


FEASIBILITY STUDY – FINAL PROJECT REPORT

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TABLE of CONTENTS

EXECUTIVE SUMMARY	1
REE Source Material	1
Fly-Ash Characterization	1
Resource Availability	1
REE Extraction Process	2
Technical Performance Assessment	3
Techno-Economic Evaluation	3
Feasibility of Proposed System	3
 SECTION A PROJECT DESCRIPTION AND TIMELINE	 4
A.1 Main Goal	4
A.2 Project Approach	4
A.3 Treatment Process Approach	4
A.4 Objectives	5
A.5 Timeline	5
 SECTION B OVERALL PROJECT EVALUATION	 7
Introduction	7
B.1 Identification of REE Source Materials	7
B.2 Characterization of Fly Ash	7
B.3 Fly Ash and REE Resource Estimate	8
B.4 Selection of Unit Processes	9
B.5 Evaluation of Unit Processes	10
B.5.1 Design Variables and Operating Conditions	10
B.5.2 Encountered Problems	10
B.6 Optimization of Extraction Process	12
B.6.1 Increasing REE Recovery	12
B.6.2 Decreasing Operating Costs	12
B.7 Project Performance Metrics	13
B.8 Techno-Economic Evaluation	14
 SECTION C TASK 2: SAMPLING AND CHARACTERIZATION OF PROPOSED FEEDSTOCKS	 16
C.1 Identification, Sampling, and Selection of Source Material	16
C.1.1 Identification of Source Materials	16
C.1.2 Sampling of Targeted Source Materials	17
C.1.3 Characterization of Targeted Source Materials	19
C.1.4 Selection of Source Material	20
C.2 Characterization of Selected Fly-Ash	20
C.2.1 Optical Evaluation	21

C.2.2 QEMSCAN	21
C.2.3 X-ray Diffraction (XRD)	24
C.2.4 Sieve Size Fractionation	24
C.2.5 Scanning Electron Microscopy	24
C.2.6 Particle Size Analysis (PSA)	25
C.2.7 Chemical Assay	26
C.3 Material Resource Estimate	26
C.3.1 Estimation of Coal Reserves	26
C.3.2 Estimation of Fly-Ash “Reserves”	27
C.3.3 Material Resource Summary	27
SECTION D TASK 3: FEASIBILITY STUDY - INITIAL PROCESS DEVELOPMENT	30
D.1 Evaluation of Pretreatment Strategies	30
D.1.1 Physical Pretreatment – Thermal Shock	30
D.1.2 Physical Pretreatment – Grinding	30
D.1.3 Physical Pretreatment – Magnetic Separation	30
D.1.4 Chemical Pretreatment – Type of Caustic Solution	31
D.1.5 Chemical Pretreatment – Concentration of NaOH	32
D.1.6 Chemical Pretreatment – Solids wt% in Pretreatment Slurry	33
D.1.7 Chemical Pretreatment – Temperature	34
D.1.8 Chemical Pretreatment – Time	34
D.1.9 Chemical Pretreatment – Optimization	35
D.2 Evaluation of Digestion Strategies	36
D.2.1 Type of Acid Solution	36
D.2.2 Concentration of HCl	37
D.2.3 Solids wt% in Digestion Slurry	38
D.2.4 Digestion Reaction Temperature	38
D.2.5 Digestion Reaction Time	39
D.2.6 Digestion Optimization	40
D.3 Uranium and Thorium Removal	42
D.3.1 Operating pH for U/Th Sequestration	43
D.3.2 Evaluation and Selection of Adsorptive Media	44
D.3.3 U/Th Column Empty-Bed-Contact Time	45
D.4 Evaluation of Chromatographic Separation of REEs	47
D.4.1 Column Hydraulic Loading Rate	47
D.4.2 Bolus Volume	48
D.4.3 Bolus Concentration	50
D.4.4 Column Aspect Ratio	51
D.4.5 Carbon Media Particle Size	51
D.5 Conventional Load/Strip Separation of REEs	52
D.5.1 Column Hydraulic Operation	52
D.5.2 Column Aspect Ratio	53
D.5.3 Strip Bolus Size	54

D.5.4 Strip Bolus Concentration	54
D.5.5 Repeated Cycle Loading	55
D.6 Wastewater Treatment	56
D.7 Zeolite Production	57
D.7.1 Zeolite Production Process	57
D.7.2 Type of Zeolite Produced	59
SECTION E TASK 4: PROCESS DESIGN AND PERFORMANCE	60
E.1 Proposed Process Design	60
E.1.1 Final Process Design	60
E.1.2 Final Process Mass Balance	62
E.2 Process Recovery and Yield	63
E.2.1 REE Extraction – NaOH Pretreatment	63
E.2.2 REE Extraction – HCl Digestion	63
E.2.3 REE Extraction – U/Th Removal	65
E.2.4 REE Extraction – REE Extraction Columns	67
E.2.5 REE Product Production	72
E.3 Techno-economic Analysis of Process	75
SECTION F PROJECT EXTENSION	78
F.1 Project Extension Details	78
F.1.1 Motivation	78
F.1.2 Goals and Objectives	78
F.1.3 Tasks	78
F.2 Project Extension Details	79
F.2.1 REE Extraction Optimization – Chloride Addition	79
F.2.2 Dual Digestion U-Th Removal	83
APPENDIX A REPRESENTATIVE SAMPLING	86
Background	86
Error Estimates and Required Sample Size	87
Representative Sampling from Laboratory Bulk Samples	88
APPENDIX B PROCESS DESIGN CALCULATIONS	89

Executive Summary

This final report provides a complete summary of the activities, results, analytical discussion, and overall evaluation of the project titled “*Economical and Environmentally Benign Extraction of Rare Earth Elements (REES) from Coal & Coal Byproducts*” under DOE Award Number DE-FE-0027155 that started in March 2016 and ended December 2017. Details pertaining to the overall project plan, task execution, problems encounters, system development and optimization, and techno-economic feasibility of the REE extraction process is presented in separate sections throughout the main body of this document.

