2017 Project Review Meeting for Crosscutting Research, Gasification Systems, and Rare Earth Elements Research Portfolios

Economical and Environmentally Benign Extraction of Rare Earth Elements from Coal & Coal Byproducts

DOE Contract Number DE-FE0027155

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Outline

- Project Goals and Objectives
- Overall Approach
- Methodology
- Results
- Accomplishments
- Summary
- Status
- Future Work

Project Goals and Objectives

Goals

- Develop a bench-scale REE extraction process for coal fly-ash materials
- Utilize pretreatment and leaching processes along with proprietary metal sorption media to process 1-kg batches
- Deliver a REO product meeting or exceeding DOE requirements

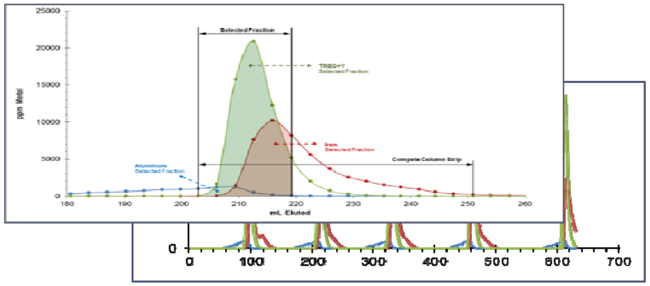
Objectives

- Identification/selection of coal by-product sources
- Develop leaching procedure for selected by-products
- REE sequestration and recovery
- Radioactive material separation*
- Waste water treatment for metal removal
- Scale-up of process to +2-kg coal by-product per batch

Background

- **Selection of Coal By-Product**
  - Coal *fly-ash* chosen as source material
  - Knowledge regarding the pretreatment and digestion of inorganic source materials
  - Experience with extracting REEs from phosphor powders and ore materials

- **Isolation of REEs**
  - Expertise in the separation of REEs from other metal constituents in process streams using proprietary media
  - Preliminary research on the isolation of metal constituents from ore digest liquors



Overall Approach

- Develop system utilizing pretreatment + digestion followed by U/Th removal, REE isolation, and subsequent precipitation (production) of REOs.
- Assess system performance
- Determine scaling parameters
- Evaluate economic viability

