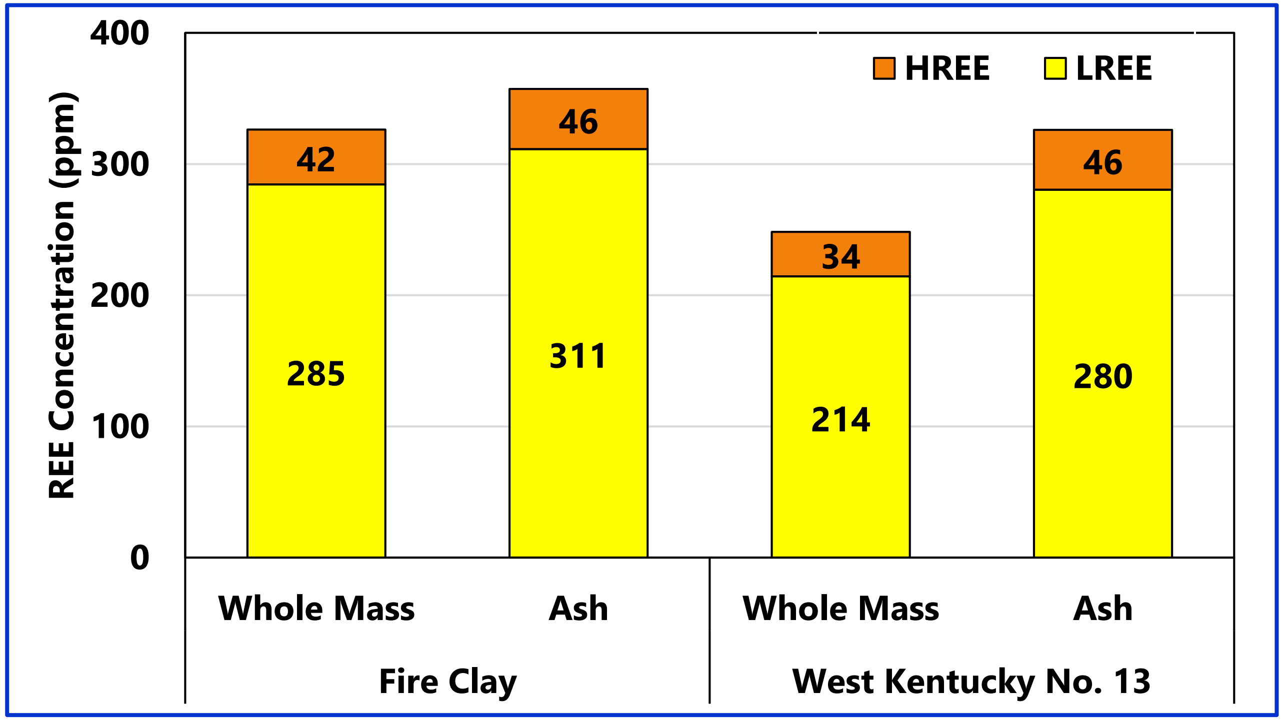
$$e^- + O_2 \rightarrow O_2^{\ +} + 2e^- \rightarrow O^+ + O \quad (1)$$
$$e^- + O_2 \rightarrow O_2^{\ 2+} + 3e^- \rightarrow O^+ + O^+ \rightarrow O^{2+} + O \quad (2)$$
$$e^- + O_2 \rightarrow O_2^{\ 3+} + 4e^- \rightarrow O^{2+} + O^+ \quad (3)$$





McConkey et al., 2008; Hozumi, 1977

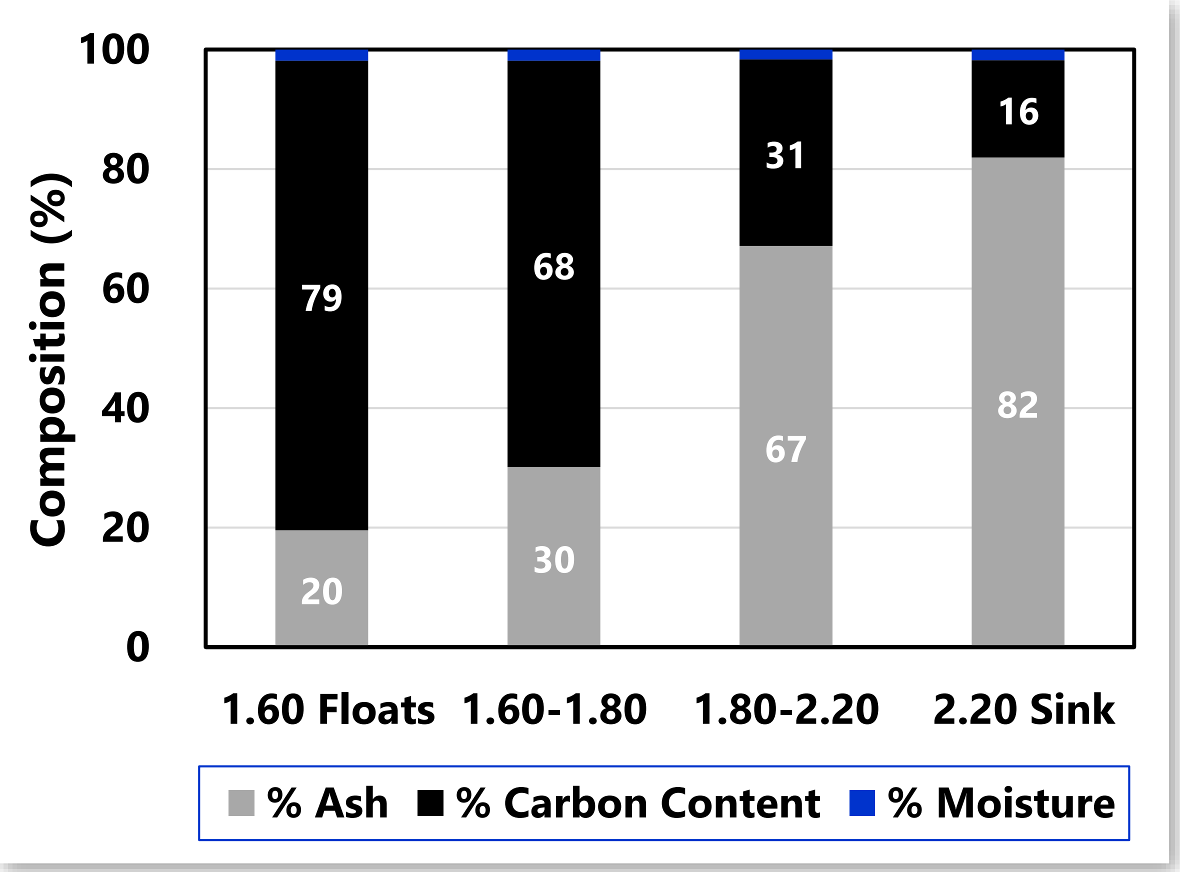
Feed Characterization



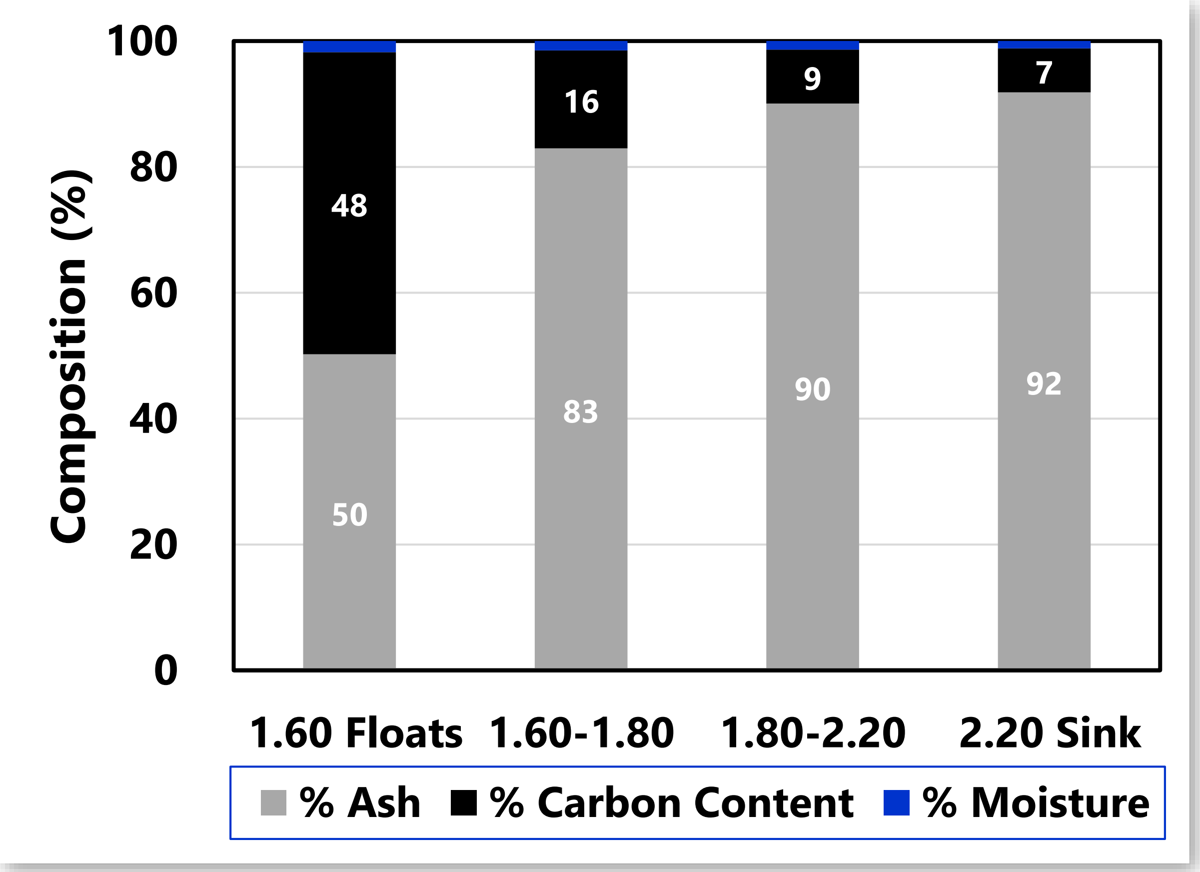
- Coarse refuse samples collected from plants treating West Kentucky No.13 and Fire Clay seam sources.
- Fractions of 1.60 SG Float, 1.60-1.80 SG,1.80-2.20 SG and 2.20 SG Sink were size reduced and analyzed for the REE concentrations.
- Fire Clay-CR composite sample had total REE concentration higher than 300ppm while the Dotiki-CR composite sample contained 250 ppm TREE.

Feed Characterization

West Kentucky No.13 Coarse Refuse

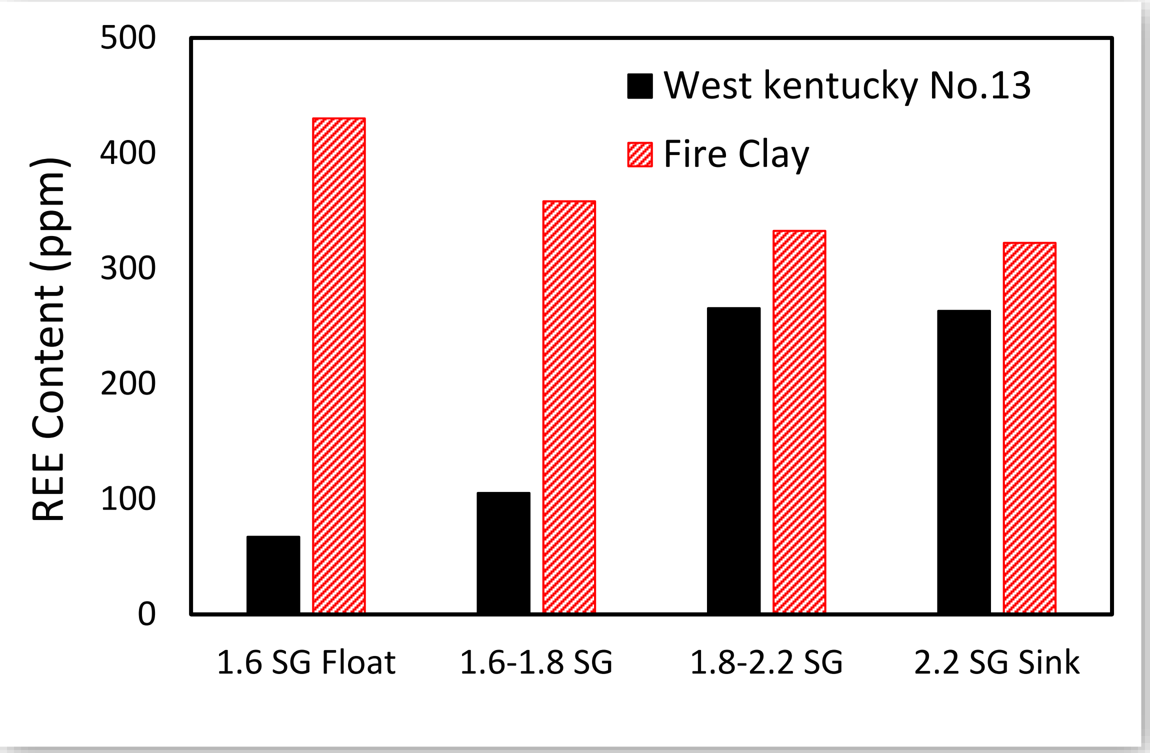


Fire Clay Coarse Refuse

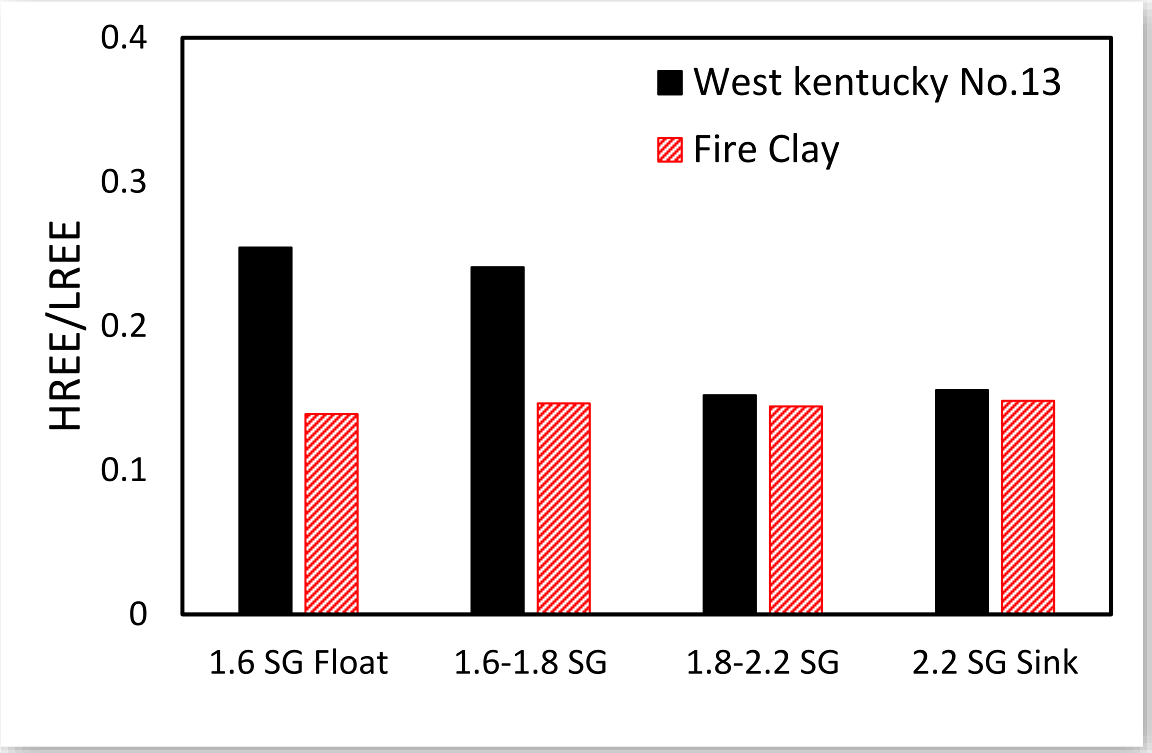


Feed Characterization

REE Contents (Dry Whole Mass Basis)