REE Source Material

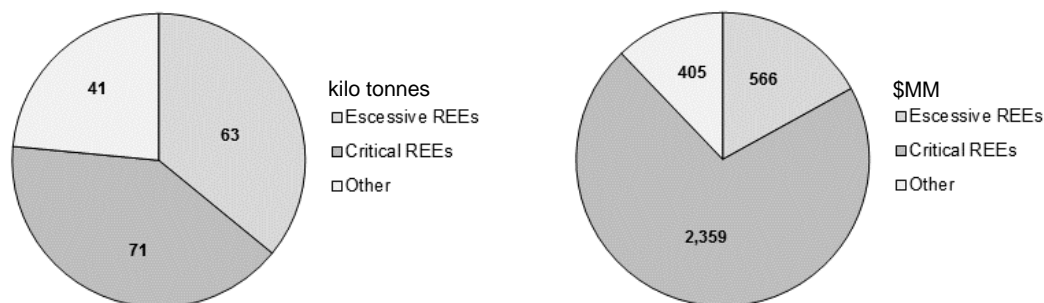
Fly ash was selected as the coal-byproduct source material due to fact that it is readily available with no need for extensive methods to obtain the material, it is produced in large quantities (>50 million tons per year) and had REE concentrations similar to other coal-byproducts. Candidate sources were identified by analyzing information provided on NETL’s website with over 700 potential fly ash sources evaluated to meet the >300ppb REE selection criteria. From this review, six (6) fly ash sources were identified that had critical REE concentrations between 400-535 ppm with outlook ratios between 1.456 to 1.535, and sources that were readily available. Samples from each fly ash source were evaluated for REE content with the most favorable selected for follow-on characterization. The selected fly ash used throughout this project was from the Mill Creek power generating facility operated by Louisville Gas and Electric located in Louisville, KY.

Fly-Ash Characterization

The selected fly was subjected to a variety of physical and chemical characterization tests. Results of the ICP-MS analysis of lithium borate fusion extractions revealed that the selected fly-ash had a TREE+Y concentration of approximately 480 ppm with critical REEs having a concentration of 200 ppm. The fly ash had an outlook ratio of 1.25 and an estimated value of \$16 worth of salable REEs present in 1-tonne of material. Additional characterizations by optical evaluation, QEMSCAN, XRD, size fractionation, and SEM analysis showed the fly ash material consisted of small glassy spherules with a size range between 1 to 110 µm (average diameter of 13 µm), was heterogeneous in chemical composition (main crystalline phases identified as aluminum oxides and iron oxides), and was primarily an amorphous material (75 to 80%).

Resource Availability

A simple stepped approach was completed that included the identification of potential fly-ash sources that had high REE content (>300 ppm), REE characterization of the representative samples, evaluation of fly-ash availability, and final determination estimated resource availability with regards to REE grade on a regional and national scale. Results summarized in the following graphs.



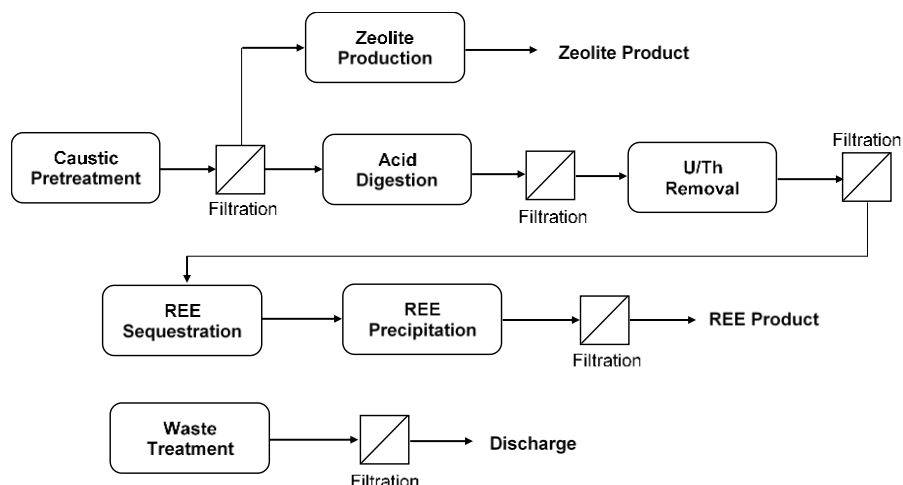
This data represents the best available information and is based upon the assumptions that the power generating facility where the fly-ash was obtained will use the same coal sources (actual mines were identified), the coal materials will have relatively consistent REE concentrations, and the REE extraction process developed during this project can achieve 42% REE recovery (validated and confirmed). The data indicates that the estimated REE resource is approximately 175,000 tonnes with a current estimated value of \$3,330MM. These values are further

separated into excessive REEs, critical REEs, and other REEs. The critical REE estimated resource is approximately 71,000,000 tonnes with a value of \$2,350MM.

REE Extraction Process

The proposed REE extraction and production process developed during this project utilized four fundamental steps; 1) fly-ash pretreatment to enhance REE extraction, 2) REE extraction by acid digestion, 3) REE separation/concentration by carbon adsorption and column chromatography, and 4) REE oxide production. Secondary processing steps to manage process residuals and additional processing techniques to produce value-added products were incorporated into the process during the project. These secondary steps were not only necessary to manage residuals, but also provided additional revenue streams that offset operational and capital expenditures.

The final developed REE process system incorporated seven main unit operational areas. A generalized process approach is summarized in the following schematic.



The process produces one value product stream (production of zeolite Na-P1), a solids waste stream, and one liquid stream that met RCRA discharge requirements. Based upon final design criteria and operational parameters, the proposed system could produce approximately 200 grams of REOs from 1-tonne of fly-ash, thereby representing a TREE+Y recovery of 42% (project target of > 25%). A summary of critical design and operating parameter values determined through project experimentation for each unit process (excluding wastewater treatment) are provided in the table below

	Caustic Pretreatment	Acid Digestion	U/Th Removal	REE Sequestration	REE Precipitation	Zeolite Production
volume (l/kg-fly ash)	0.65	0.76	0.05	0.063	0.41	2.16
reaction/contact time (hr)	4	4	0.12	0.15	2	96
temperature (°C)	80	80	ambient	ambient	ambient	95
NaOH (kg/kg-fly ash)	0.07	---	0.06	---	0.065	recycled
HCl (kg/kg-fly ash)	---	0.077 (2.67M)	---	0.02	---	---
water (l/t-fly ash)	2,300	4,500	---	---	---	---
pH adj. of reaction liquor	no	to 2.5	to 4	no	no	no
media (kg/m ³ -solution)	---	---	0.25	2.5	---	---
fluid velocity (m/hr)	---	---	5.1	5.1	---	---

These parameters were used to design a full-scale processing system and for system performance modeling used during a detailed techno-economic analysis.