Overall Work Plan

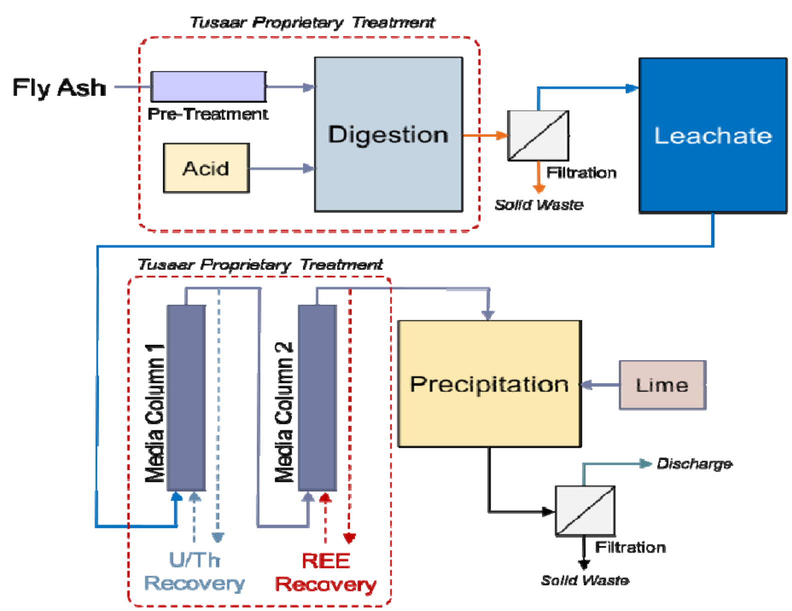
Task 1 Project Management and Planning

Task 2 Sampling an Characterization of Feedstocks

Task 3 Feasibility Study

Task 4 Process Integration

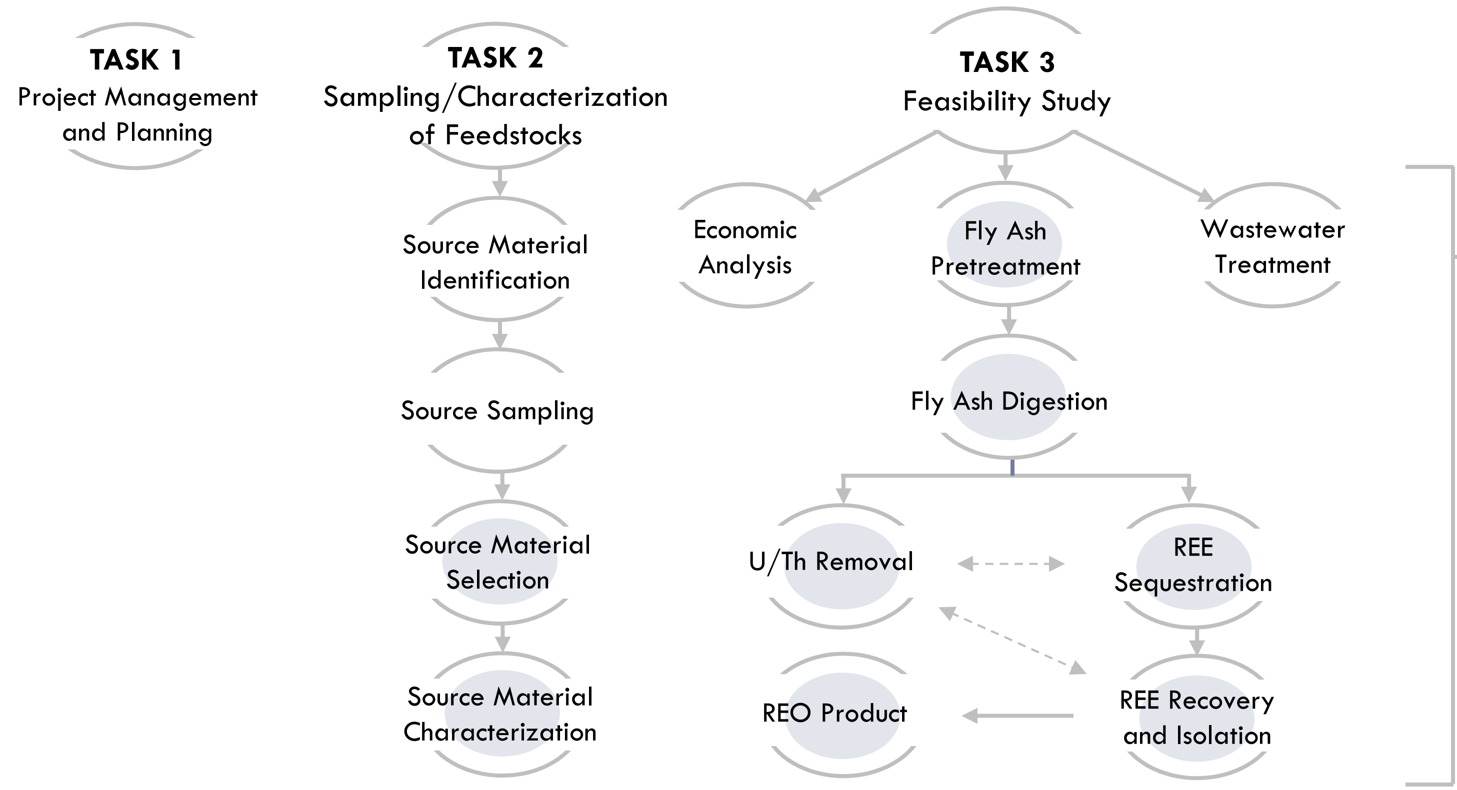
Proposed Test System



Milestones

- Selection of fly ash source
- Source material characterization
- Selection of best pre-treatment method
- Selection of best digestion method
- Ability to remove U/Th from digestion liquor
- Demonstrating and overall recovery of REE from the source fly ash of >25%
- Produce an REO product that had a final REEs concentration > 2.0 wt. %.
- Verify that waste residuals from the process could meet RCRA limits and local metal discharge requirements

Methodology



Results

Summary of Results

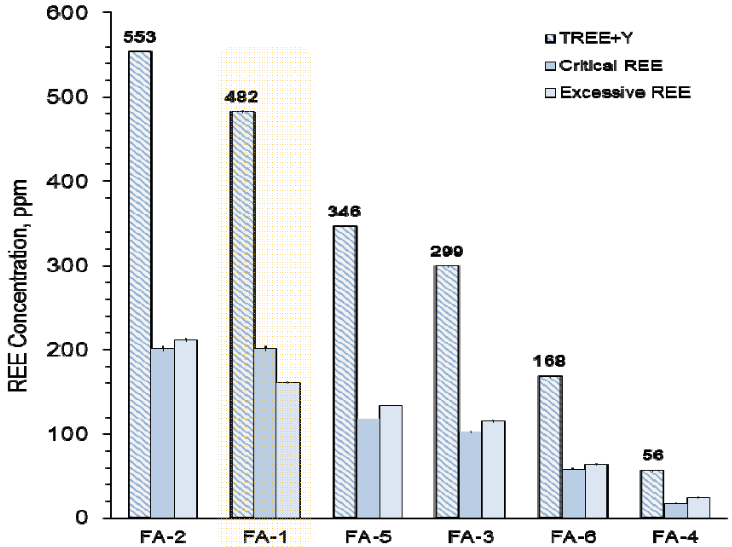
- Major project results discussed
- Separated by main process units
- Results presented represent project activities up to Go/No Go decision point

- Fly Ash Materials
  - Selection
  - Characterization
- Proposed Process
  - Fly Ash Pretreatment
  - Digestion
  - U/Th Removal
  - REE Isolation and Recovery
  - REO Product

Results

Fly Ash Selection

- Reviewed over 700 potential sources including material locations, REE content, and availability
- Six fly ash sources selected that had documented:
  - critical REE concentrations between 400-535 ppm
  - outlook ratios between 1.456 to 1.535
  - accessible for sampling
  - available in large quantities



	FA-1	FA-2
Chemical Assay (ppm and %)		
TREE+Y	482	553
TREE	387	467
Critical REE	201	201
Excessive REE	161	212
La+Ce (% of TREE+Y)	44%	51%
Outlook Ratio	1.25	0.95
Other Factors		
Fly Ash Availability	yes	limited
In-place Sampling	yes	no
Long-Term Sourcing	yes	limited
Historical Information	yes	no

Results

Fly Ash Characterization

Chemical Assay

Fly Ash Elemental Composition, wt%											
Be	0.0014%	V	0.0553%	Ga	0.0165%	Mo	0.0104%	Sm	0.0016%	Yb	0.0010%
Na	0.4712%	Cr	0.0238%	Ge	0.0075%	Sn	0.0006%	Eu	0.0004%	Lu	0.0001%
Mg	0.3950%	Mn	0.0207%	As	0.0077%	Sb	0.0008%	Gd	0.0020%	Hf	0.0006%
Al	10.6%	Fe	18.1%	Rb	0.0116%	Ba	0.0951%	Tb	0.0003%	Ta	0.0002%
Si	14.5%	Co	0.0046%	Sr	0.0375%	La	0.0068%	Dy	0.0020%	W	0.0018%
K	1.876%	Ni	0.0260%	Y	0.0105%	Ce	0.0139%	Ho	0.0004%	Pb	0.0025%
Ca	1.795%	Cu	0.0185%	Zr	0.0263%	Pr	0.0017%	Er	0.0011%	Th	0.0025%
Ti	0.5998%	Zn	0.0252%	Nb	0.0020%	Nd	0.0070%	Tm	0.0002%	U	0.0035%