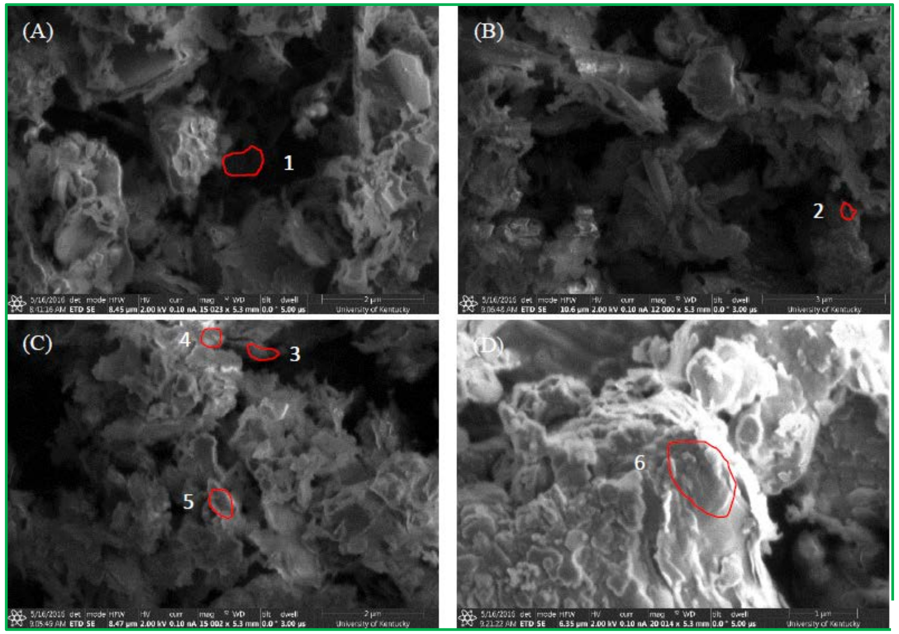


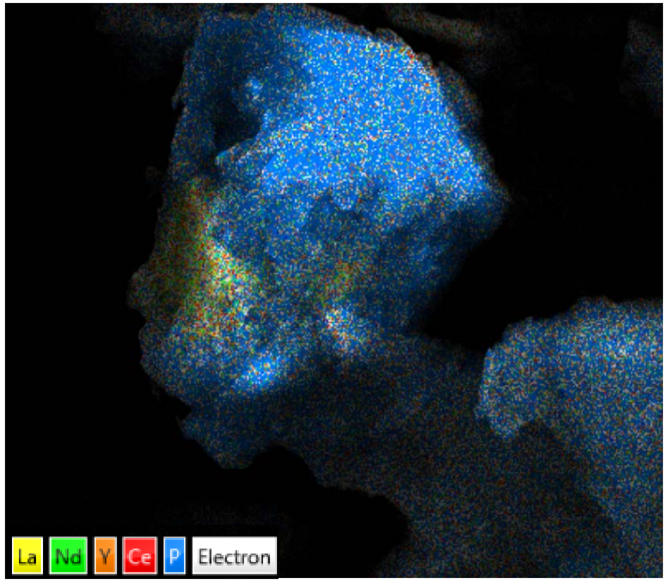
HREE/LREE

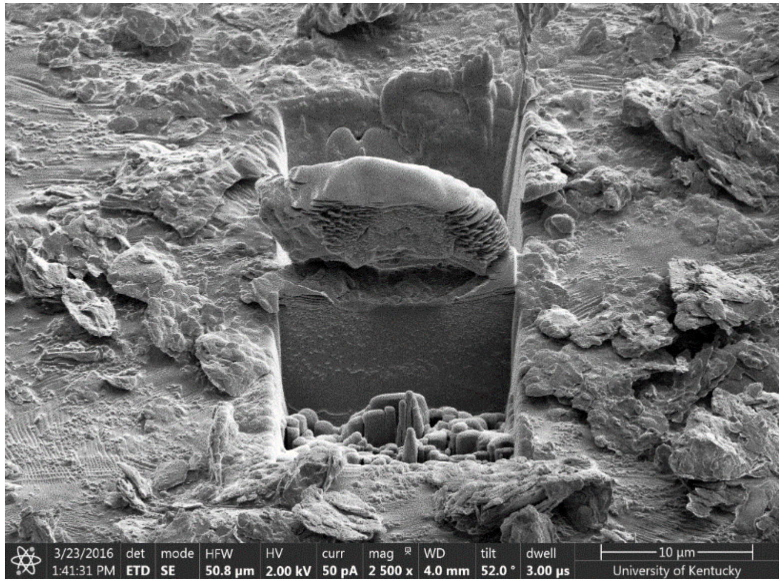


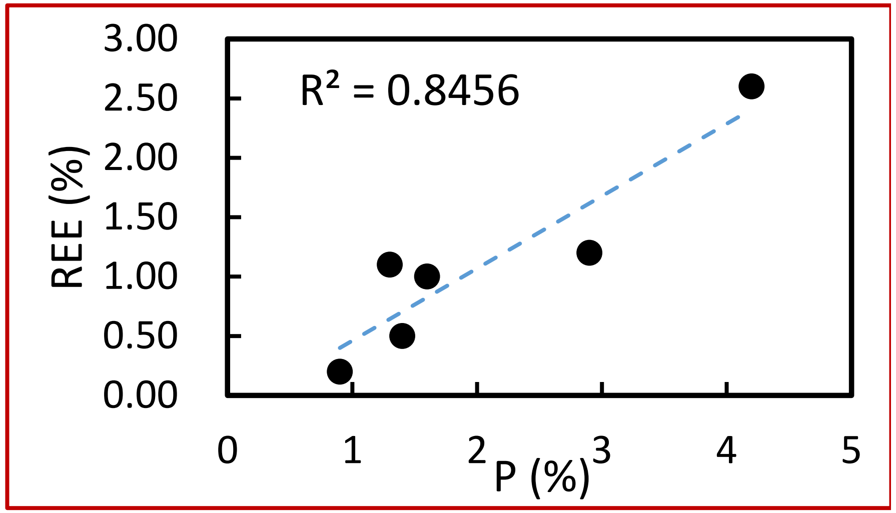
- Rare earth phosphates originating from volcanic activity contributed the higher REE content in the Fire Clay low density fractions
- The relatively higher HREE/LREE ratio in the West Kentucky No. 13 seam is likely due to stronger organic affinity.

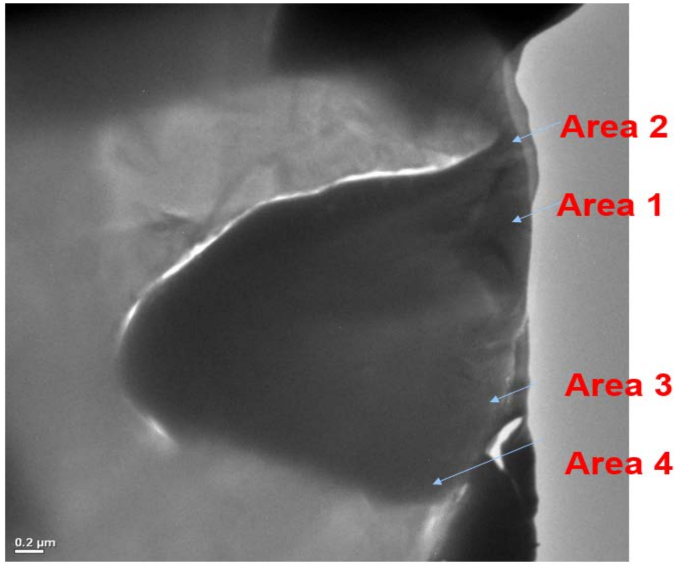
Feed Characterization-REE Phosphates in Fire Clay Coal

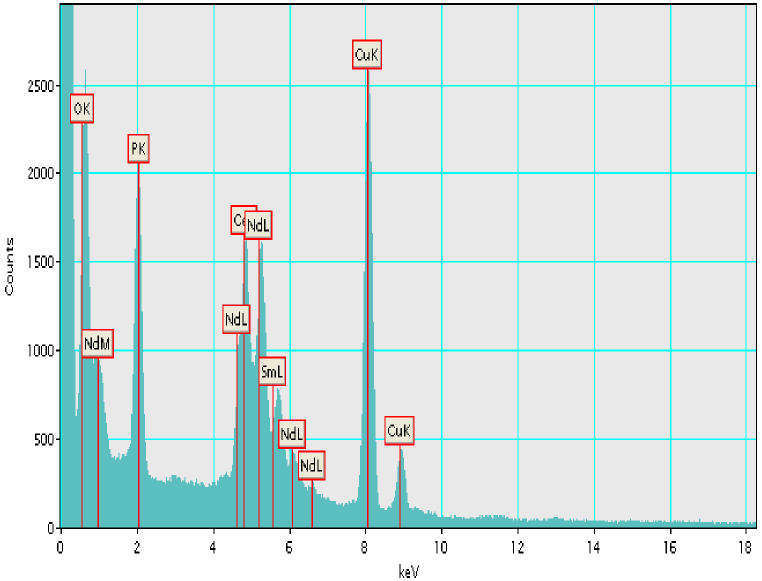




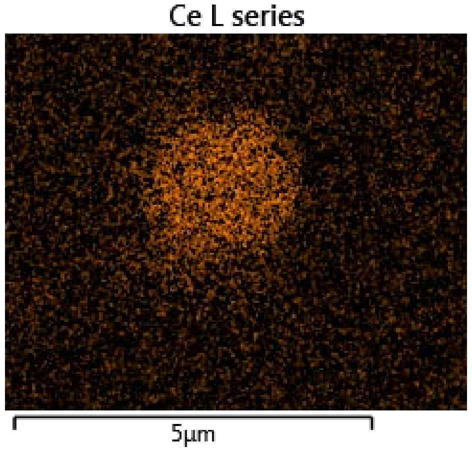


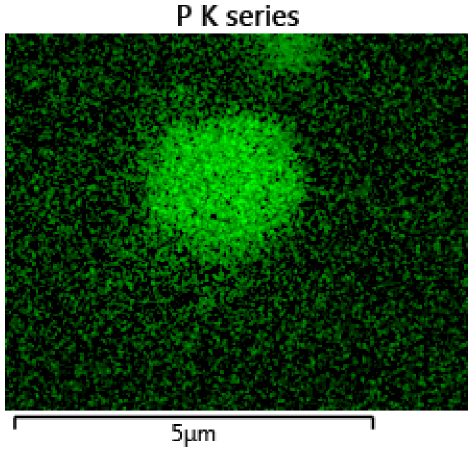






Feed Characterization-REE Phosphates in West Kentucky No.13





- Solely one rare earth phosphate particle was found through two batches of large area mapping, which indicated the lack of rare earth minerals in the West Kentucky No.13 coal.

Feed Characterization-XRD

Major Minerals

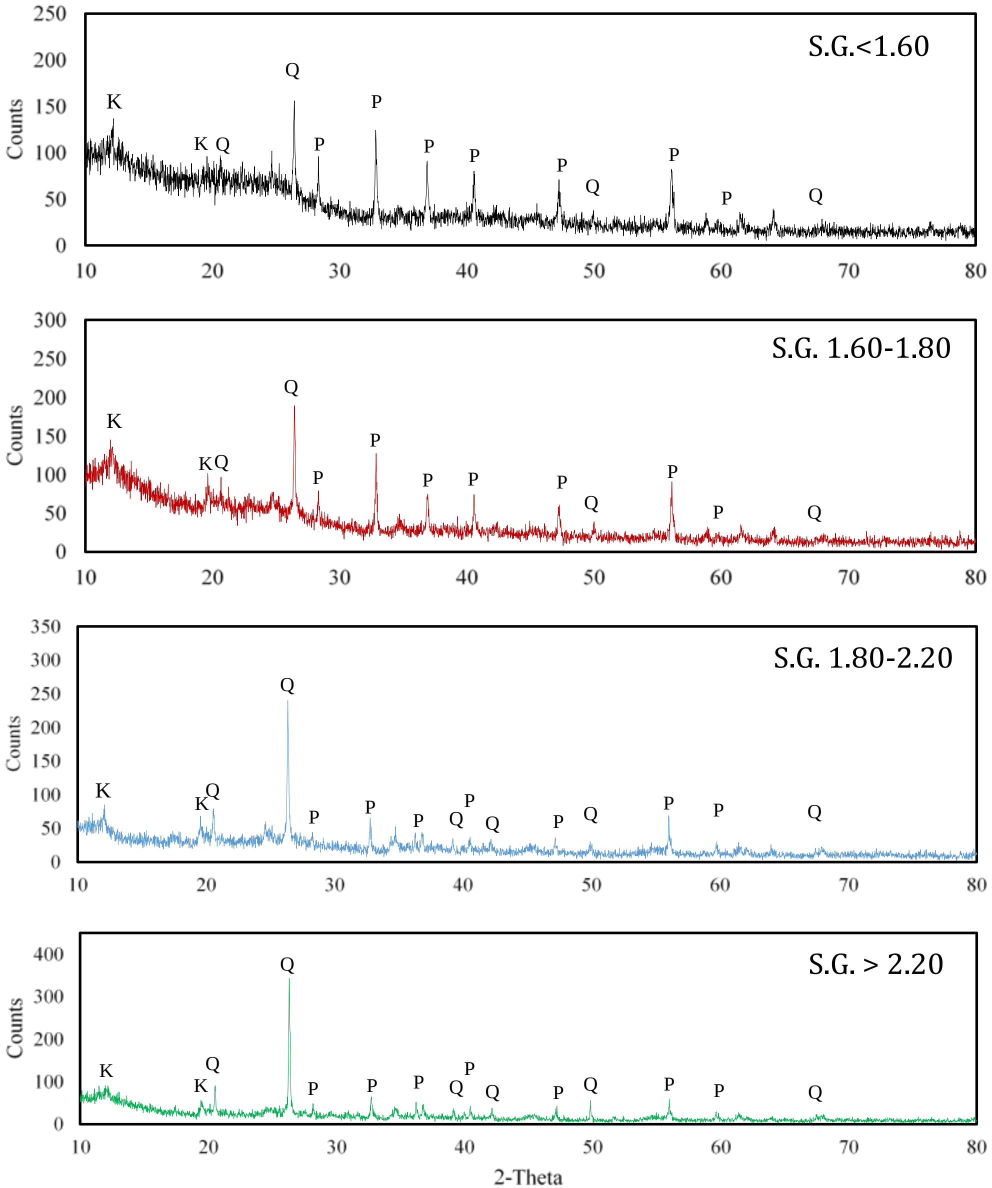
Q-Quartz
(SiO_2)