Technical Performance Assessment

There were six (6) criteria set at the start of the project that established the performance guidelines. These guidelines were targeted during the project. A comparison between observed performance to the benchmarks is provided in the table below.

	Criteria	Metric Value	Actual Value	Criteria Met (Y/N)
1	Overall REE Recovery from Source Fly Ash >25%	25%	29%-42%	Y
2	Final REE Concentration Approaches 2% by Weight (dry mass basis)	2 wt% (dry mass basis)	1.2 - 3.2%	Y
3	> 50% Removal of U-Th from Source Fly Ash	>50% for both U and Th	90+% - U 90+% - Th	Y
4	U-Th to REE Ratio in Final Product is Less-than Ratio in Source Material	Mass U-Th/Mass REE in Product < Mass U-Th/Mass REE in Fly Ash	0.8% < 15.1%	Y
5	Aqueous Waste Streams Meet RCRA Discharge Requirements	Measured ppm for As, Ba, Cd, Cr, Pb, Hg, Se, and Ag are below RCRA discharge limits	All non-detect except Ba which is 65% lower than standard	Y
6	Reasonableness of Economic Justification	Potential Revenue > System Cost	System Cost >> Potential Revenue	N

Overall performance assessment shows that all but one of the performance metrics were met including two critical ones, namely the ability to recover more-than 25% of REE from fly ash materials and that a final REO product could be produced with more than 2wt% REE. The only criterion not met was the economic justification of the process. This conclusion was based upon the fact that estimated OPEX and CAPEX were greater than total anticipated revenues from REEs and the value-added product (zeolite Na-P1) obtained from the process.

Techno-Economic Evaluation

A detailed economic model was developed to evaluate both CAPEX and OPEX estimates for systems with varying capacities between 100 kg to 200 tonnes of fly ash processed per day. Cost estimate data shows a standard power-law relationship between capital and operating costs to system size. Using a standard system capacity of 10 tonne/day system, capital costs were estimated at \$88/kg fly ash while operating costs were estimated at approximately \$450/kg fly ash. This operating cost estimate includes a revenue of \$495/tonne of fly ash processed from the value-added product produced from the system (zeolite Na-P1).

Although operating cost savings due to zeolite production is significant, the capital + operating cost for a 10 tonne system is still more expensive than the total dollar value of REEs present in the fly ash material. Specifically, the estimated cost per 1-tonne of fly ash treated is approximately \$540 while the estimated value of REEs in the fly ash is \$18-\$20/tonne. This is an excessive difference showing that the proposed process is not economically feasible strictly on the basis of REE revenue compared to extraction costs.

Feasibility of Proposed System

Although the current proposed system does not produce sufficient quantities of REEs or additional revenue sources to offset operational and capital costs, supplementary factors including US strategic concerns, commercial demands, and defense department requirements must be factored. The strategic need to the US and Europe for such a technology and ready resource cannot be over stated. At this time, we strongly believe that the process developed during this project provides foundational information for future development of relatively simple processes that require low capital investment and one that will extract a valuable quality and quantity of REE oxides from industrial waste.

A.1 Main Goal

The overall goal of the project was to develop and optimize a REE extraction process utilizing a series of unit operations integrating the use of the recipient's proprietary media to produce a final mixed rare earth element (REE) product concentrate that was greater-than 2% by weight (dry basis) from fly-ash produced from coal fired power generation.

A.2 Project Approach

Project activities were separated into three main phases:

1. Fly-ash source selection, characterization, and beneficiation
2. Small-scale unit operation selection, testing, and performance evaluation
3. Recommended process design and validation testing

The phases were chosen as a logical progression from REE source material characterization, identification of the best treatment operations to extract REEs based upon the source material characteristics (physical and chemical), testing and evaluation of the selected treatment operations, and finally validation of the developed extraction process. Section A.5 Timeline provides a detailed summary of the project phases and timeline.

A.3 Treatment Process Approach

The original process concept to extract REEs from fly ash was designed to use multiple unit operations including; fly-ash pretreatment, acid digestion, U/Th removal by adsorption, REE recovery by adsorption, and final precipitation of an REE product. Figure A.1 illustrates this simple concept.

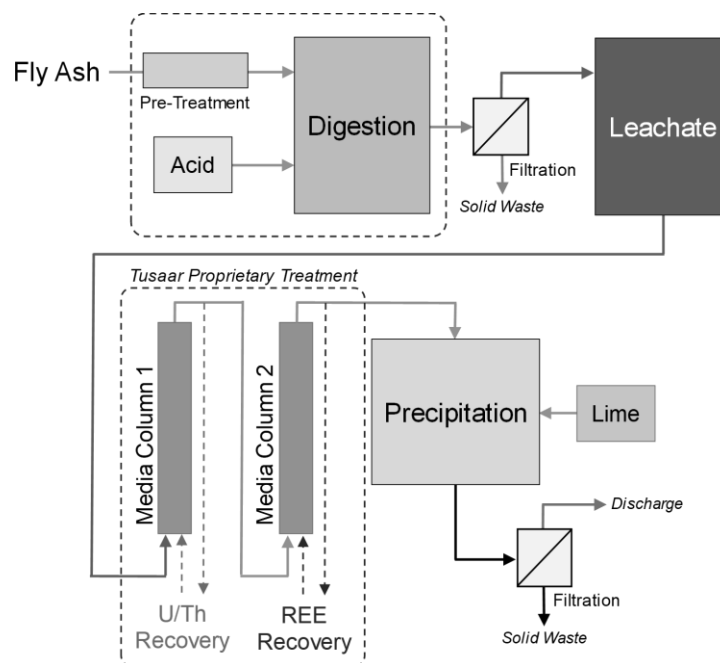


Figure A.1 Initial concept of treatment process to extract REEs from fly ash.

Planned project tasks, experiments, and evaluation was based upon this simplified scheme. As project activities were completed and knowledge of the process increased, modifications and additions to the process were made to optimize performance (see Sections C, D, and E).