TREE+Y ≈ 0.05%

SEM

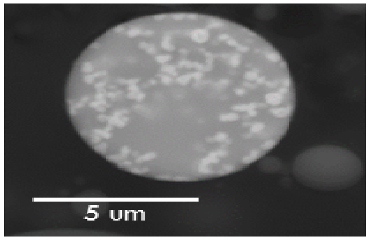
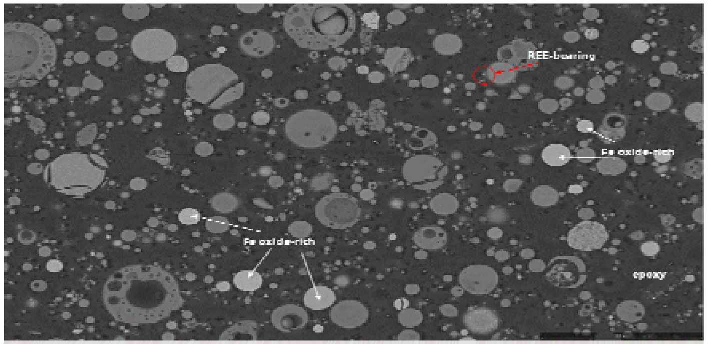


Image of a small siliceous glass spherule with inclusions of rare earth oxides

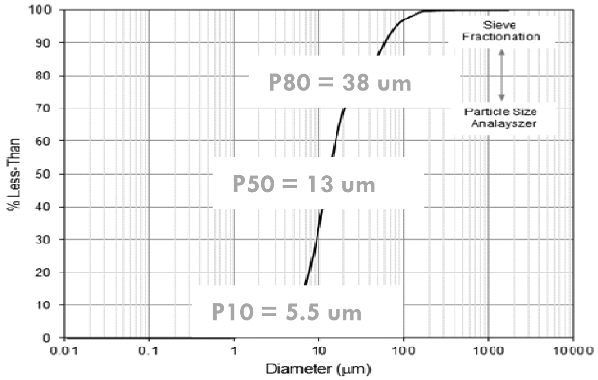
QEMSCAN



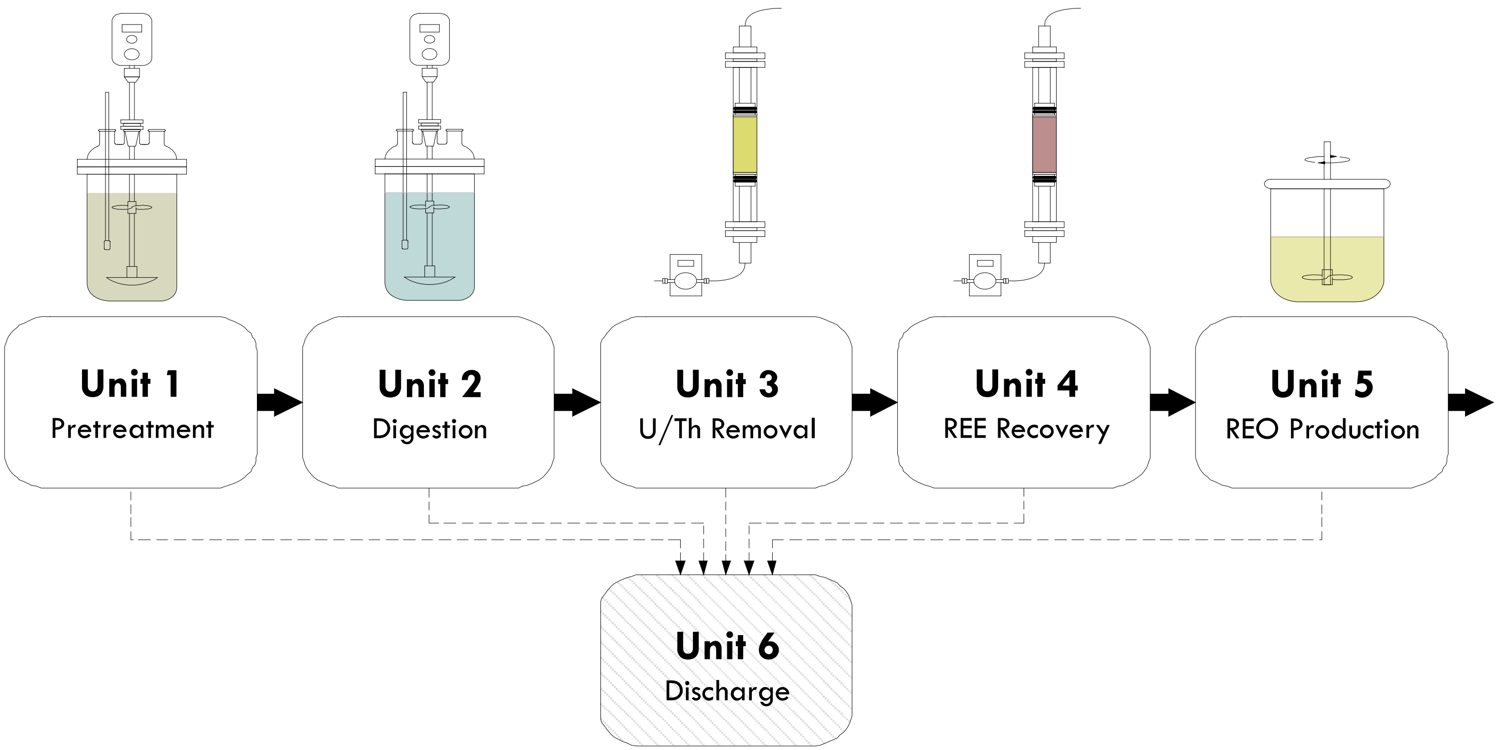
Phase	Mass%
Fe oxide	9.8
Fe oxide in glass	10.5
Si–O	2.6
Si(high)–Al–K–O	3.2
Al–K–Fe–Si–O	38.4
Al–Fe(high)–K–Si–O	28.3
Al–Fe(high)–Ti–K–Si–O	2.0
Ti-rich glass	0.2
Al–Ca–Fe–Si–O	2.3
Ba-bearing (barite)	0.02
Ca–Al–S–O (ettringite)	0.9
Ca sulfate	0.5
Ce-bearing	0.01
Miscellaneous	0.3
Others	1.2
Total	100