K-Kaolinite
($Al_2Si_2O_5(OH)_4$)

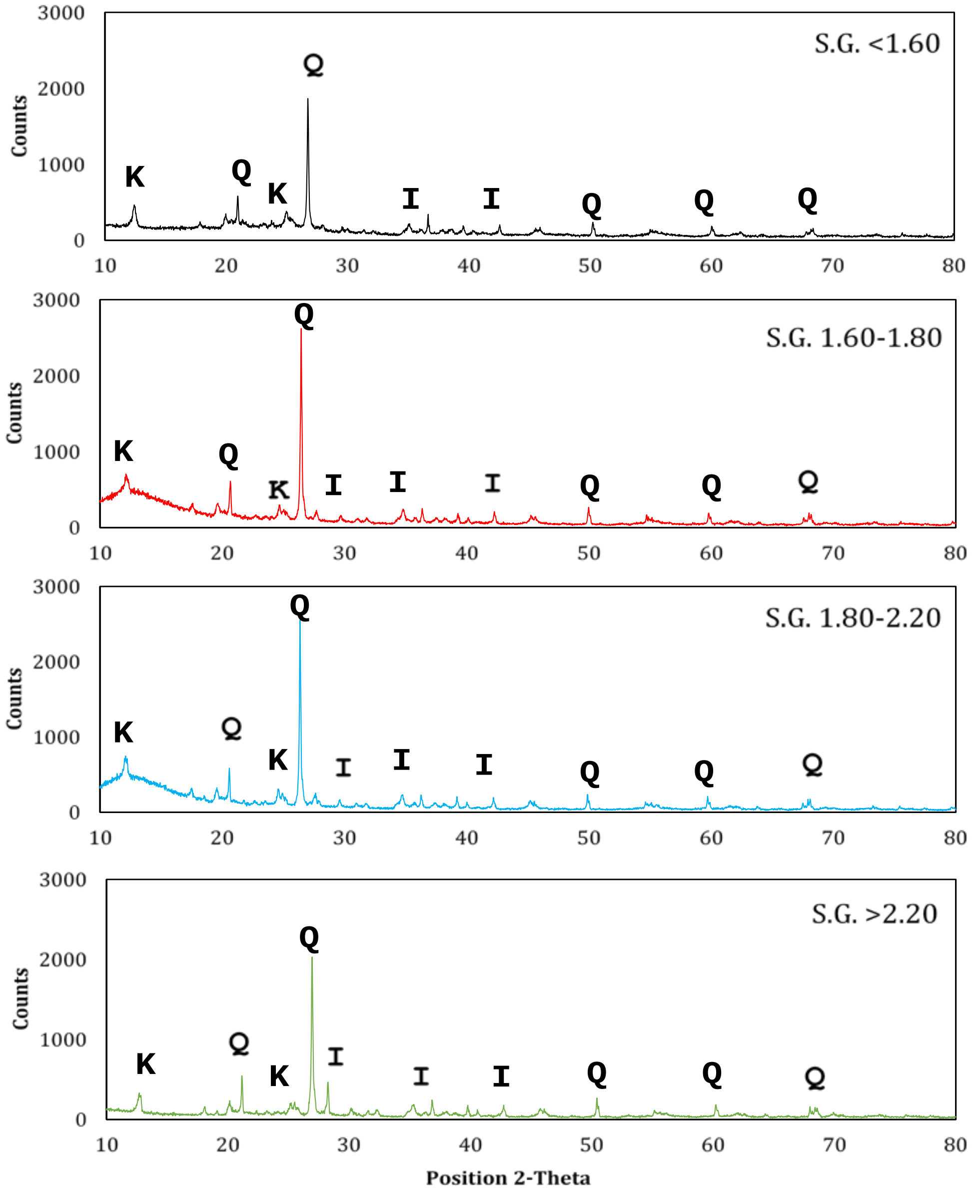
I-Illite
($(K,H_3O)(Al,Mg,Fe)_2(Si,Al)_4O_{10}[(OH)_2,(H_2O)]$)

P-Pyrite
(FeS_2)

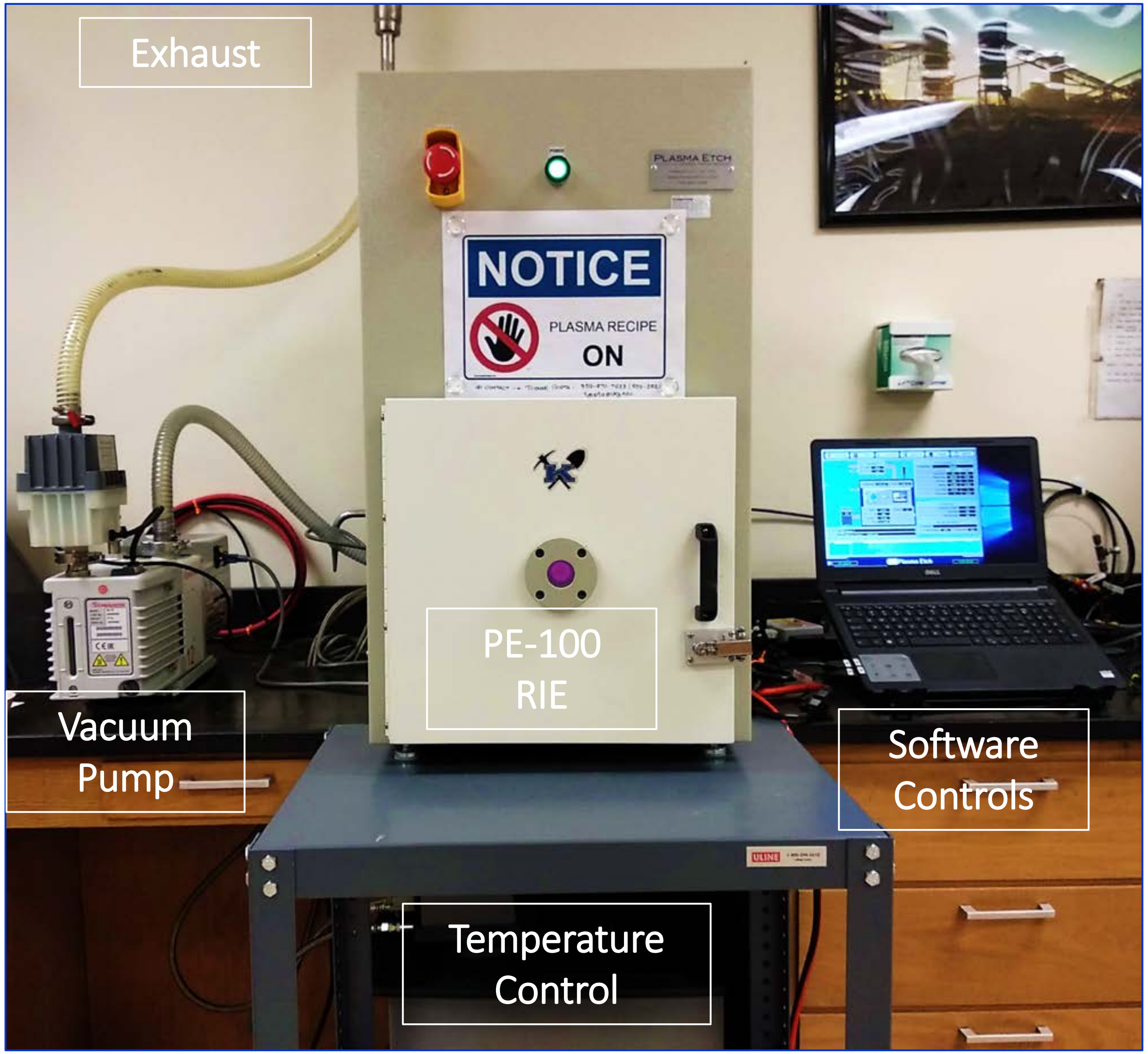
West Kentucky No.13

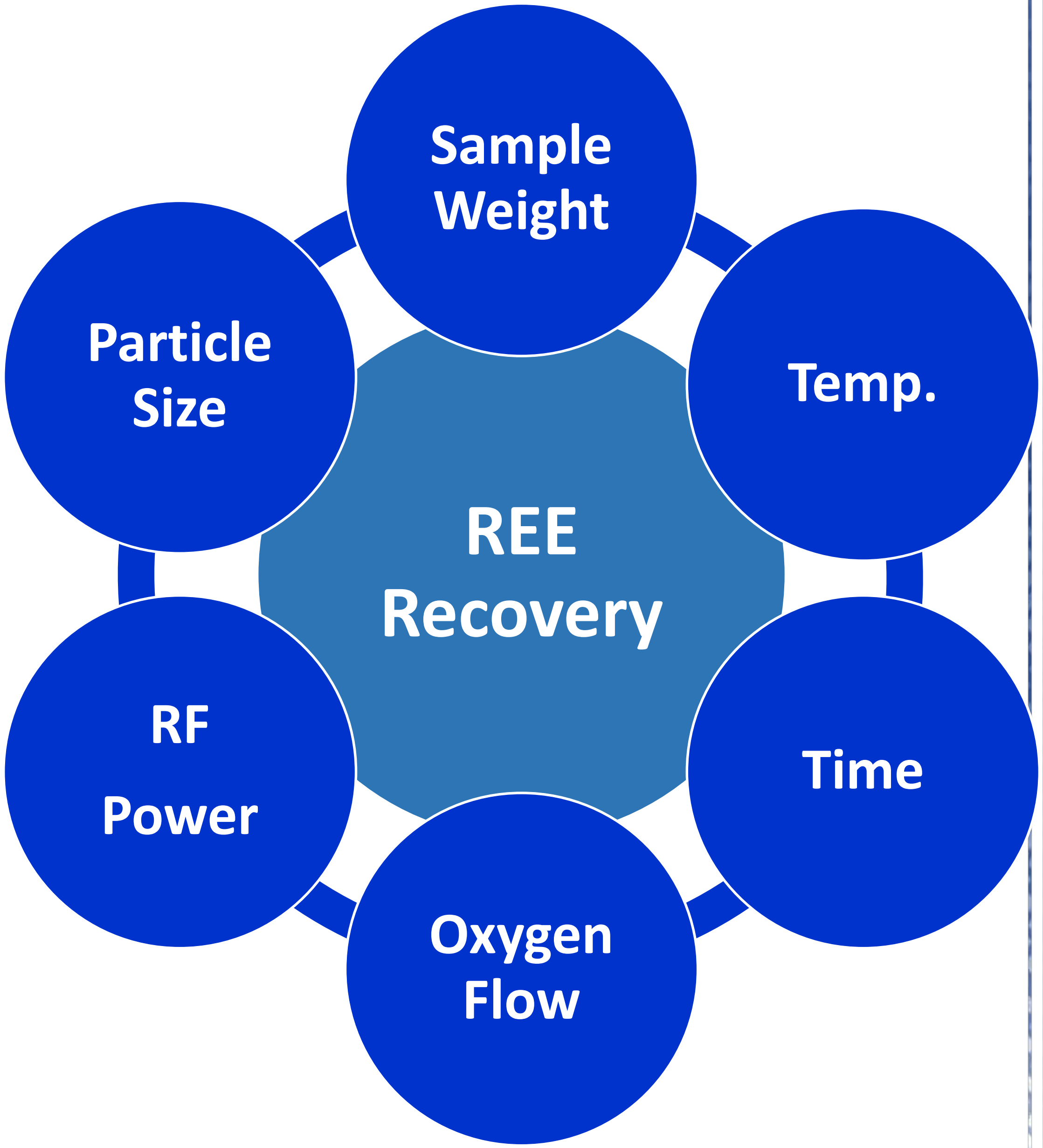


Fire Clay



Low Temperature Plasma Parametric Study





Two-Factorial Parametric Study

1.8-2.2 S.G. Fraction

		Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Factor 6	Response 1
Std.	Run	A:Temp	B:RF Power	C:Oxygen	D:Time	E:Weight	F:Size	REE Recovery
		Celsius	Watts	CC/min	Hours	Grams	Microns	%
8	1	60	250	35	3	20	180	10.09
6	2	60	100	35	1	20	75	10.40
1	3	30	100	25	3	20	180	9.92
7	4	30	250	35	1	10	180	10.35
2	5	60	100	25	1	10	180	10.91
4	6	60	250	25	3	10	75	13.56
5	7	30	100	35	3	10	75	11.86
3	8	30	250	25	1	20	75	10.67

Two-Factorial Parametric Study

West Kentucky No.13 1.8-2.2 S.G. Fraction

		Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Factor 6	Response 1
Std.	Run	A:Temp	B:RF Power	C:Oxygen	D:Time	E:Weight	F:Size	REE Recovery
		Celsius	Watts	CC/min	Hours	Grams	Microns	%
8	1	60	250	35	3	20	180	10.09
6	2	60	100	35	1	20	75	10.40
1	3	30	100	25	3	20	180	9.92
7	4	30	250	35	1	10	180	10.35
2	5	60	100	25	1	10	180	10.91
4	6	60	250	25	3	10	75	13.56
5	7	30	100	35	3	10	75	11.86
3	8	30	250	25	1	20	75	10.67

Fire Clay 1.8-2.2 S.G. Fraction

		Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Factor 6	Response 1
Std.	Run	A:Temp	B:RF Power	C:Oxygen	D:Time	E:Weight	F:Size	REE Recovery
		Celsius	Watts	CC/min	Hours	Grams	Microns	%
8	1	60	250	35	3	20	180	41.17
6	2	60	100	35	1	20	75	38.68
1	3	30	100	25	3	20	180	36.66
7	4	30	250	35	1	10	180	38.32
2	5	60	100	25	1	10	180	37.72
4	6	60	250	25	3	10	75	40.14
5	7	30	100	35	3	10	75	39.56
3	8	30	250	25	1	20	75	38.71