A.4 Objectives

Based upon the general project goal and designated approach, project objectives focused on the required experiments to evaluate proposed unit operations and ultimately develop a technically robust, economically viable, and environmentally friendly treatment process for the extraction of mixed REEs from a domestic coal-generated fly-ash. Specific project objectives included:

1. Identify fly-ash source materials that had total REE concentrations greater than 300 ppm
2. Analyze and characterize fly-ash source materials and select a fly-ash source rich in REEs (>300 ppm), high in critical REE percentage, and available in large quantities for future process scale-up activities
3. Select unit processes based upon the fly-ash characterization to test
4. Evaluate the performance of selected processes
5. Optimize process for the recovery of REEs from fly-ash
6. Produce a final product that meets all of the project performance metrics set forth by DOE.
7. Complete a techno-economic evaluation of the developed extraction process and assess market viability

A.5 Timeline

Project activities were separated into five main Tasks along with a project extension period (described in later sections). The defined project tasks were:

- Task 1 Project Management and Planning (PMP)
- Task 2 Sampling and Characterization of Proposed Feedstocks
- Task 3 Feasibility Study - Development of Process
- Go/No Go Decision Point
- Task 4 Process Design and Integration
- Project Extension
- Task 5 Final Process Technical Report and Presentation

Details of major activities and milestones for each major task, as well as the required time effort required are summarized in Figure A.2.

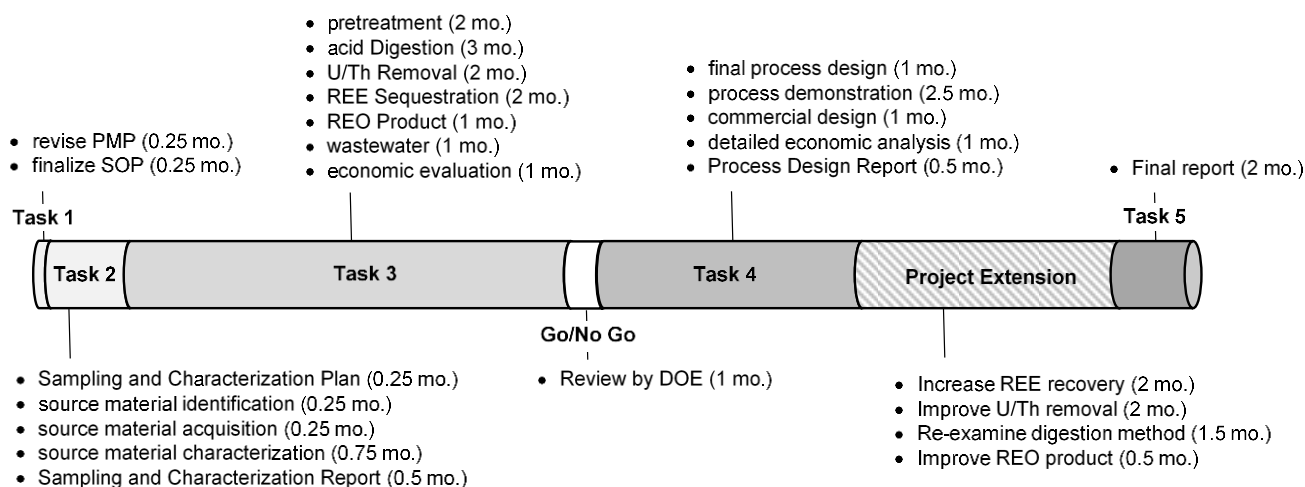


Figure A.2 Project activities within each major task including required time to complete each activity.

The initial time-frame of the project was 18 months but was later changed to a 24-month period with the inclusion of a project extension. Project activities and experiments started in February of 2016 and ended in December of 2017. Although project funding was approved for a start date of March 2016, efforts were initiated to find suitable coal by-product sources. The number of months required for each project tasks were; Task 1 (0.5 mo.) Task 2 (2 mo.), Task 3 (12 mo.). GO/NO GO decision point (1 mo.), Task 4 (6 mo.), project extension (6 mo.), and final report generation (2 mo.).

Project activities and results were summarized every quarter and submitted to DOE as required by the project management plan (PMP). Quarterly reviews also provided important assessment, critical guidance, and most importantly on-going modification of project activities to meet stated goals. Specific, second-tier goals aside from the main project goals were formulated each quarter. Within these quarterly goals, specific activities were identified, therein providing the framework for all laboratory activities. Table A.1 summarizes these activities.

Table A.1 Specific Second-Tier Goals During Quarter and Corresponding Activities.

Quarter	Goals	Activities
1	<ul style="list-style-type: none"> finalize Sampling and Characterization Plan complete PMP evaluate fly-ash source materials 	<ul style="list-style-type: none"> select fly-ash sampling locations obtain fly-ash samples initial evaluation of selected fly-ash materials
2	<ul style="list-style-type: none"> evaluation of available fly ash materials final fly ash selection characterization of the chosen fly ash initial processing of fly-ash material 	<ul style="list-style-type: none"> characterization of obtained fly-ash materials evaluation of acid digestion pretreatment methods investigation of different digestion methods
3	<ul style="list-style-type: none"> SEM evaluation of fly ash materials optimization of the fly digestion method laboratory set-up for U/Th sequestration and REE recovery 	<ul style="list-style-type: none"> finalization of fly-ash digestion method optimizing U/Th removal REE recovery evaluation exploration of producing value-added products
4	<ul style="list-style-type: none"> establish a material resource estimate Increase removal of uranium and thorium separate and concentrate REEs finalizing preliminary process design produce a final REO product define and optimize wastewater and residuals management complete initial techno-economic evaluation 	<ul style="list-style-type: none"> determine best method for U/Th removal evaluate chromatographic separation of Al and Fe optimize REE loading and recovery investigate zeolite production complete treatment system process design and mass balance analysis simulation of entire production process wastewater/residuals treatment analyses determine operating and capital cost estimates
5	<ul style="list-style-type: none"> REE product recovery in a continuous process scheme removal of uranium and thorium (U/Th) scale-up of REE sorption columns REE product production 	<ul style="list-style-type: none"> determine best conditions for U/Th removal evaluate chromatographic separation of Al and Fe optimize sorptive media REE loading and stripping simulation of entire production process to obtain REO product material
6	<ul style="list-style-type: none"> REE product recovery in large batches increase REE removal efficiency by optimizing process conditions decrease REE loss through process 	<ul style="list-style-type: none"> improve filtration efficiency of REEs by reducing retained oxidation liquor in the filter cake optimization of REE media columns by determining the optimal flow rate
7	<ul style="list-style-type: none"> increase REE removal efficiency by optimizing pretreatment and digestion process conditions investigate dual-digestion method to increase removal of uranium and thorium 	<ul style="list-style-type: none"> define operational parameters using chloride salt addition to maximize REE extraction evaluate dual-digestion sequence to remove REEs followed by a second digestion to remove uranium/thorium
8	<ul style="list-style-type: none"> Assess impact of new digestion method Determine updated process economics 	<ul style="list-style-type: none"> Final project assessment

Introduction

This section summarizes overall project evaluation and is more detailed than the Executive Summary, providing a “snapshot” of experiments conducted, corresponding analysis, and context to the project goals and objectives. The reader will notice that some information in this section is repeated in subsequent sections that summarize all results of the project.