XRD analysis indicated 80-85% amorphous content, mineral constituents: Magnetite, Mullite, Hematite, Quartz, Portlandite

Particle Size Analysis

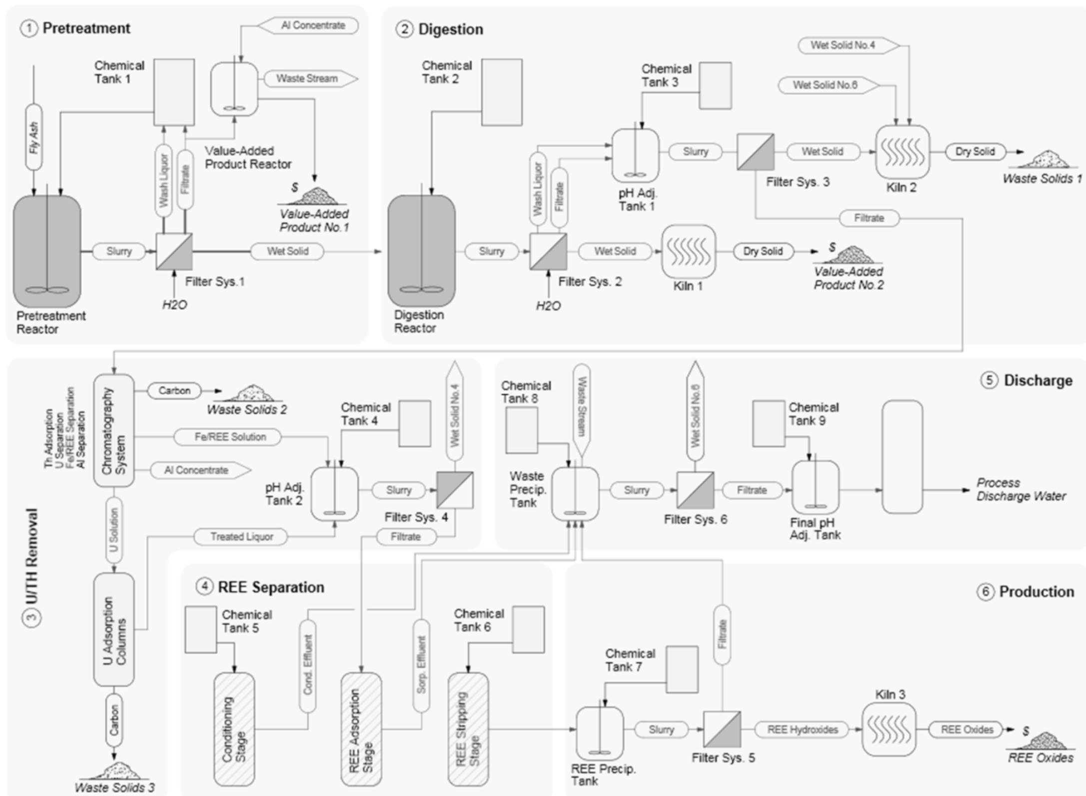


Process Strategy: REE Extraction from Coal Fly-Ash



Results

Developed Process



Results

Physical Pretreatment

Targeted effort to develop physical process methodology followed by acid digestion to enhance REE recovery rates.

Tests included:

- Thermal shock
- Grinding
- Magnetic Separation

Base Chemical Pretreatment

Optimization of pretreatment process by utilizing various pretreatment methods followed by standard acid digestion

Tests included:

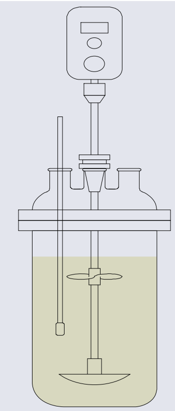
- Type of Base Solution
- Concentration of Base Solution
- Solid wt% Slurry
- Temperature
- Reaction Time