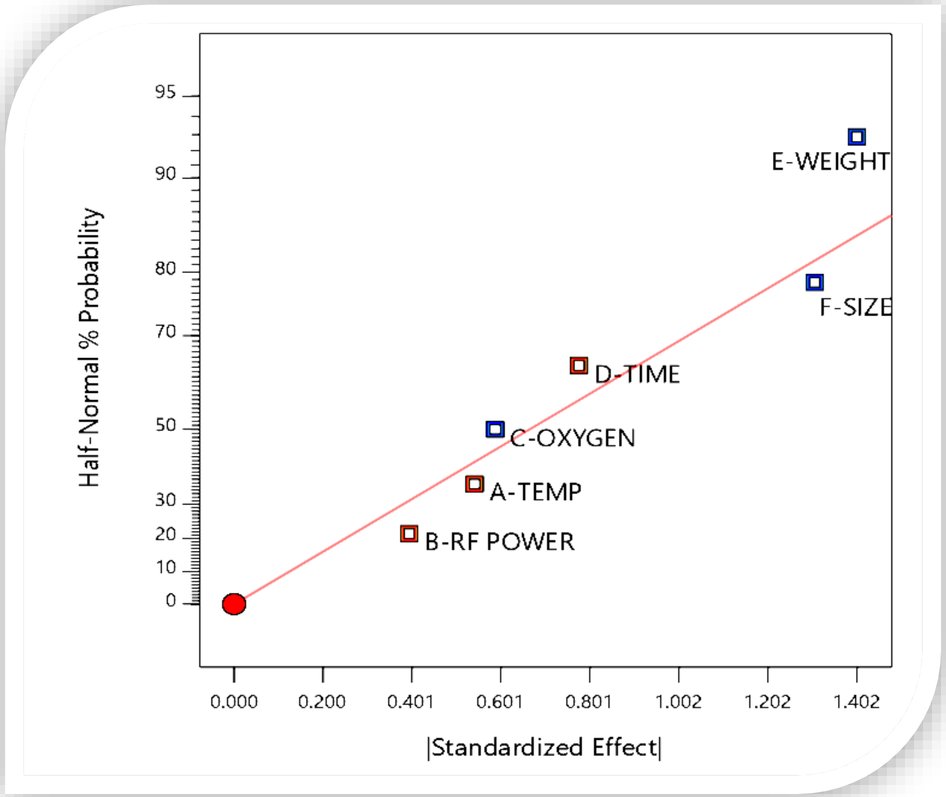
Two-Factorial Parametric Study

West Kentucky No.13 1.4 SG Float

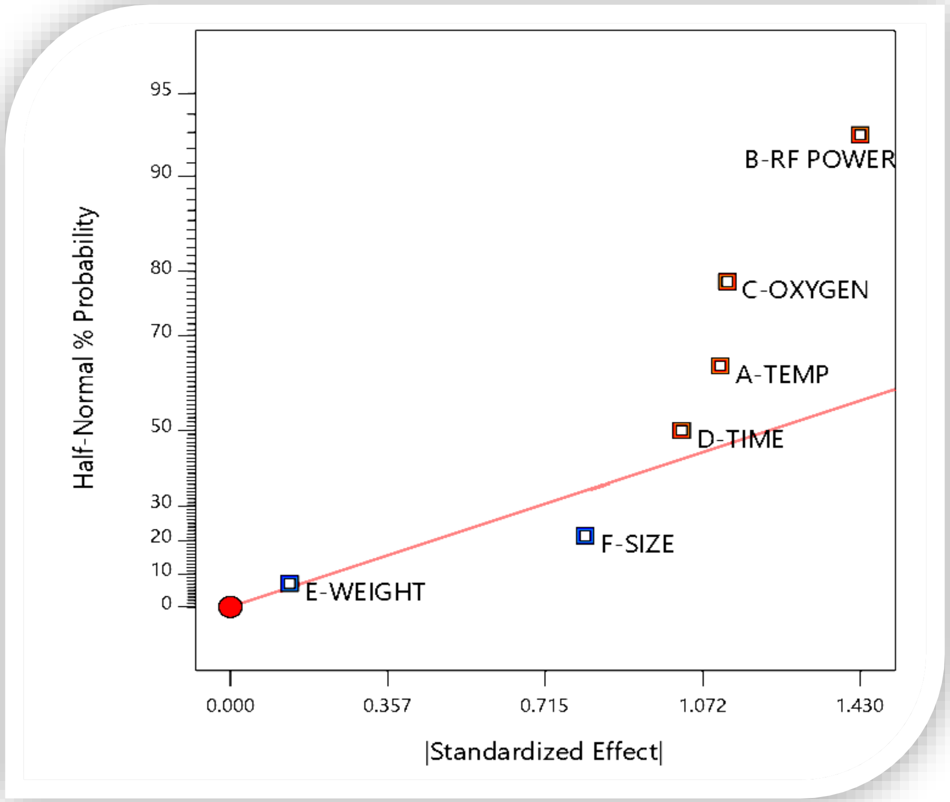
		Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Factor 6	Recovery
Std	Run	A:TEMP	B:RF POWER	C:OXYGEN	D:TIME	E:WEIGHT	F:SIZE	
		CELCIUS	WATTS	CC/MIN	HOURS	GRAMS	MICRONS	%
8	1	60	450	40	5	30	180	24.8
6	2	60	100	40	1	30	75	24.6
1	3	30	100	25	5	30	180	20.6
7	4	30	450	40	1	10	180	20.7
2	5	60	100	25	1	10	180	14.2
4	6	60	450	25	5	10	75	30.2
5	7	30	100	40	5	10	75	27.3
3	8	30	450	25	1	30	75	20.3

Two-Factorial Parametric Study

West Kentucky No.13

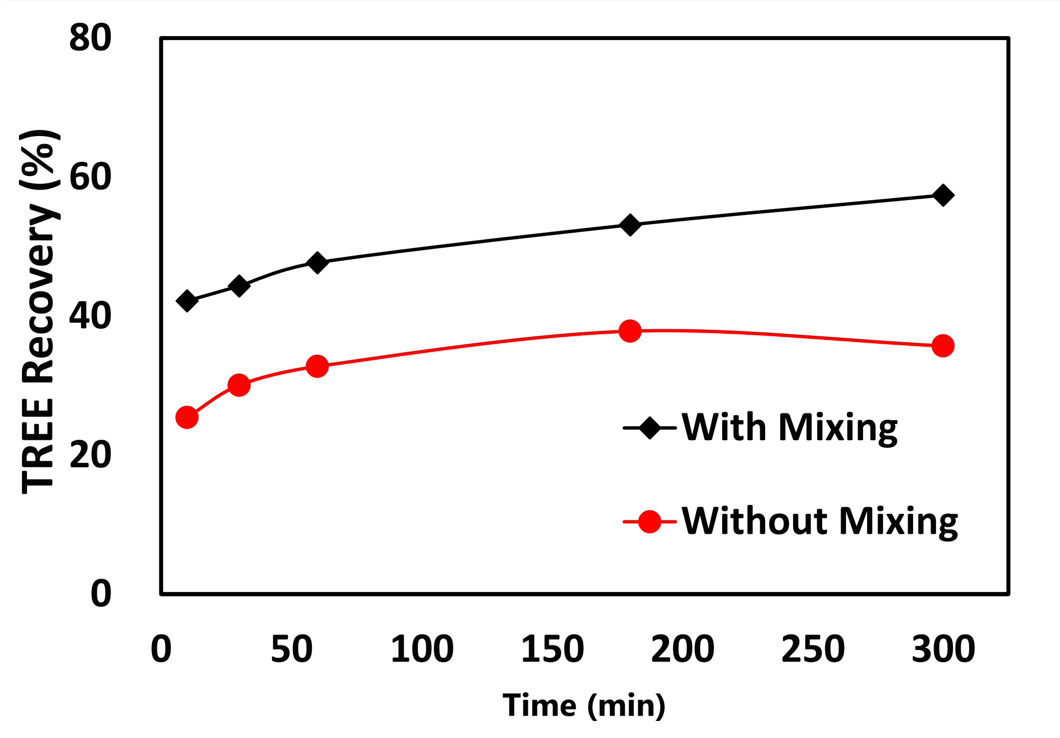


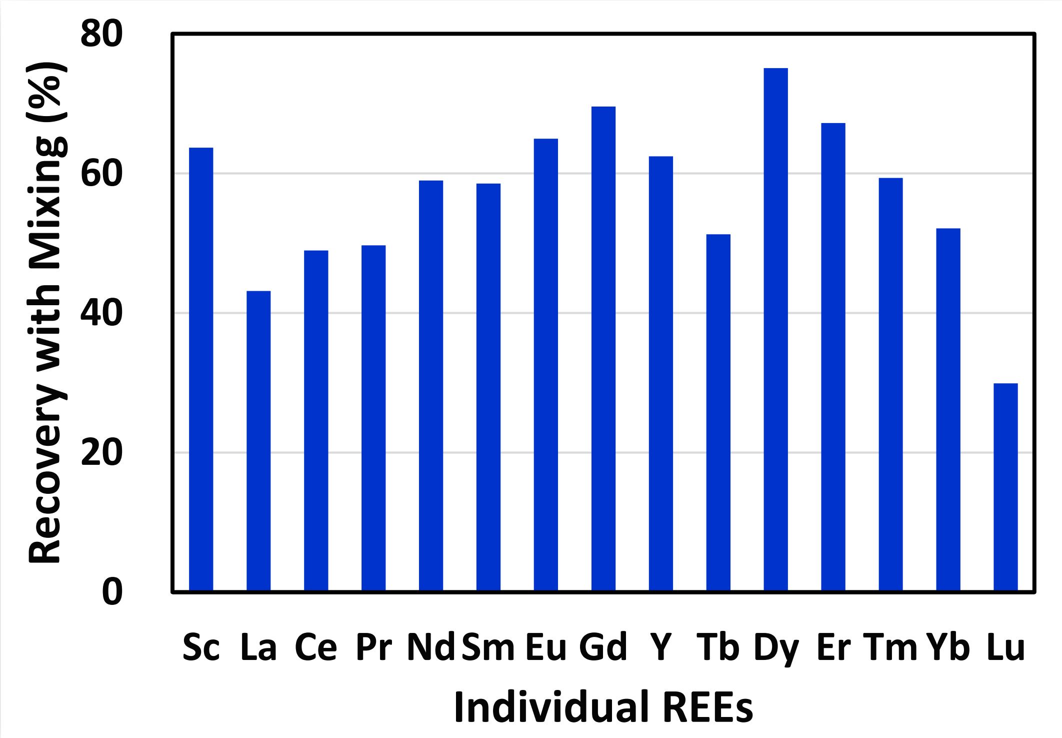
Fire Clay

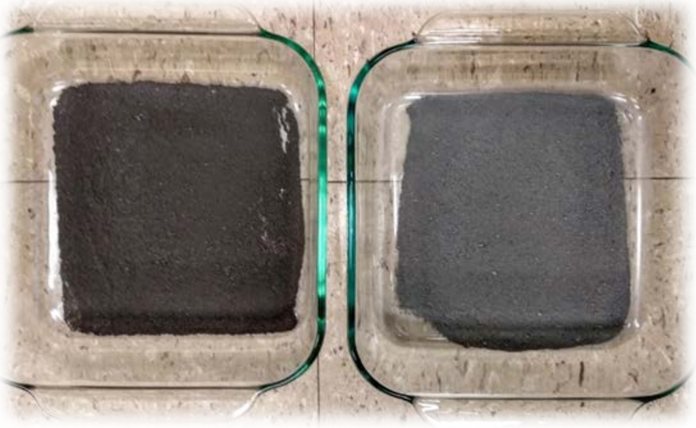


- The variables shaded orange are positively associated with the response variable while the ones shaded blue are negatively associated with REE recovery.

Time Based Plasma Treatment



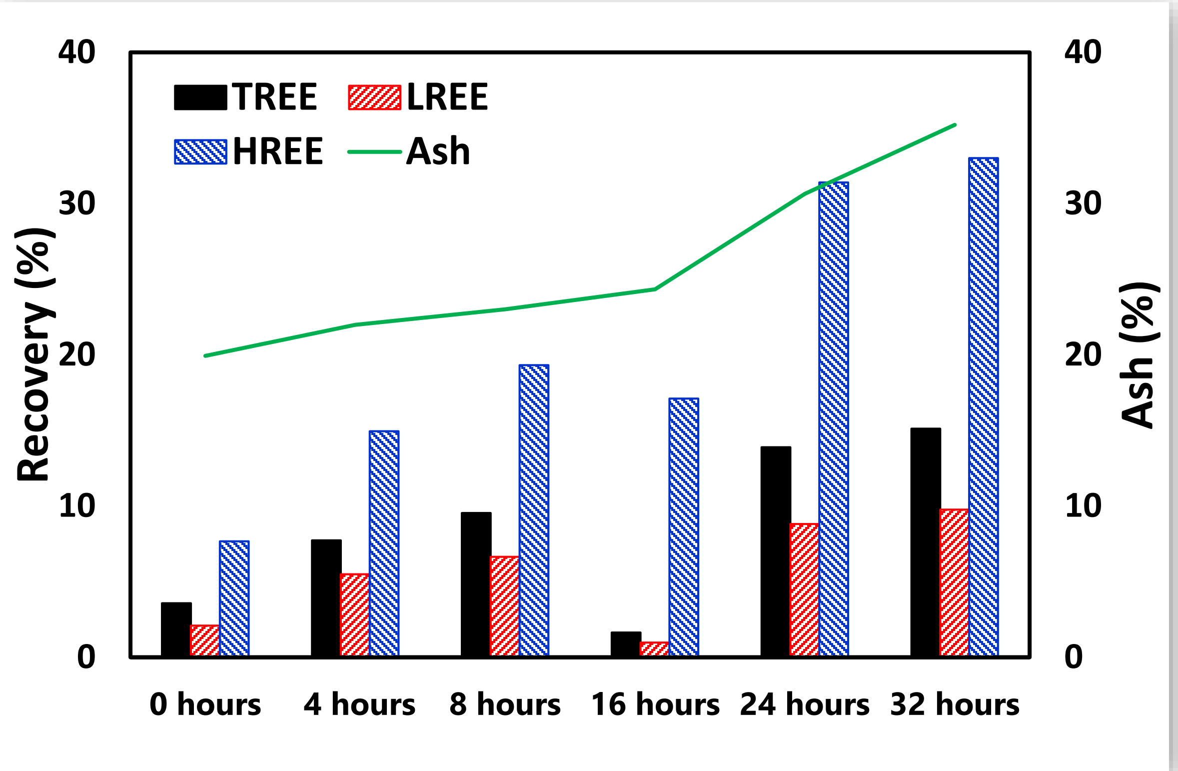




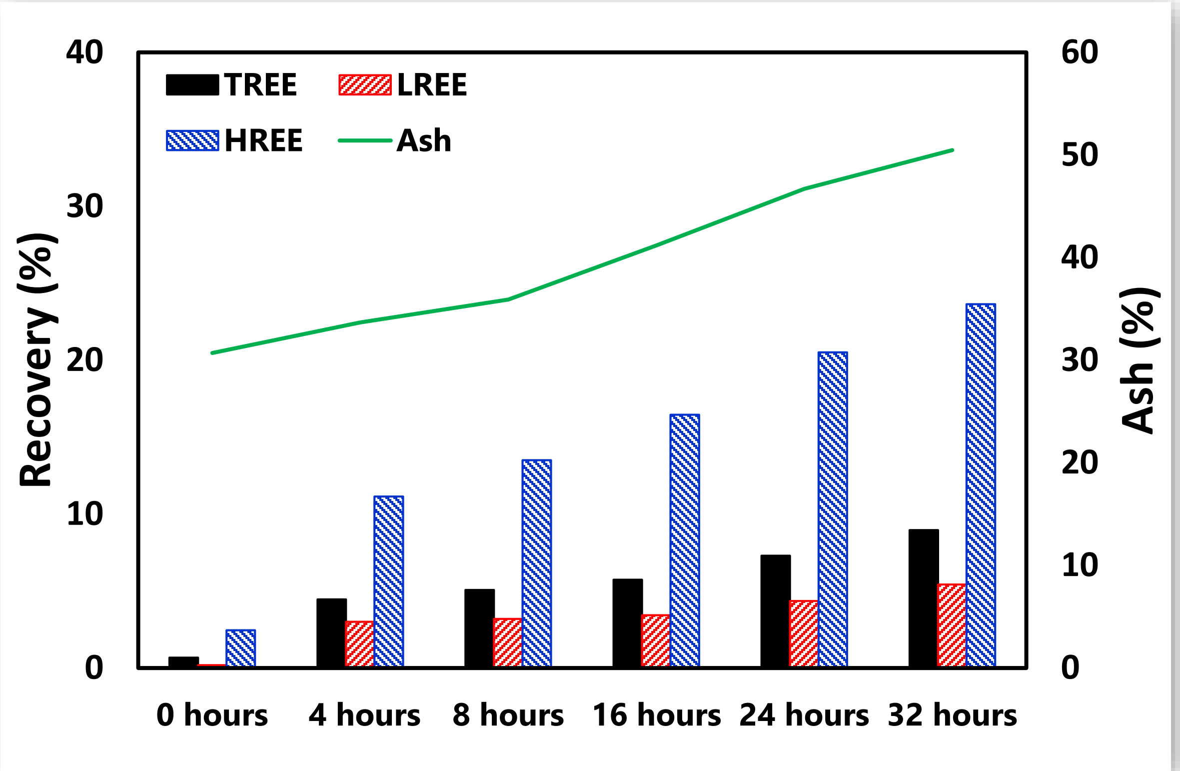
- Bottom layers of the sample limits exposure to the oxygen plasma.
- LTP treatment with periodic mixing provides better leaching kinetics due to a more thorough treatment of the sample.