B.1 Identification of REE Source Materials

Fly ash was selected as the coal-byproduct source material due to fact that it is readily available with no need for extensive methods to obtain the material, it is produced in large quantities (>50 million tons per year) and had REE concentrations similar to other coal-byproducts. Initial review of fly ash sources focused on sources that had REE content exceeding 300 ppm along with high critical to excess REE ratios. Candidate sources were identified by analyzing information provided on NETL’s website with over 700 potential fly ash sources evaluated. From this review, six (6) fly ash sources were identified that had critical REE concentrations between 30-200 ppm with outlook ratios between 1.456 to1.535, and sources that were readily available. Geographically, the sources of coal that generated the six fly-ash materials came from two regions; the Interior Region and Appalachian region. Within these regions, two distinct coal basins provided coal to the power generating facilities that produced the six targeted fly ash materials, the Illinois Basin and the Central Appalachian Basin. Samples from each of these fly ash sources were evaluated for REE content with the most favorable selected for follow-on characterization.

The selected fly ash used throughout this project was from the Mill Creek power generating facility operated by Louisville Gas and Electric located in Louisville, KY.

B.2 Characterization of Fly Ash

The selected fly was subjected to a variety of physical and chemical characterization tests. Lithium borate fusion followed by ICP-MS analysis was used to determine the total REE content of the selected fly ash and was used as the reference baseline to determine extraction efficiencies for REEs, U, and Th. Obtaining a representative sample from the fly ash material shipped to the Recipient’s laboratories was approached by balancing both probabilistic and judgmental sampling approaches. From a probabilistic perspective, multiple fractional samples at multiple locations within the 5-gallon container were acquired and then combined to form a final, representative composite sample. Probabilistic sampling was not possible due to limitations within onsite sampling when practical issues such as required sample sizes, safety, transport, and financial constraints are factored.

Multiple representative fly ash samples were analyzed. Results of the ICP-MS analysis of extracted REEs is summarized in Table B.1.

Table B.1 REE Chemical Assay of Selected Fly Ash	
TREE+Y	482
TREE	387
Critical REE	201
Excessive REE	161
La+Ce (% of TREE+Y)	44%
\$-REE/tonne fly-ash	\$15.74
Outlook Ratio	1.25

The baseline value for TREE and TREE+Y was used to ascertain unit process performance (see Sections C and D). Extended chemical assay of the fly ash material is Summarized in Table B.2.

Table B.2 Extended Chemical Assay of Selected 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%

From fusion analysis, the mass of aluminum, iron, and silica combined accounts for 48% of the fly ash mass. If the oxide forms of these constituents are estimated, even in an amorphous state, then SiO₂, FeO₃, and Al₂O₃ would account for 32%, 34% and 20% of the total fly ash mass respectively. These values are consistent with a bituminous coal source.

Additional characterizations by optical evaluation, QEMSCAN, XRD, size fractionation, and SEM analysis were performed (see Section B). Based upon these analyses the fly ash material consisted of:

- Small glassy spherules with a size range between 1 to 110-um with an average diameter of 13 um
- A heterogeneous composition, both chemically and spatially, with main crystalline phases identified as aluminum oxides, iron oxides, and possibly quartz
- A material that was 75 to 80% amorphous

B.3 Fly Ash and REE Resource Estimate

Material resource estimates were calculated by using the coal basin reserve estimates for the power generating facility, the fly-ash production rate per tonne of coal processed, the REE content in the fly ash material (by fusion analysis), and by the efficiency of the REE extraction process (an average of 42%). Details of the analysis can be found in sections C and D. Based upon this analysis, the maximum TREE+Y that could be extracted and total potential revenue (based on current prices) from the entire coal source would be approximately 175,000 tonnes and \$3.33 billion. A detailed breakdown of these resource estimates into critical REEs/excessive REEs for both mass and potential revenue is provided in Figure B.1.

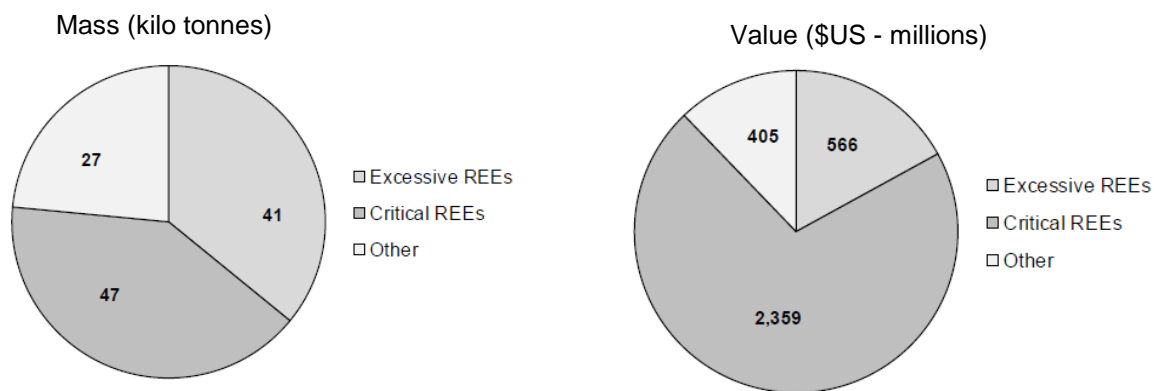


Figure B.1

Total adjusted REE resource estimates for total mass and estimated value (based upon current REO prices).

The represented data in Figure E.1 clearly shows that the critical REEs account for over 70% of the potential REE revenue from the material source. At the current critical REE production rate from the total fly ash produced at the Mill creek facility of 535 tonnes/yr, the reserve would last approximately for well over 100 years. This estimate seems high since other factors such as increased future coal usage at other facilities will lower this estimate. In any event, the REE resource appears to be a long-term source.