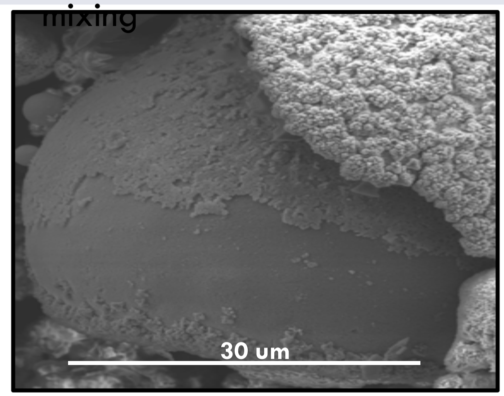
Test Apparatus

- 2L reaction kettle
- Heating mantle
- Temperature control
- High-speed mixer

Operation

- 1-kg fly ash batches
- 80-100°C
- 100-400 rpm mixing

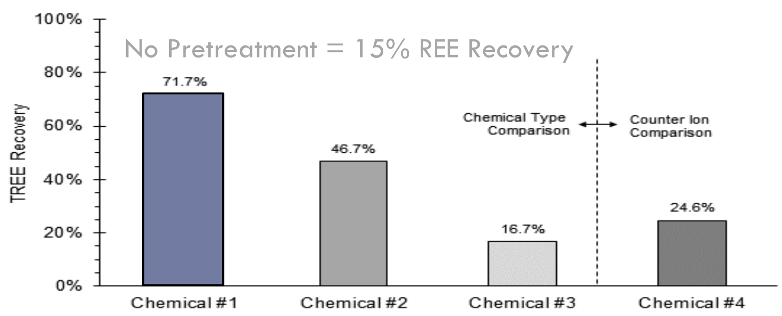




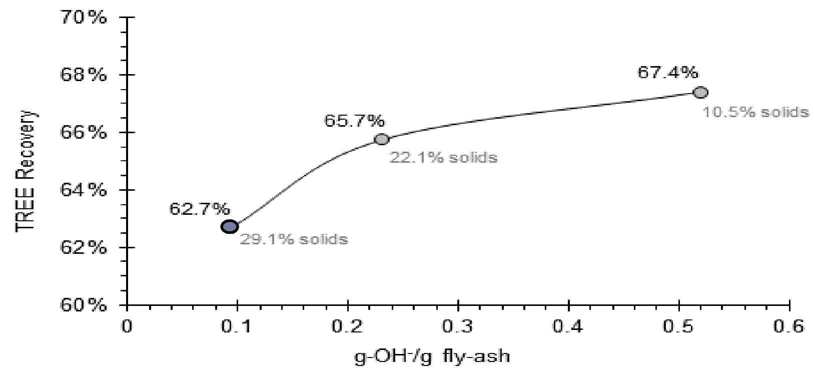
Results

Unit 1
Pretreatment

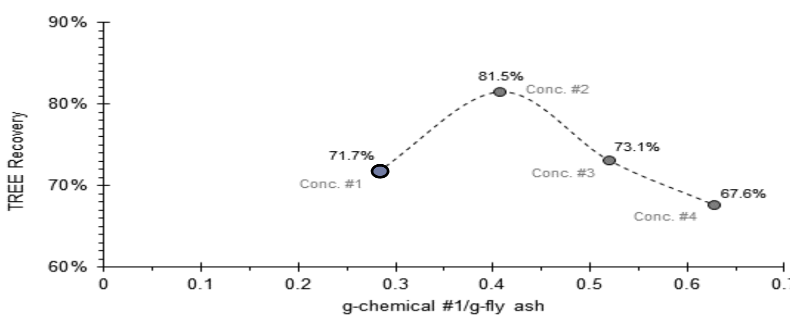
Type of Base Solution



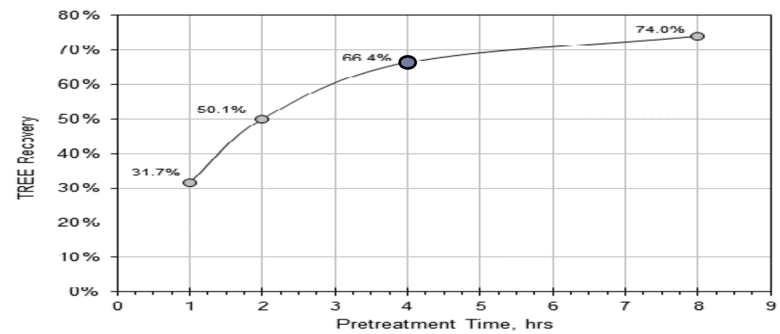
Solid wt% Slurry



Base Solution Concentration



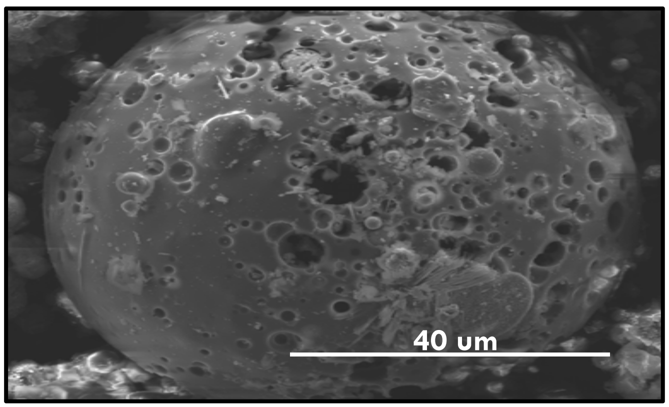
Reaction Time



Results

Acid Pretreatment

- Type of Solution
- Concentration of Solution
- Solid wt% Slurry
- Temperature
- Reaction Time