West Kentucky No.13 - 0.1M Ammonium Sulfate

1.6 SG Float



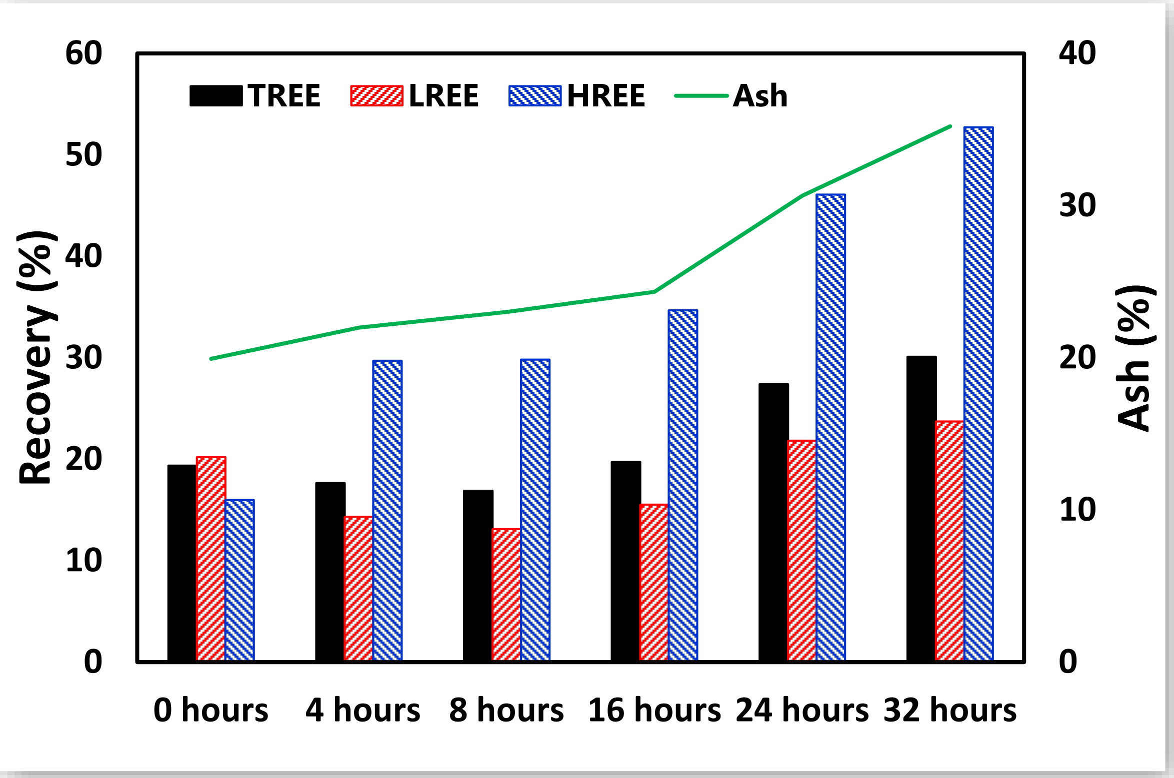
1.6-1.8 SG



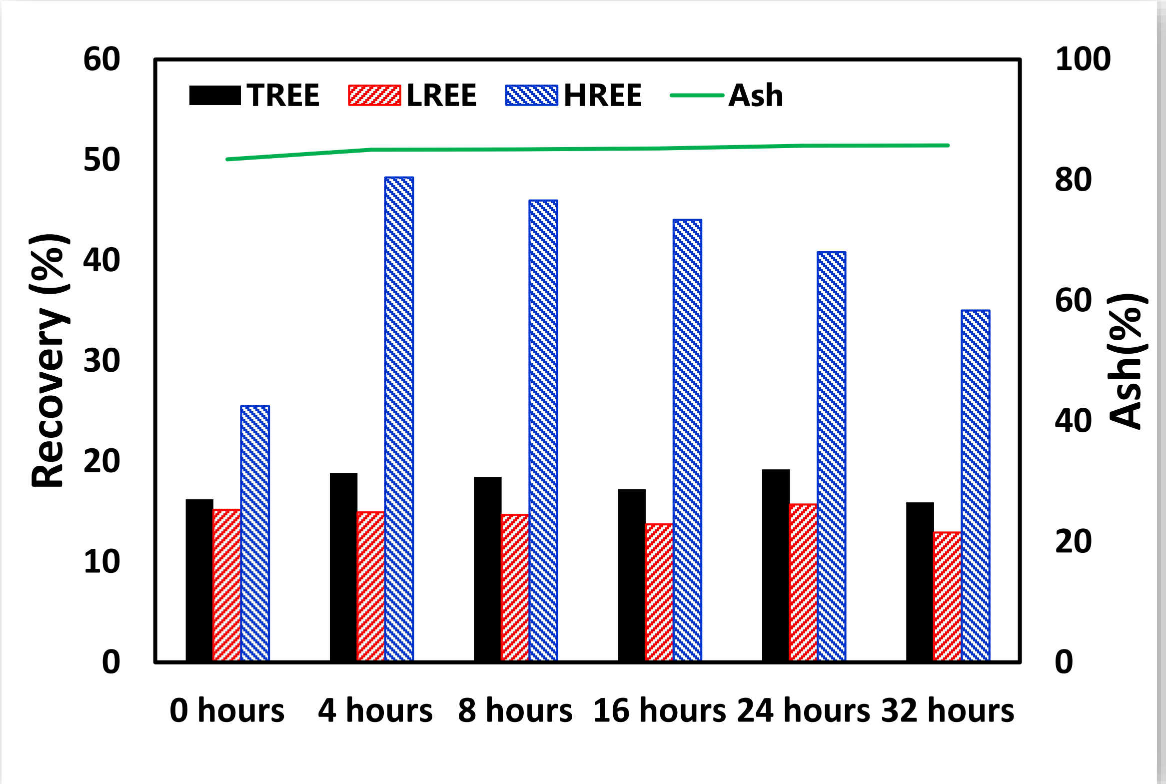
- LTP treatment liberated some REEs especially HREEs which can be readily extracted
- HREEs can be recovered by benign methods such as by using 0.1 M ammonium sulfate solution at a pH of 6.

West Kentucky No.13 - 1.2M Sulfuric Acid

1.6 SG Float

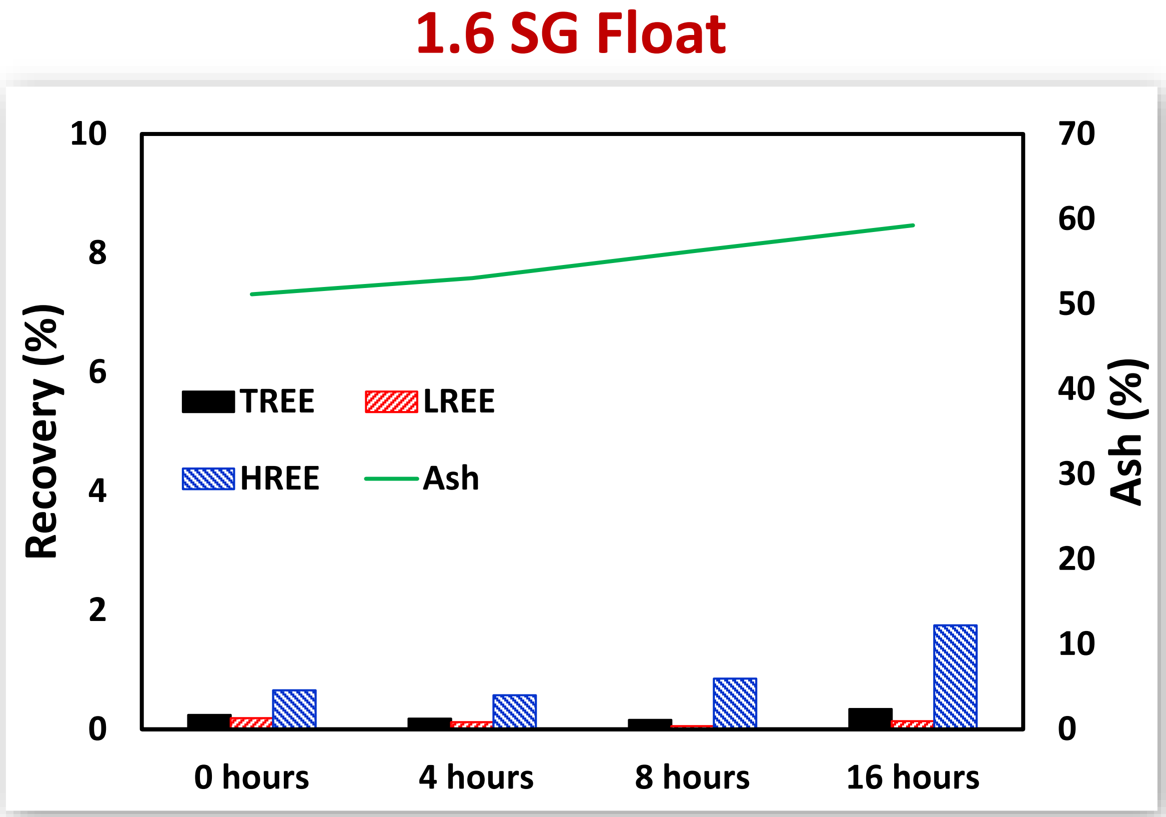


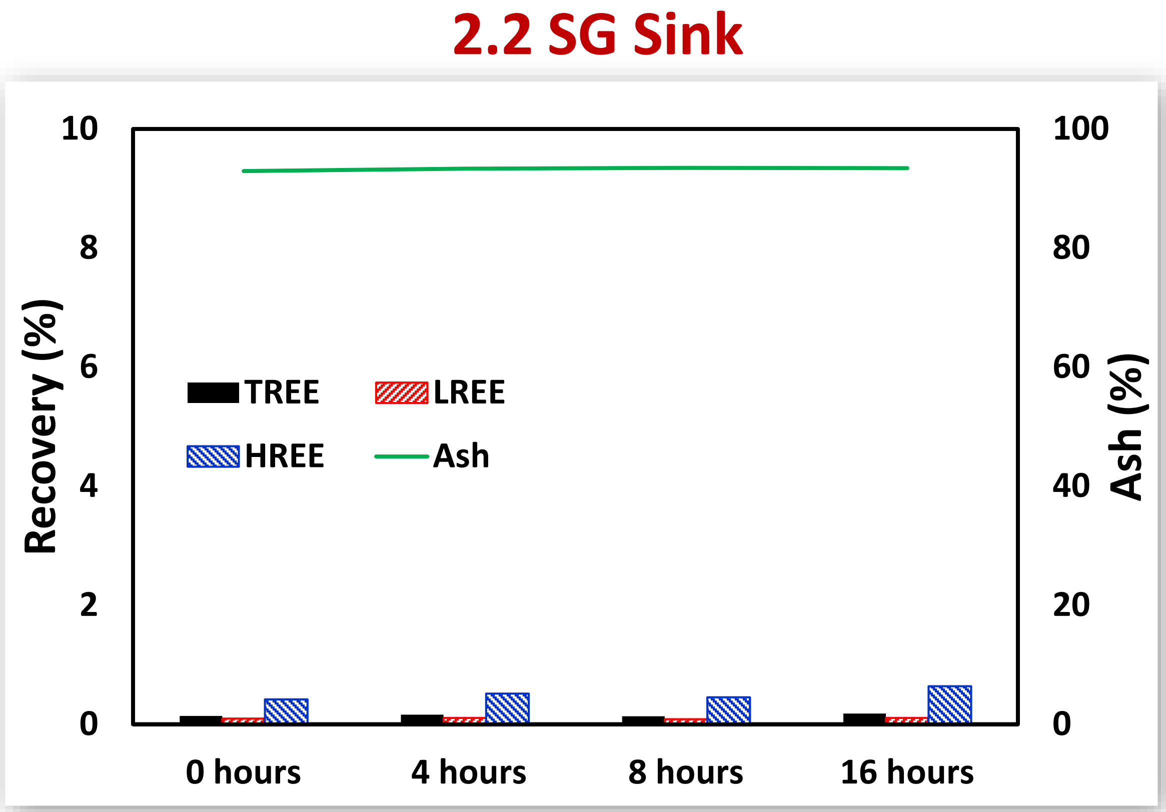
2.2 SG Sink



- The LTP pretreatment of West Kentucky No.13 material improved the total REE recovery for lower density fractions.
- LTP pretreatment exhibits selectivity for HREEs for the high ash fractions of West Kentucky No.13 sample.