Based upon current generation rates at the Mill Creek power generation facility, the maximum value of REEs that could be obtained within a year would be \$5.2MM (see Table B.6 in Section B.3.2). This is assuming that all of the fly ash produced from the burning of 9.8 million tonnes of coal, over 920,000 tonnes of fly-ash, is processed. If 100% of the TREE+Y was extracted from all of the fly ash produced, then the TREE+Y mass extracted would be approximately 535 tonnes per year (0.05wt% in fly ash). This TREE+Y extraction rate would require a system capacity of 3,600 tonnes per day.

B.4 Selection of Unit Processes

It was decided during the proposal submission stage that an acid digestion technique would be used in conjunction with column adsorption/chromatography (with the recipient's proprietary media) to isolate and concentrate extracted REEs would be the core of the developed process. Based upon literature review and discussions with industry experts, it was clear from the onset of the project that fly ash would need to be pretreated to increase the extraction efficiency of REEs above 20 to 30% with stand-alone acid digestion strategies. A targeted effort was initiated to develop a pre-treatment process utilizing caustic solutions to enhance acid digestion efficiencies. It was also known early on in the project that a specific unit process for U-Th removal unit process would also be required. Figure E.2 below summarizes the unit processes selected for testing during initial project activities.

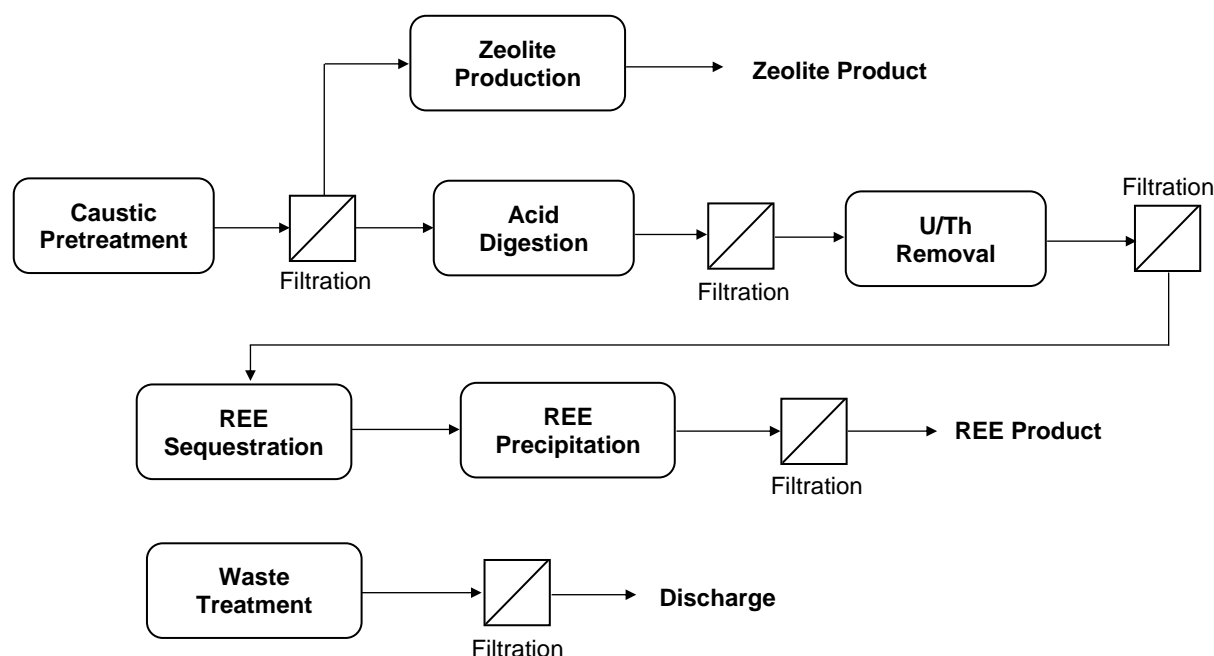


Figure B.2

General treatment concept showing main unit processes.

Testing and evaluation of these unit processes consumed a large portion of project activities and resources. Section B.5 discusses the evaluation of these processes, while Section B.6 discusses the testing and optimization of the final proposed process sequence.

B.5 Evaluation of Unit Processes

Seven major unit process including 1) caustic pretreatment, 2) acid digestion, 3) U-Th removal, 4) REE sequestration, 5) REE Precipitation, 6) zeolite production, and wastewater treatment were evaluated. Along with these main unit operations, filtration was an integral part of the evaluation process (see Figure E.2). A series of experiments were performed for each unit operation to derive operational parameters and to provide influent process stream characteristics for downstream unit processes. Details of specific experimental results and analysis of each unit process can be found in Section C.

B.5.1 Design Variables and Operating Conditions

Once the general treatment process and individual unit operations were identified, as described in the previous section, a large number of experiments were completed to determine the best operating conditions (type of chemical, concentration, time, reaction temperature, pH, etc.) and overall design parameters. A summary of critical design and operating parameter values for each unit process (excluding wastewater treatment) is provided in Table B.3.

Table B.3 Operational and Design Parameters

	Caustic Pretreatment	Acid Digestion	U/Th Removal	REE Sequestration	REE Precipitation	Zeolite Production
volume (l/kg-fly ash)	0.65	0.76	0.05	0.063	0.41	2.16
reaction/contact time (hr)	4	4	0.12	0.15	2	96
temperature (°C)	80	80	ambient	ambient	ambient	95
NaOH (kg/kg-fly ash)	0.07	---	0.06	---	0.065	recycled
HCl (kg/kg-fly ash)	---	0.077 (2.67M)	---	0.02	---	---
water (l/t-fly ash)	2,300	4,500	---	---	---	---
pH adj. of reaction liquor	no	to 2.5	to 4	no	no	no
media (kg/m ³ -solution)	---	---	0.25	2.5	---	---
fluid velocity (m/hr)	---	---	5.1	5.1	---	---

Additional operational and design parameters for the filtration steps shown in Figure B.2 were determined with general operation at 15 to 60 psi pressure with a 1 um effective filtration size.