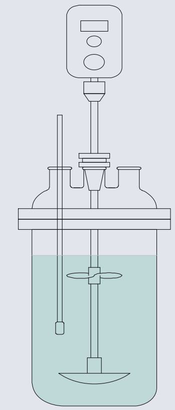


Test Apparatus

- 2L reaction kettle
- Heating mantle
- Temperature control
- High-speed mixer

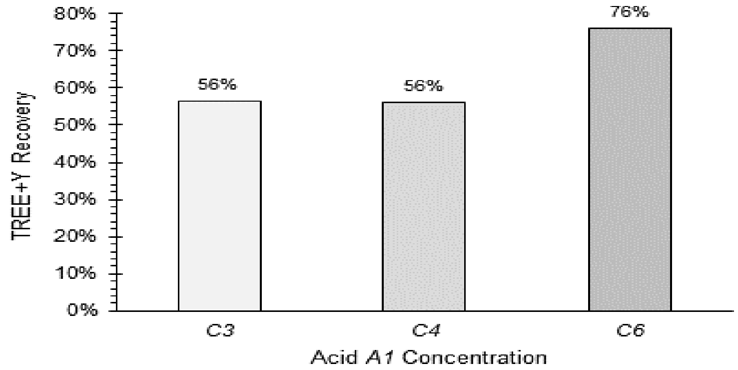
Operation

- 1-kg fly ash batches
- 80-100°C
- 100-400 rpm mixing

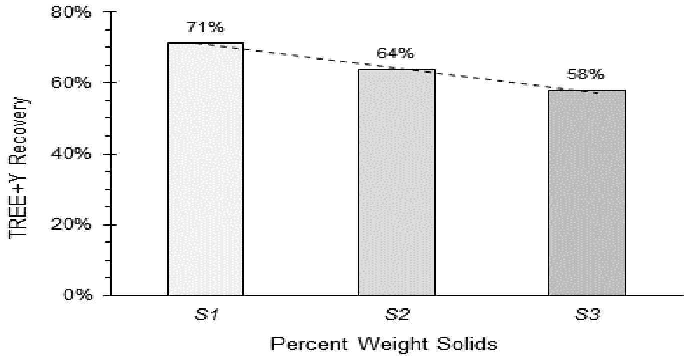


Results

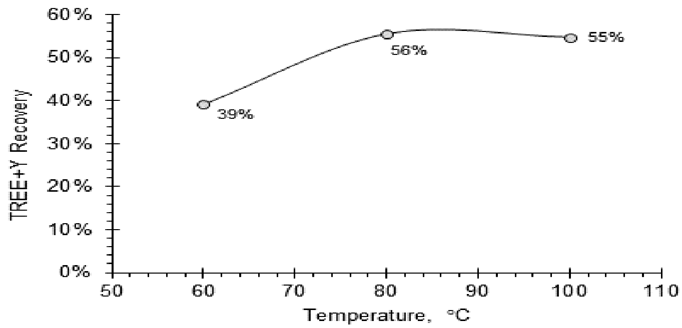
Acid Solution Concentration



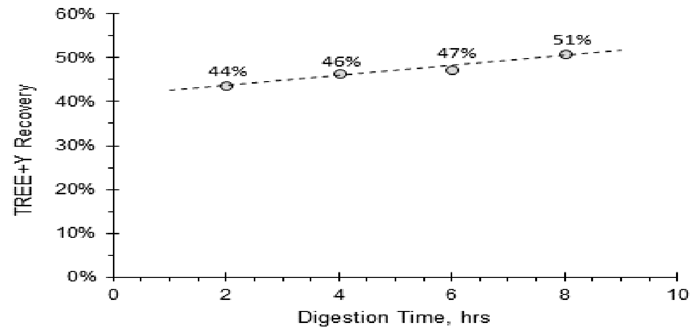
Solid wt% Slurry



Reaction Temperature



Reaction Time



Results

Unit 3
U/Th Removal

Overall Approach

Unit process utilizes an adsorptive bed to bind U and Th while allowing REEs and other ions in solution to pass through for downstream processing.

Operational Constraints

Adsorptive bed requires influent solution to be particle free and at pH 2 to eliminate media bed clogging and to maximize U and Th sequestration.

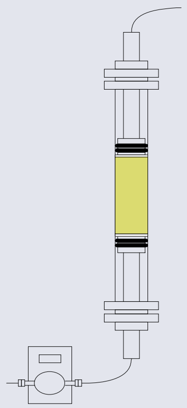
Evaluation

Tests included:

1. Determining Operation pH Range for U/Th Sequestration (selective precipitation)
2. Evaluation and Selection of Adsorptive Media
3. Adsorptive Column Performance

Test Apparatus
- 1cm Ø x 50 cm column
- Adjustable bed height
- Diffusers (both ends)
- Inf./Eff. pH measurement
- Precision metering pump

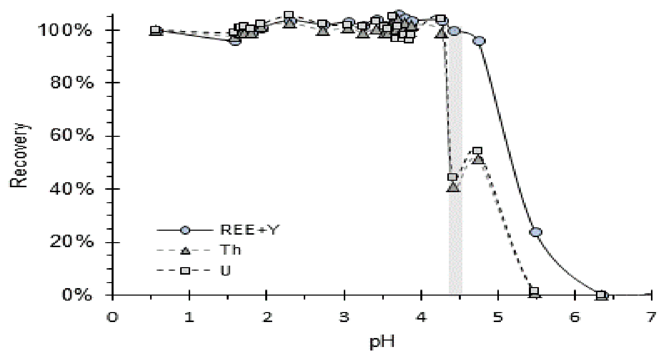
Operation
- 1g to 20g media
- 0.01 to 5 ml/min
- 0.01 to 3M Acid