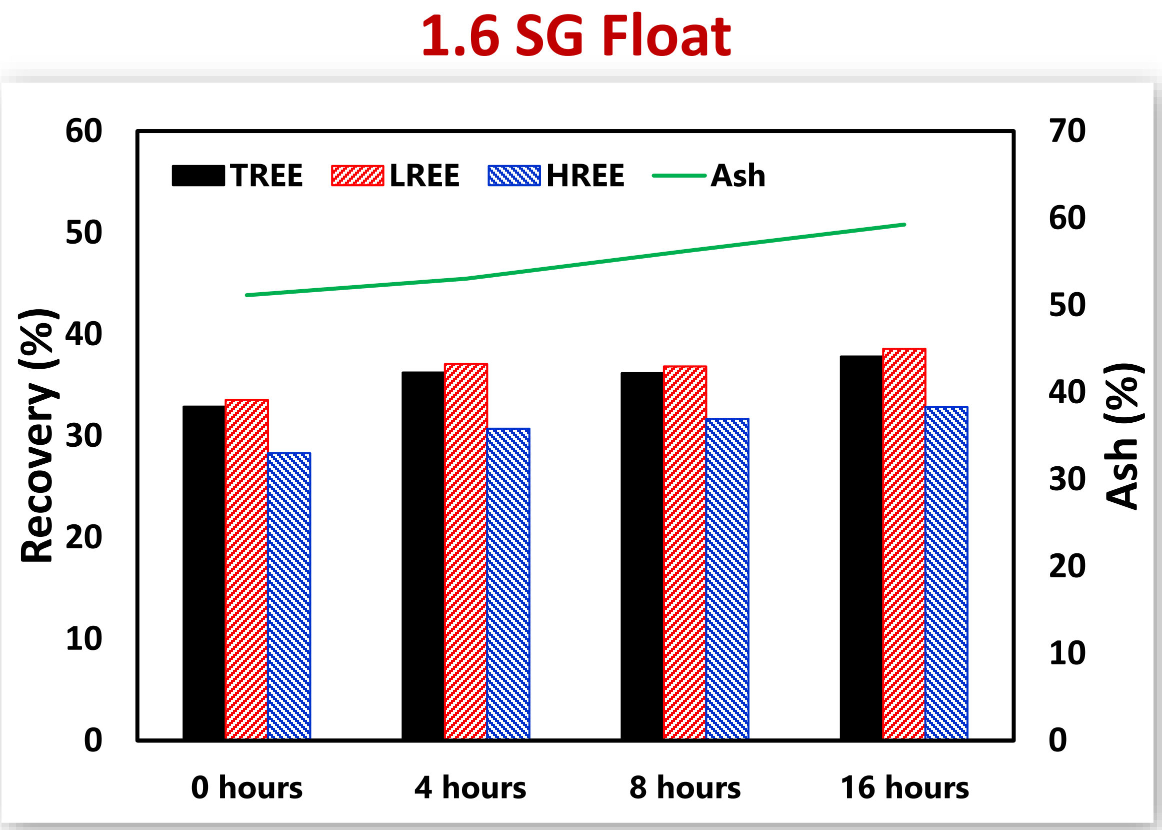
Fire Clay - 0.1M Ammonium Sulfate

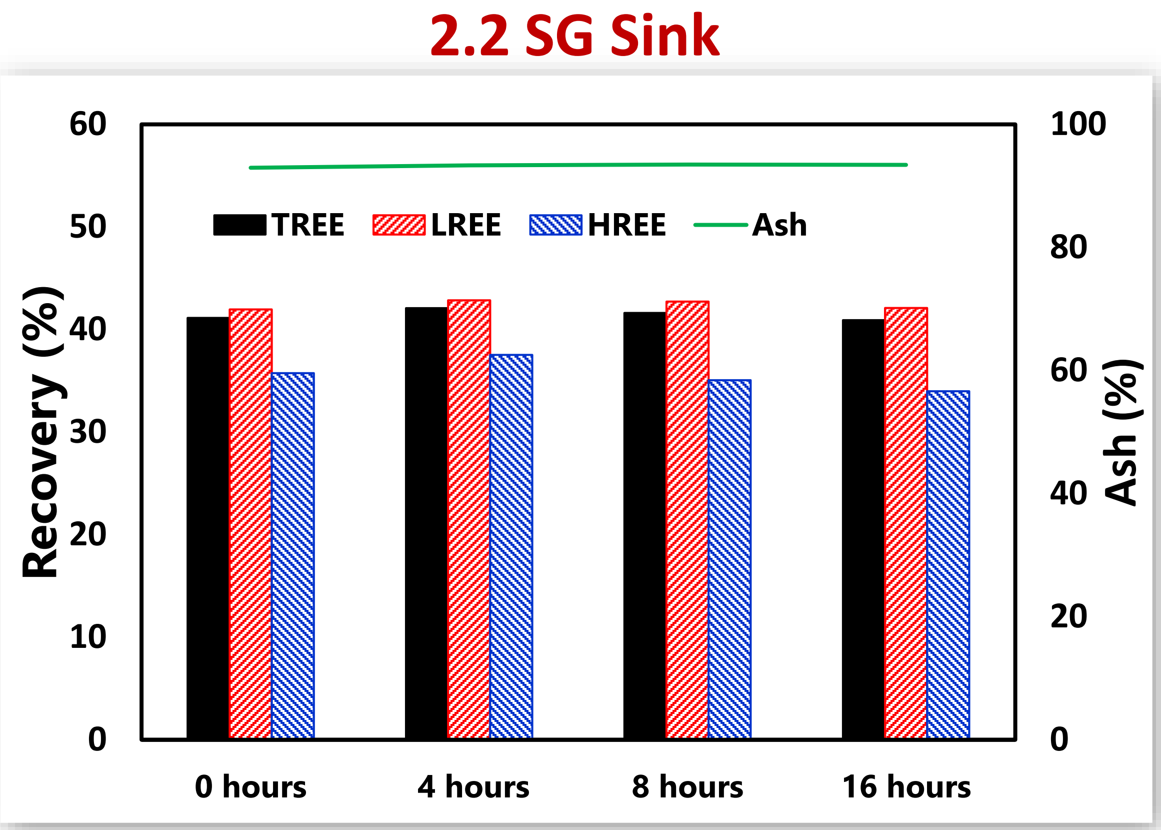




- Poor leachability with ammonium salts for Fire Clay density fractions.
- However, the trend for HREE leaching characteristics is similar to that for West Kentucky No.13 material.
- Some HREEs appear to be associated in an the organic matter in coal.

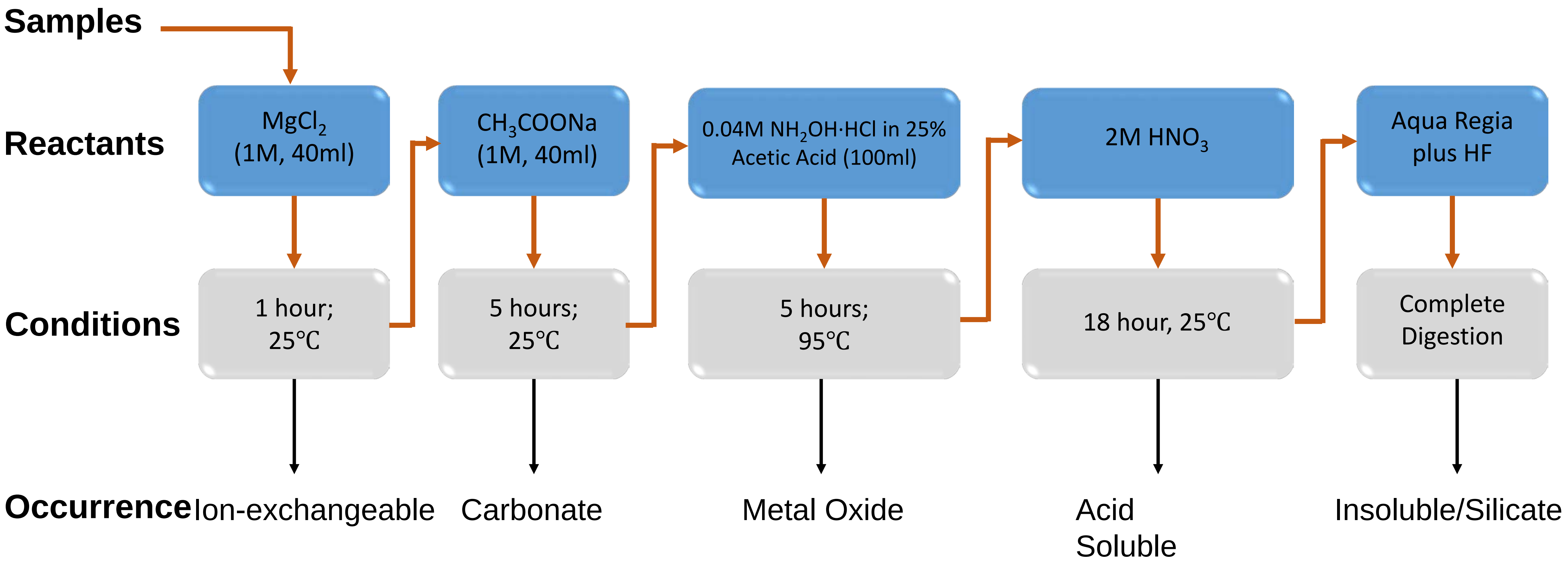
Fire Clay - 1.2M Sulfuric Acid





- No significant change in REE recovery was observed despite 16 hours of LTP treatment.
- The association of REEs in the Fire Clay material is different to the West Kentucky No.13 material.
- The small increase in the ash content of the LTP material shows very limited effect of plasma oxidation on the Fire Clay sample.

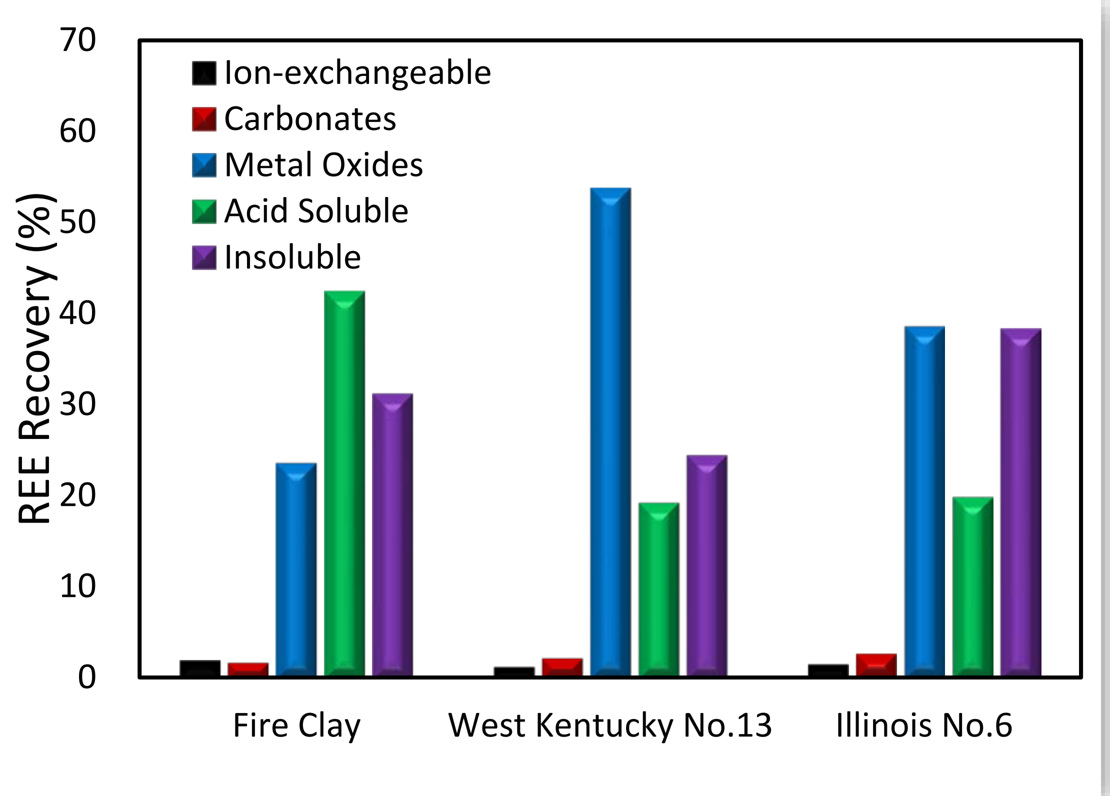
Modes of Occurrence of REEs in Coal (Sequential Extraction)