The overall wastewater production rate from filtration wash water, media column washing, and spent treatment liquors was 3.3 liters per kg-fly ash processed. Neutralization of the wastewater solution for the precipitation and removal of metals utilized 0.212 kg-NaOH/kg-fly ash. The wastewater treatment basin requires a 2-hour retention time prior to filtration and ultimate discharge.

The design parameters and operational values in Table B.3 were used to scale-up the size of bench-scale test from 50 to 400 g-fly ash per batch up to 2 kg-fly ash batch processes. Evaluation of the process at this larger scale is discussed in Section B.6.

B.5.2 Encountered Problems

In general, each unit operation in the process sequence (see Figure B.2) worked well as stand-alone experiments. As with any process development, each unit process had a few technical challenges. These issues were readily solved and resulted in an optimized process. However, there were some problems encountered during this evaluation stage that were difficult to solve, with process design “workarounds” used as final solutions. Problems identified during this stage included:

- Separation of fly ash from acid digestion solution was difficult due to slow filtration times
- REEs were lost during each filtration step
- REE recovery rates were sensitive to solids loading during processing

The issues with filtration after acid digestion proved to be one of the most challenging problems to address during the project. It was observed that when larger solids wt% loadings were used during acid digestion, required filtration time and the percentage of retained liquid in the digested solids increased. Figure B.2 illustrates this point for one series of experiments. In addition, the size of the reactor vessel also impacted filtration efficiency as Figure B.4 illustrates this point.

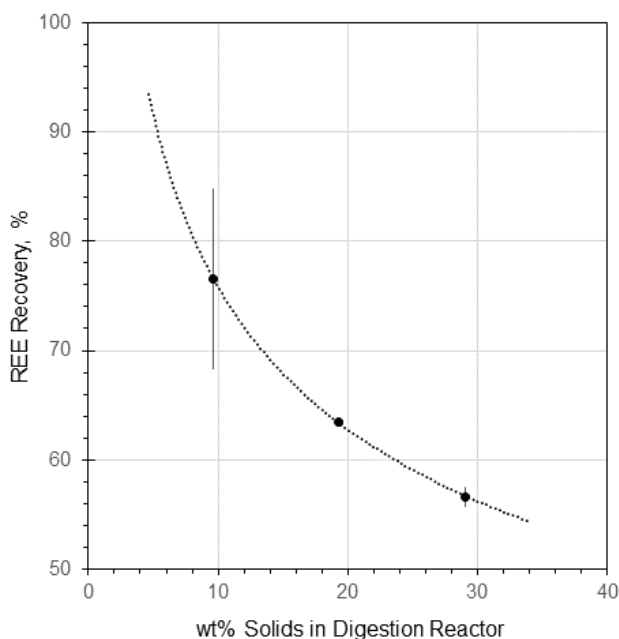


Figure B.3

Resulting percentage of digestion solution remaining in filter solids versus the size (g-fly ash) of the digestion batch.

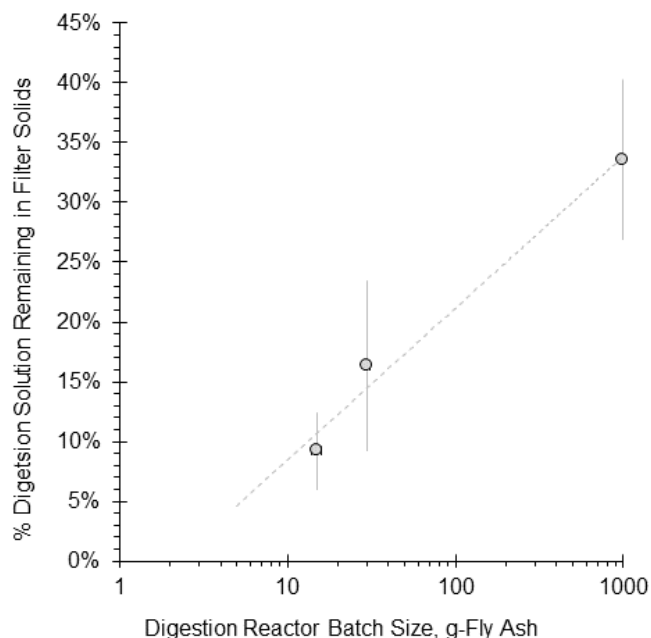


Figure B.4

Relationship between reactor size used during digestion and resulting % solution remaining in filter solids.

The decrease in REE recovery versus solids wt% in Figure B.3 of 20% from solids increase in the digestion reactor from 10 to 30 wt% is significant. These results, coupled with the results shown in Figure B.4 where batch reactor size dramatically impacted REE recovery, shows that the use of a high solids loading during acid digestion in conjunction with a large reactor size, resulted in REE losses could exceeding 50%.

It was determined from detailed observations that, when wt% solids increased and/or the reactor size increased, the reaction solution started to thicken in the top regions of the solution and in some cases turned into a “gel like” substance. This formation would decrease mixing and uniform heating efficiencies within the reaction vessel. Two observations provided information that was helpful in formulating an explanation and strategies to solve the decrease in REE recovery. It was observed that during digestion, if the solution temperature exceeded 85°C, the solution would thicken and not mix well. Additional observations revealed that if the digestion solution was maintained at 80°C, then filtered to separate residual fly-ash solids from the liquor containing extracted REEs, the solid – liquid matrix would thicken to the point that the solution appeared to be “gelatinous”. These changes to the solution and solids did not occur during fly-ash digestion if the ash was not subjected to pretreatment. Therefore, linking pretreatment conditions to the conditions during digestion gave insight into the possibility of silicic acid formation during processing. At high temperatures (>85°C) it was likely that short-chain silicic acids condensed to form complex polymeric structures that interacted with one another resulting in a “gelatinous” fluid. The situation was exacerbated during filtration because as water is removed from the digestion liquor, short-chain silicic acids weakly interact with one another to form a “gelatinous” mass once again.

The best solution to this problem was to operate both pretreatment and acid digestion reactors with a 10 wt% loading at a temperature maintained less-than 80°C. It is anticipated in an actual production system with more powerful and efficient mixing and filtration equipment, solids loading up to 30% can be used to minimize reaction vessel and ancillary equipment sizes.

B.6 Optimization of Extraction Process

During the project, over 150 experiments were completed to develop an efficient extraction process and to ultimately optimize the REE extraction process. Tests were scaled from 40 to 400-gram reaction batch sizes up to 1-kg batches not only to provide data for scale factors, but also to produce sufficient quantities of materials for more detailed testing and evaluation.