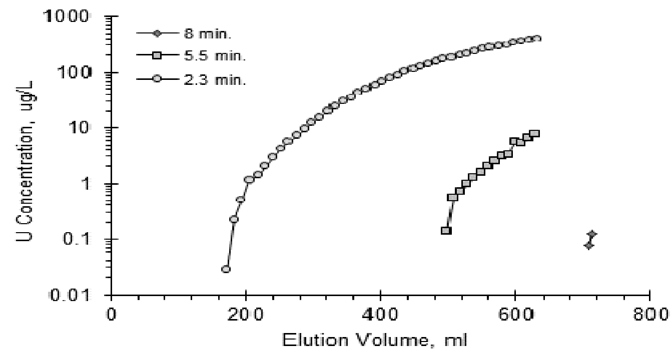
Results

Unit 3
U/Th Removal

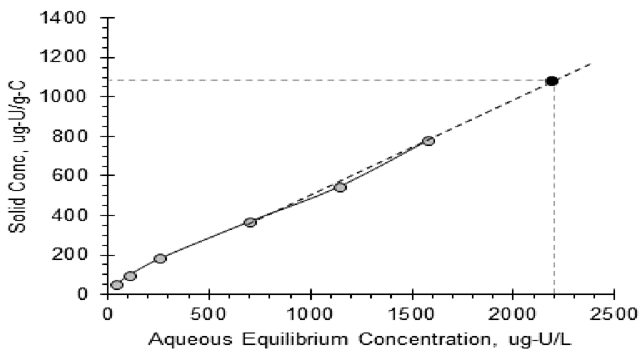
pH of Influent Solution



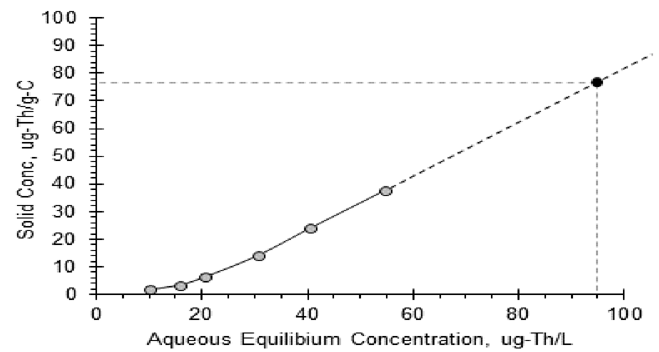
Column Retention Time



U Operational Isotherm



Th Operational Isotherm



Results

Overall Approach

Unit process utilizes an adsorptive bed to bind REEs and other ions with subsequent acid “stripping” to produce concentrated REE solution with decreased amounts of ancillary metals.

Operational Constraints

Adsorptive bed requires influent solution to be particle free and at pH 4 to eliminate media bed clogging and to maximize REE sequestration and isolation.

Evaluation

Tests included:

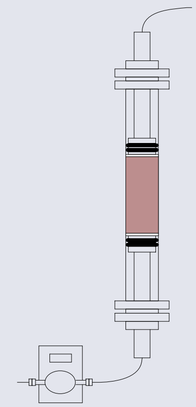
1. Flow Rate
2. “Push”/Strip Volume and Concentration
3. Feed Volume
4. Media Size
5. Aspect Ratio

Test Apparatus

- 1cm Ø x 50 cm column
- Adjustable bed height
- Diffusers (both ends)
- Inf./Eff. pH measurement
- Precision metering pump

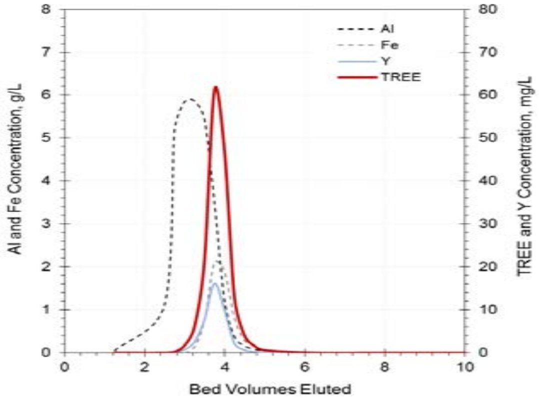
Operation

- 1g to 20g media
- 0.01 to 5 ml/min
- 0.01 to 3M Acid

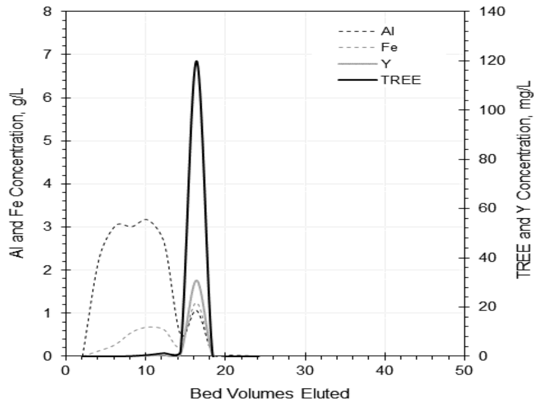


Results

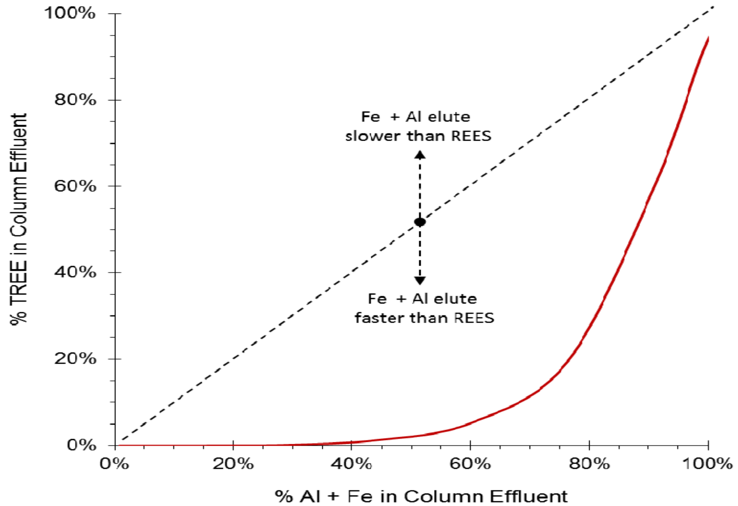
Chromatography



Load & Strip



TREE vs. Al+Fe in Column Effluent



Can remove upwards of 60% of Al and Fe from process solution while only losing 5% REEs

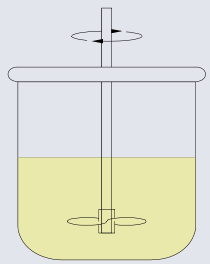
- Translates into 2.5x increase in TREE wt%
- Removal of 15 to 20% of unwanted cations