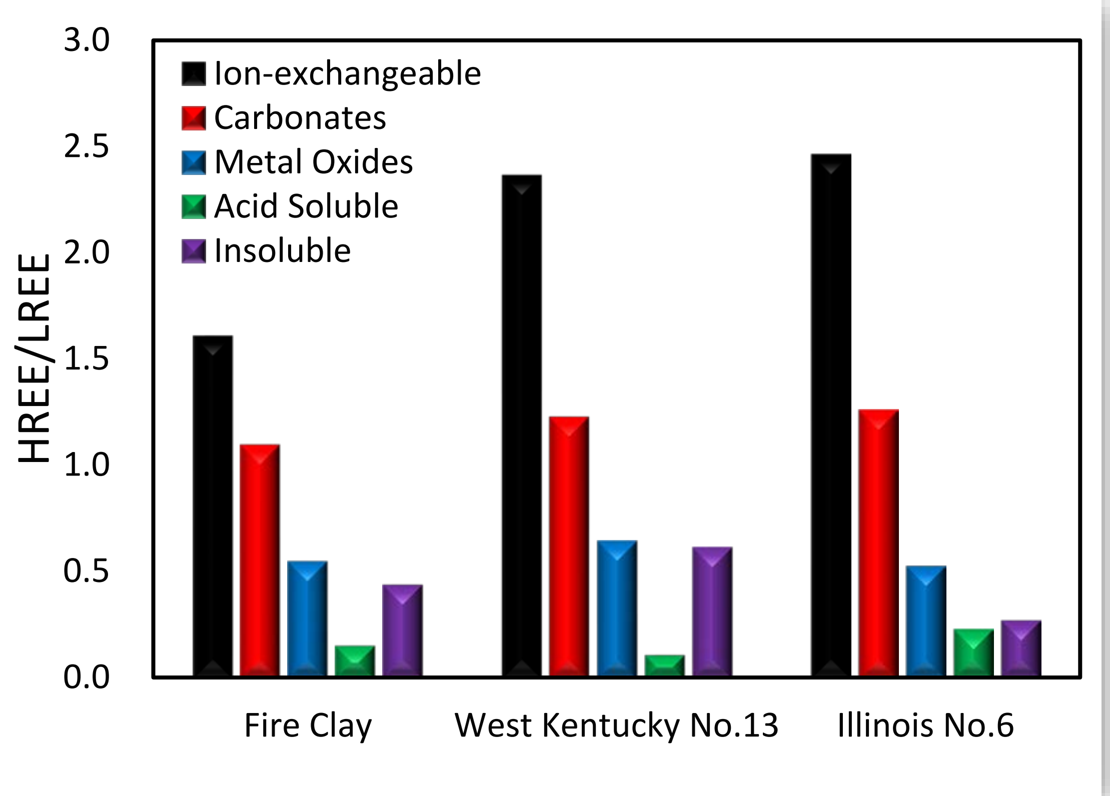


Chou et al., 2009; Finkelman et al., 2018; Pan et al., 2009

Modes of Occurrence of REEs in Calcined Coals

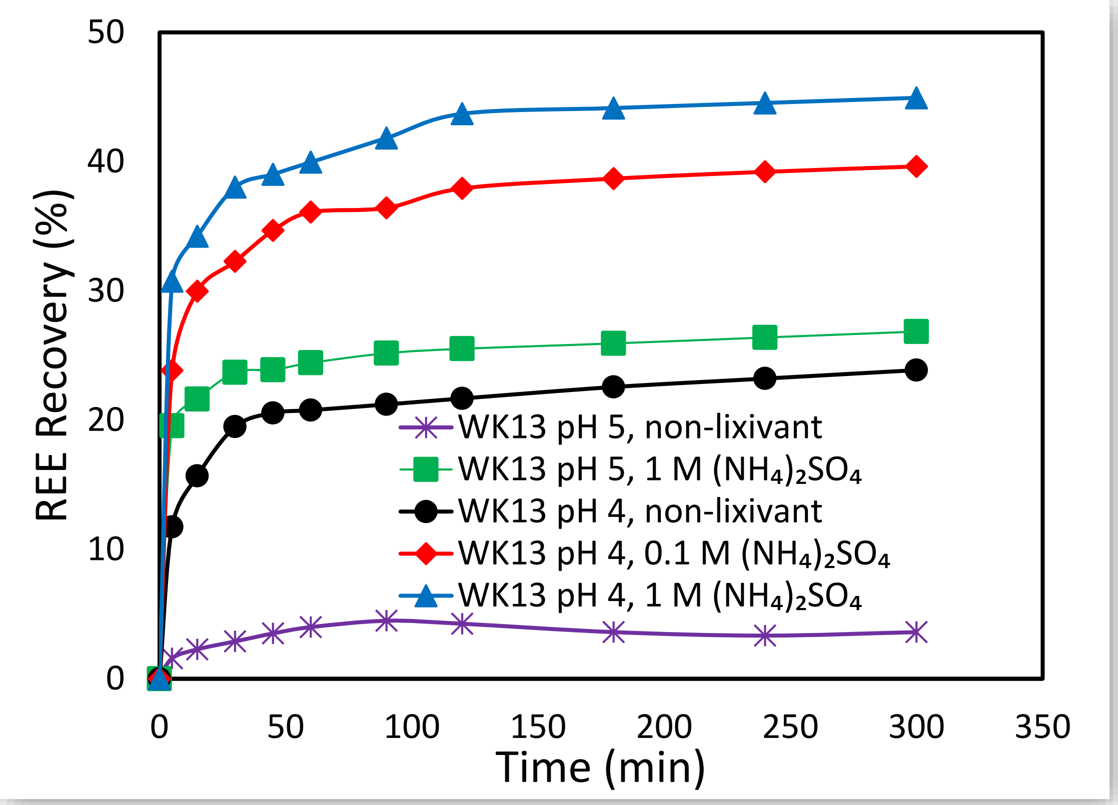
1.4 SG Float/600°C 2 hours



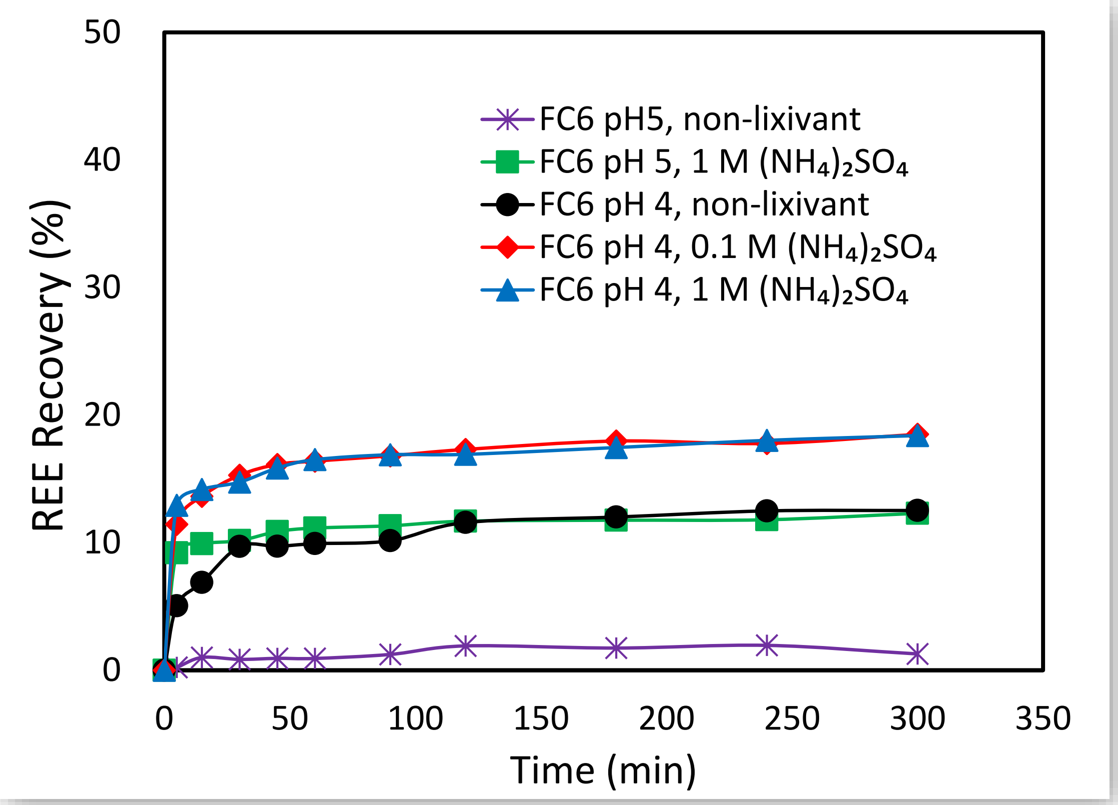


Modes of Occurrence of REEs in Calcined Coals

West Kentucky No.13
1.4 SG Float/600℃ 2 hours

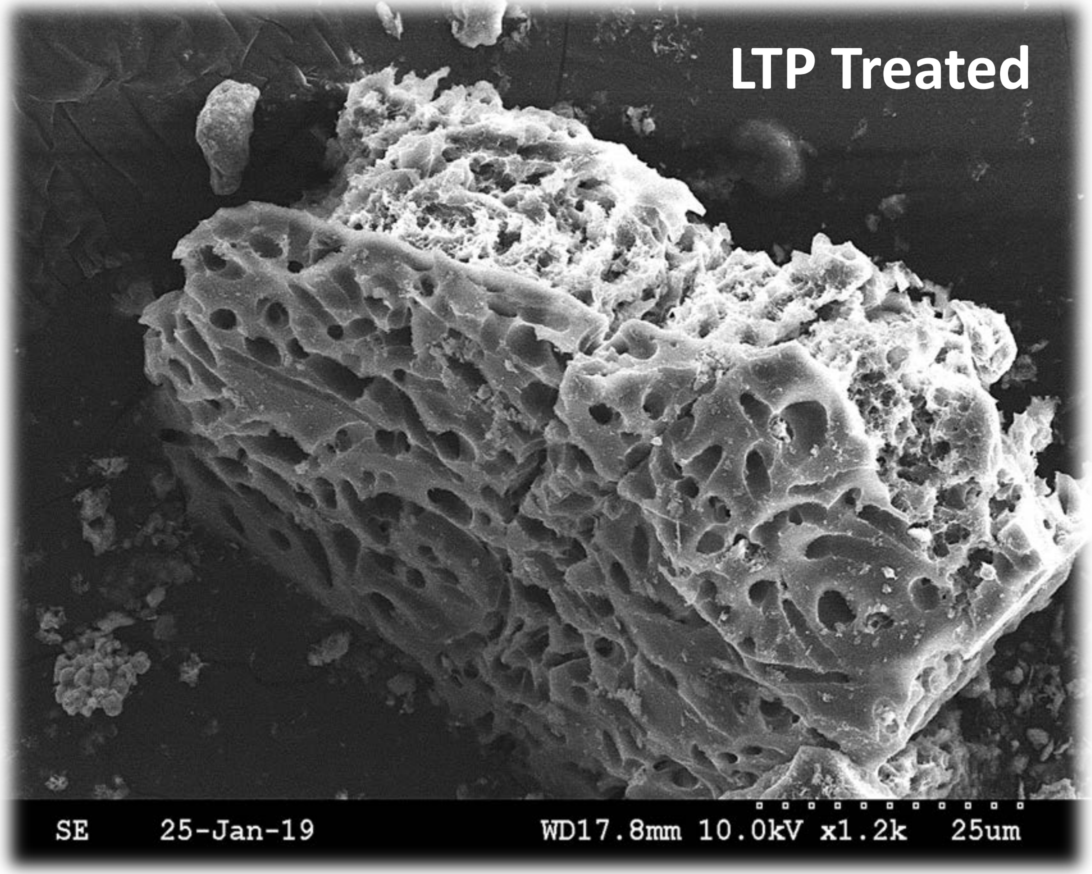


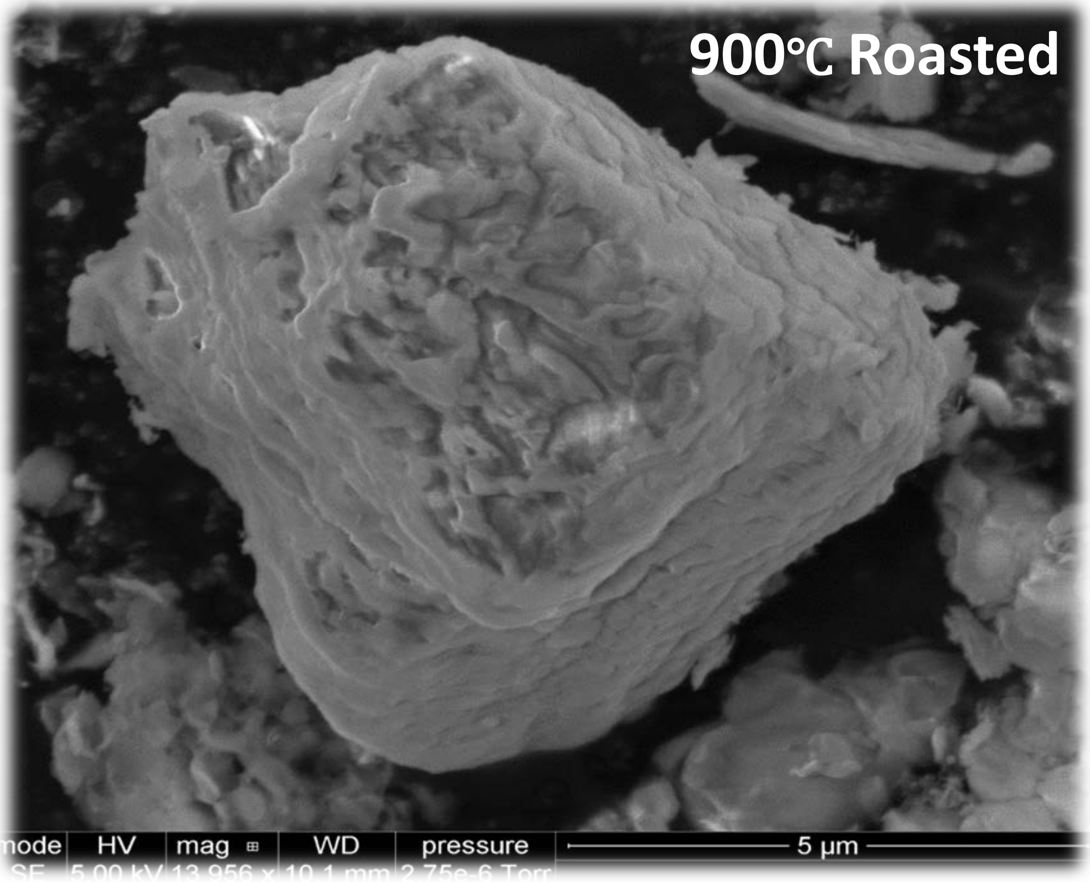
Fire Clay
1.4 SG Float/600℃ 2 hours



Low vs High Temperature Oxidation

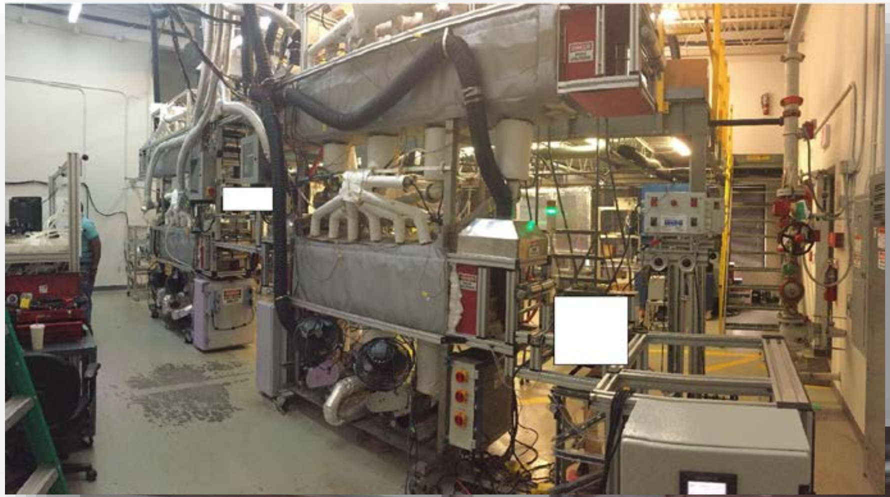
- SEM-EDX studies of West Kentucky No.13 LTP treated material show the presence of particles with increased porosity, surface area and pore volume.





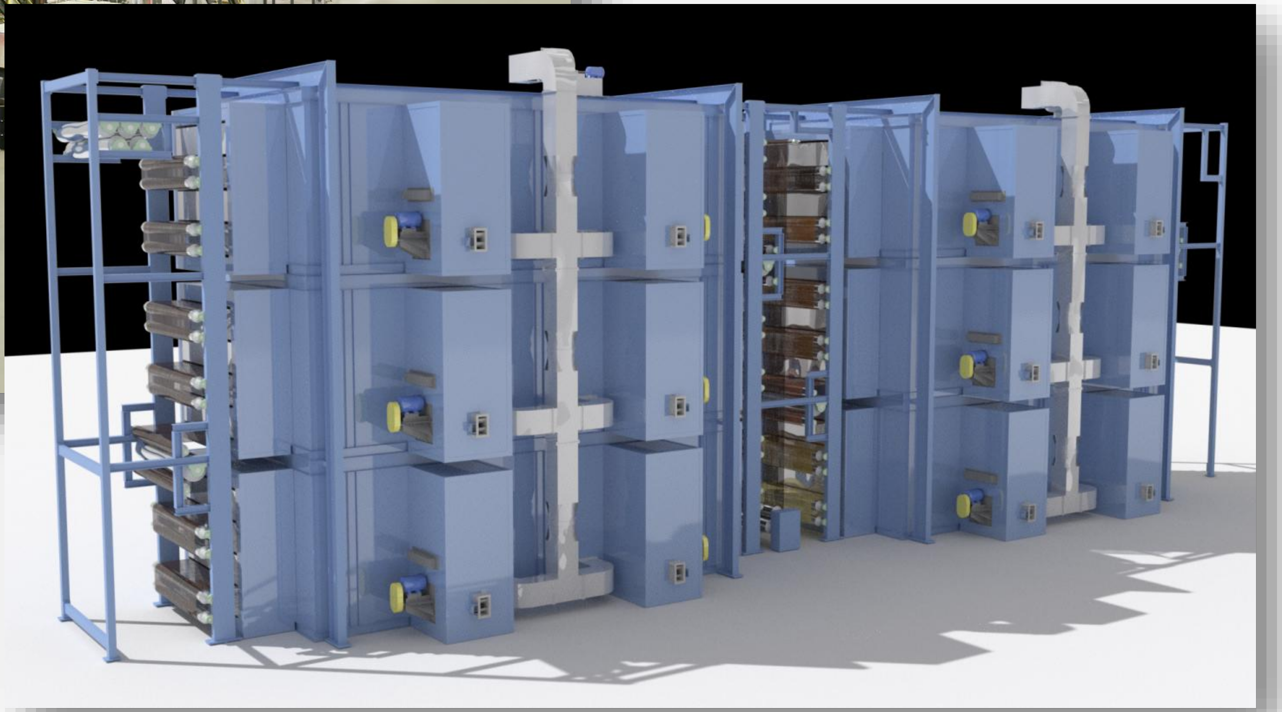
Industrial Plasma Oxidation Systems

- Plasma Oxidation is a proven technology for the manufacture of carbon fibers.
- Multi-year DOE-funded R&D technology demonstration already completed.
  - Joint effort between RMX Technologies (RMX) and Oak Ridge National Laboratory (ORNL).
  - 2004 – first benchtop unit
  - 2014 – first 1 MT prototype
- Claimed benefits:
  - Lower energy (75% less)
  - Increased kinetics (300% faster)
  - Smaller footprint (67% lower)
  - Less costly (20% reduction)
  - Better fiber (30% stronger)
- Pushed by EPA for automotive manufacturing.