Results

Unit 5
REE Production

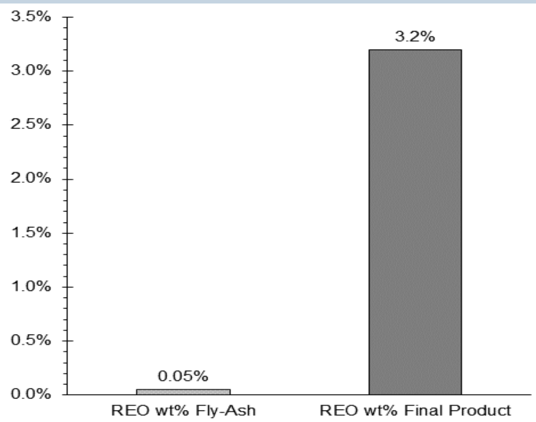
Experimental Procedure

- Hydroxide precipitation at pH 10
- Filtering of solids and drying at 50°C
- Oxidizing at 550°C
- Re-dissolution of metal oxides
- Elemental analysis by ICP

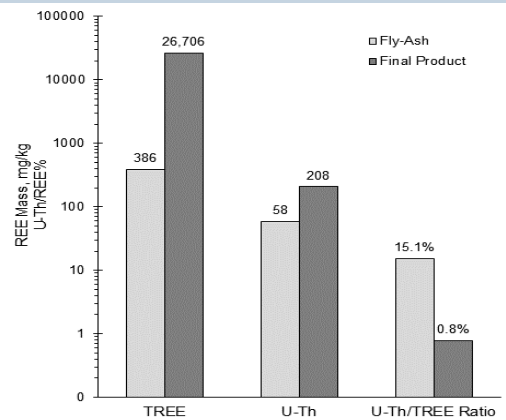


- Wt% of REOs in final product increased by over 65x compared to original fly-ash material

REO wt%



TREE and U/Th wt%



Summary

Operational Parameters

Pretreatment

Base, 0.4-0.6 g/g-fly ash, 100°C, 4 hrs, 10-30wt% solids

Digestion

Acid, 0.4-1 g/g-fly ash, 80°C, 4 hrs, 10-30wt% solids

REE Concentration of 30,000 ppm TREE+Y

U/Th Removal

Tusaar Media AM4, chromatography, 2,200 ppb U and 1,350 ppb Th solutions, 4-8 minutes EBCT, pH 2

REE Isolation/Recovery

Tusaar Media AM5, load/strip, 4-20 minutes EBCT, pH 4, REE concentration as high as 100,000 ppb

REE Recovery and REO Production

REE recovery is proportional to concentration

REE recoveries between 40-70%

3.2% REO wt% in final product

$13-20/ton fly ash

Process Design

Overall PID complete

Incorporates 6 unit process

Recycling of process streams

Production of zeolite material

Zeolite Production (Value-Added Product)

Na-P1 zeolite successfully produced

Used 80-100% of Al isolated within chromatography unit process

0.1kg zeolite/kg fly ash

Accomplishments

PRIMARY

- The developed treatment system achieved a **60% REE recovery** rate
- A final product was produced with more than **2.5wt% REOs**
- U/Th ratio in final product is lower than ratio in source fly ash
- System is **robust and reliable** for scale-up operations
- Waste and residuals treatment system **met RCRA discharge** requirements

SECONDARY

- Production of a zeolite (NaP1) was successfully demonstrated
- Residuals streams can be repurposed with minimization of waste disposal
- Optimization of the system may further increase the economic viability
- Developed process strategies providing scientific foundation for technology advancement

Project Status

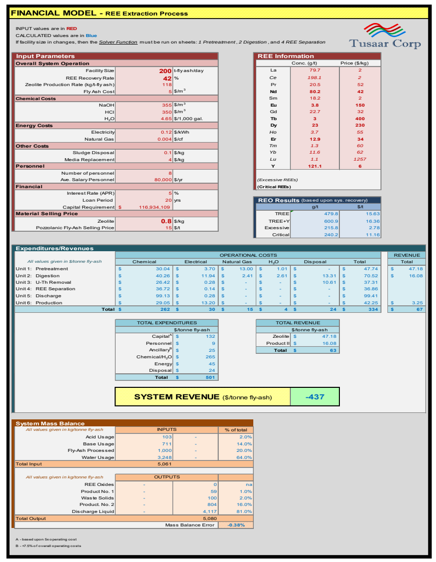
	Current Status	Next Phase
Timeline	Sampling/Characterization of Fly-ash Feedstocks Feasibility Study	Process Design, Process Demonstration Economic Analysis review sub-tasks
Process Development	Process meets/exceeds performance criteria Overall treatment system (process) design	Process instrumentation and design (P&ID) Scaled-up system bill of materials (BOM)
Validation and Scale-Up	Results are encouraging Lab-scale experiments limited to 1kg batches	Scale system up to -kg batches in laboratory Validate REO production rates over multiple runs Determine scale-up factors

Future Work

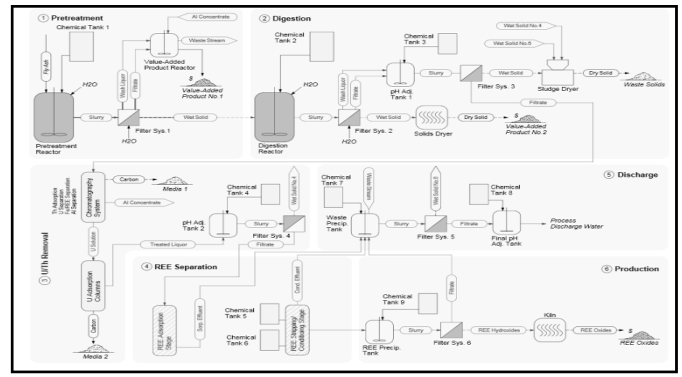
Optimize REO Production

Zeolite Production?

Financial Analysis



Process Scale-Up



Thank You

Questions