The carbon fiber pilot production line at Oak Ridge National Laboratories (ORNL, Oak Ridge, Tennessee) has provided fertile ground for the development of technologies that are helping make carbon fiber manufacture more efficient and less expensive. (Photo from Harper International – Pilot Line in operation at ORNL)

Industrial Plasma Oxidation Systems



Industrial Plasma Oxidation Systems


Office of Energy Efficiency & Renewable Energy

EERE Success Story—Plasma Oxidation of Carbon Fiber Precursor

JUNE 23, 2016

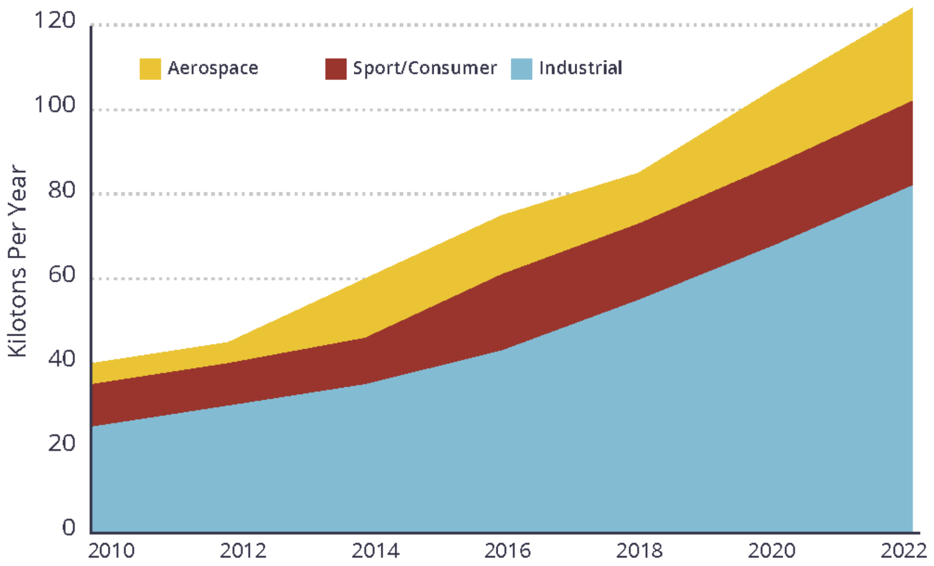
Home » EERE Success Story—Plasma Oxidation of Carbon Fiber Precursor

With the potential to reduce the weight of vehicle components by up to 60%, carbon fiber composites is one of the most promising lightweight materials available to improve vehicle efficiency. However, its current inputs and manufacturing processes are expensive, severely limiting its use in most high-volume vehicle models. Fortunately, a new manufacturing technique based on research supported by the Vehicle Technologies Office may be able to cut the total cost by 20% while also using 75% less energy in the oxidation stage and producing carbon fiber three times faster than conventional ones.

Industrial Plasma Oxidation Systems

Ref: American Jobs Project, 2017

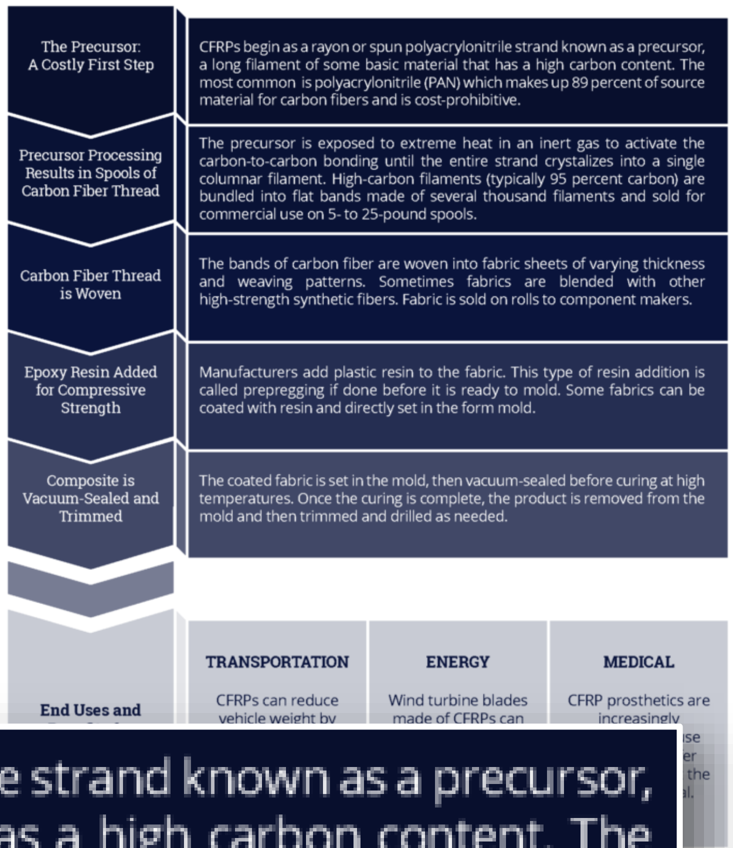
Cumulative Carbon Fiber Demand by Market Sector



Data Source: Chris Red, 2012 Global Market for Carbon Fiber, Carbon Fibers 2012

Carbon fiber demand will increase most in the industrial sector.

Carbon Fiber: How It's Made and Future Uses



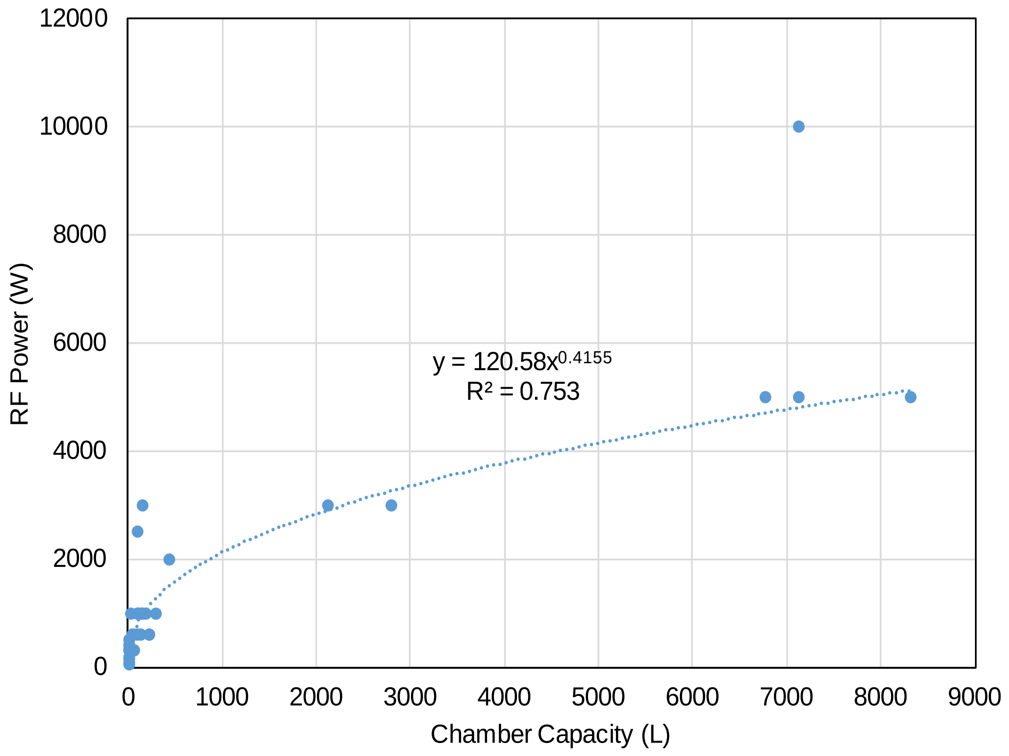
CFRPs begin as a rayon or spun polyacrylonitrile strand known as a precursor, a long filament of some basic material that has a high carbon content. The most common is polyacrylonitrile (PAN) which makes up 89 percent of source material for carbon fibers and is cost-prohibitive.

Industrial Plasma Oxidation Systems

- Carbon fibers typically manufactured from polyacrylonitrile (PAN) in a 3-step process.
  - oxidation/stabilization
  - carbonization
  - surface treatment/sizing
- Source of petroleum tar/pitch usually preferred over coal-based feedstocks.
- Contacted 4M regarding use of “coal-based feedstocks” but without reference to potential co-production of REEs.
- Representatives attended DOE stakeholders meeting/Workshop in Pittsburgh – “Improving the Competitiveness of US Coal”

Industrial Plasma Oxidation Systems

- Currently, 10 companies (10 US, 4 international) produce laboratory and production-scale plasma oxidation units.
- Technical details for these units vary within the following ranges:
  - RF Power: 50W to 10,000W
  - RF Frequency: 20 kHz to 2.45 Ghz
  - Gas Flow: 0 to 5,000 sccm
  - Chamber Volume: 1 to 8,000 L
- Scaling data shows that RF power scales exponentially (exponent = 0.4155) with chamber capacity.
- This data will be used for scaling studies and preliminary techno-economic analysis.

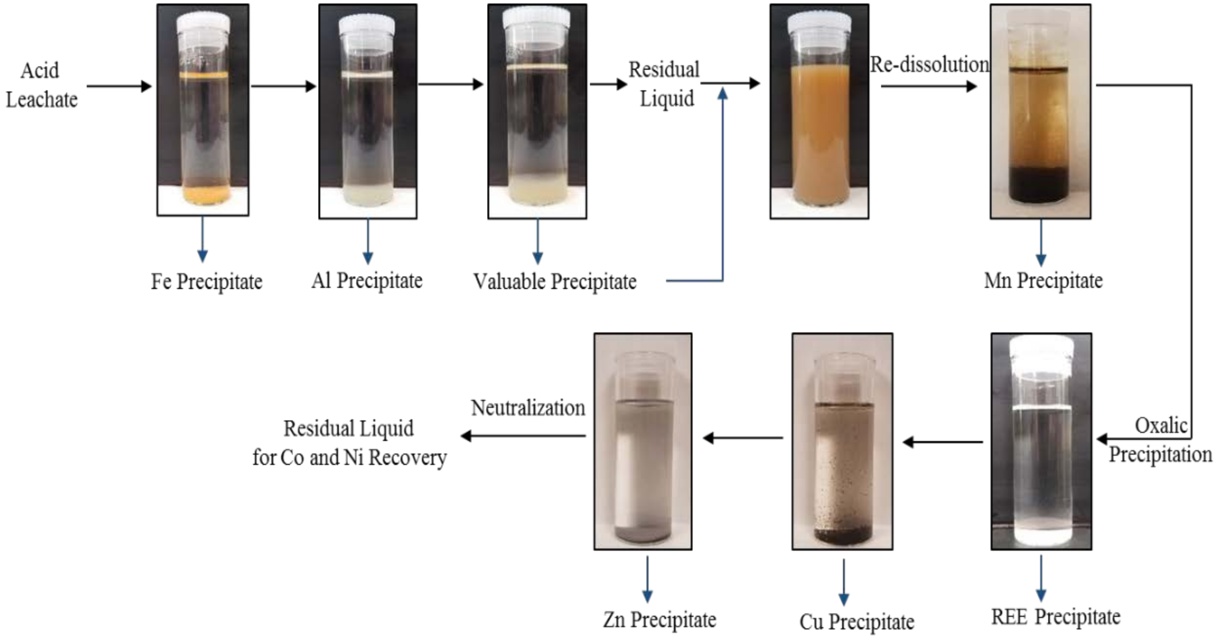


Summary & Conclusions

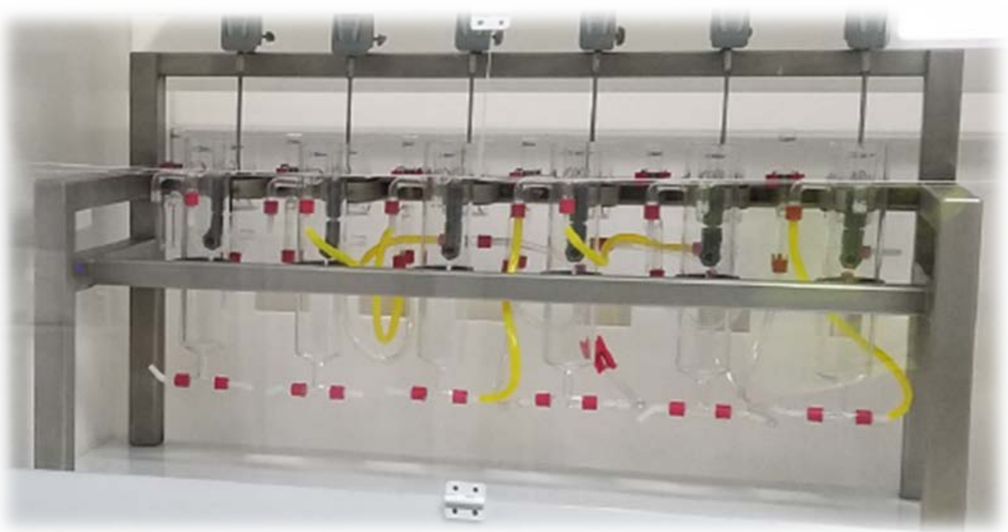
- Low-temperature plasma treats the coal on the surface of the specimen.
- Change in the deeper layers of the samples was not achieved even with prolongation of treatment time.
- The pretreatment facilitates higher REE recovery values under mild leaching conditions for West Kentucky No. 13 coal.
- Partial ashing of the feed material is sufficient to enhance REE recovery while keeping mineralogical composition unchanged.
- A significant portion of the HREEs in West KY 13 coal are bound in the organic matrix and recoverable in a salt solution.
- Association characteristics of REEs with the coal samples differ and thus leaching behaviors of REEs are distinct.
- Further studies pertaining to sequential REE leaching and effect of LTP on Solvent Extraction are undergoing.

Next Steps

Selective Precipitation



Solvent Extraction



- ❑ Final products containing more than 90% of REO will be generated using selective precipitation and/or solvent precipitation methods.