As stated in Section B.5.2, there were process issues that caused large losses of REEs, upwards of 60% of the REEs that were initially extracted from fly ash during pretreatment and digestion operations. In addition, techno-economic analysis indicated that the process, as developed during the initial stages of the project, did not produce positive revenue. Therefore, experiments targeted the improvement in filtration efficiency to decrease REE loss and to decrease overall chemical usage throughout the process.

B.6.1 Increasing REE Recovery

Increasing TREE+Y recovery was approached by maximizing filtration efficiencies through the process. Results previously presented in Section B.5.2 indicated that depending on the reactor batch size, upwards of 50% or more of TREE+Y extracted from fly ash during the pretreatment and digestion unit operations were lost during filtration. This “loss” was due to the fact that a large portion of the reaction liquors were not effectively removed from the solids, i.e. filtration efficiency was low. It was postulated that the formation of silicic acid during digestion was resulting in poor dewater characteristics of the treated fly ash solids.

Various techniques were employed to solve this problem including decreasing reaction temperatures below 80°C, limiting solids concentrations to less-than 20wt%, and decreasing acid strength during digestion. By implementing these operational changes, loss of TREE+Y during all filtration operation throughout the entire process decreased to 15 to 30% (shown in Section E.2.5). Although this loss remained higher than wanted, the efforts used did help minimize the problem.

B.6.2 Decreasing Operating Costs

It was witnessed during process development that, when the extraction process maximized REE recovery, the process also increased the extraction of aluminum and iron (the two metals with the highest concentration in the process liquor) therein impacting REE purification and final product mass percentages. Based upon these facts, it was deemed necessary to investigate digestion methodologies that could increase REE extraction efficiency while simultaneously decreasing aluminum and iron extraction percentages. In addition, any optimization that could decrease overall chemical consumption would be beneficial since over 75% of total operating cost was associated with chemical costs.

The optimization strategy focused on decreasing the quantity of HCl used during digestion since this solution had to be neutralized, i.e. more acid use also meant more NaOH use. A series of tests were performed using various concentrations of sodium chloride (NaCl) along with hydrochloric acid. The fly-ash was pretreated with the standardized project method (3M NaOH, 4 hours, 80°C, 10wt% solids loading) followed by acid digestion with varying amounts of HCl. Experiments were designed to maintain a chloride ion concentration of 2.67M (the optimal HCl concentration from earlier experiments).

Based on the observations, there was little to no impact of adding NaCl into the digestion mixture when HCl concentrations were greater-than 2M. Only when the concentration of HCl was decreased with the addition of NaCl did the extraction efficiencies for Fe and Al decrease significantly. Although there are multiple hypotheses of why this may have occurred, the most important finding was that the amount of Fe and Al in solution could be significantly reduced while maintaining a high TREE+Y extraction efficiency.

By using this optimized acid digestion method, the estimated wt% of TREE+Y in the final product increased by over 3% (absolute increase) while simultaneously decreasing HCl and NaOH usage by approximately 50%. Since HCl and NaOH chemicals accounted for roughly 70% of total operating costs (see Section E.3), reducing chemical usage by 50% translated into an operating cost reduction of 30 to 35%. This fact resulted in an estimated operating cost reduction of \$400/tonne fly ash produced.

B.7 Project Performance Metrics

There were six (6) criteria set at the start of the project that established the performance guidelines that were targeted during the project. These criteria were used as bench-mark checks to determine the technical and economic viability of the completed project work. The criteria included:

- Overall REE Recovery from Source Fly Ash >25%
- Final REE Concentration Approaches 2% by Weight (dry mass basis)
- > 50% Removal of U-Th from Source Fly Ash
- U-Th to REE Ratio in Final Product is Less-than Source Material U-Th to REE Ratio
- Aqueous Waste Streams Meet RCRA Requirements for Discharge
- Reasonableness of Economic Justification

Detailed results pertaining to the first five technical criteria are summarized in Section C, D, and F of this document. Techno-economic analysis and discussion of the proposed process are discussed in Section D.3. Results summarized in these sections were compared to the aforementioned performance metrics and are presented in Table B.4.

Table B.4 Overall Assessment of Project Performance Metrics

	Criteria	Metric Value	Actual Value	Criteria Met (Y/N)	Section
1	Overall REE Recovery from Source Fly Ash >25%	25%	29%-42%	Y	C and D
2	Final REE Concentration Approaches 2% by Weight (dry mass basis)	2 wt% (dry mass basis)	1.2 - 3.2%	Y	C and D
3	> 50% Removal of U-Th from Source Fly Ash	>50% for both U and Th	90+% - U 90+% - Th	Y	F
4	U-Th to REE Ratio in Final Product is Less-than Ratio in Source Material	Mass U-Th/Mass REE in Product < Mass U-Th/Mass REE in Fly Ash	0.8% < 15.1%	Y	C and D
5	Aqueous Waste Streams Meet RCRA Discharge Requirements	Measured ppm for As, Ba, Cd, Cr, Pb, Hg, Se, and Ag are below RCRA discharge limits	All non-detect except Ba which is 65% lower than standard	Y	C
6	Reasonableness of Economic Justification	Potential Revenue > System Cost	System Cost >> Potential Revenue	N	D

Overall performance assessment in Table B.4 shows that all but one of the performance metrics were met including two critical ones, namely the ability to recover more-than 25% of REE from fly ash materials and that a

final REO product could be produced with more than 2wt% REE. The only criterion not met was the reasonableness of economic justification of the process. This conclusion was based upon the fact that estimated OPEX and CAPEX was greater than anticipated revenues from REEs and the value-added product (zeolite Na-P1) obtained from the process.

B.8 Techno-Economic Evaluation

The proposed process design was the culmination of laboratory efforts that included the optimization of process parameters through multiple iterative evaluations and investigations into process yields and economic impacts to develop the most promising techno-economic solution. Section E.3 provides detailed information regarding the steps taken, spreadsheets developed, and assumptions made during the economic assessment of the developed process. Based upon this analysis, CAPEX and OPEX were determined for systems with varying capacities between 100 kg to 200 tonnes of fly ash processed per day. It must be noted that OPEX estimates are presented with and without the revenue generated from a value-added product (zeolite Na-P1 – see Section D.8)

Figure B.5 summarizes capital and operating cost estimates based upon the financial analysis model.

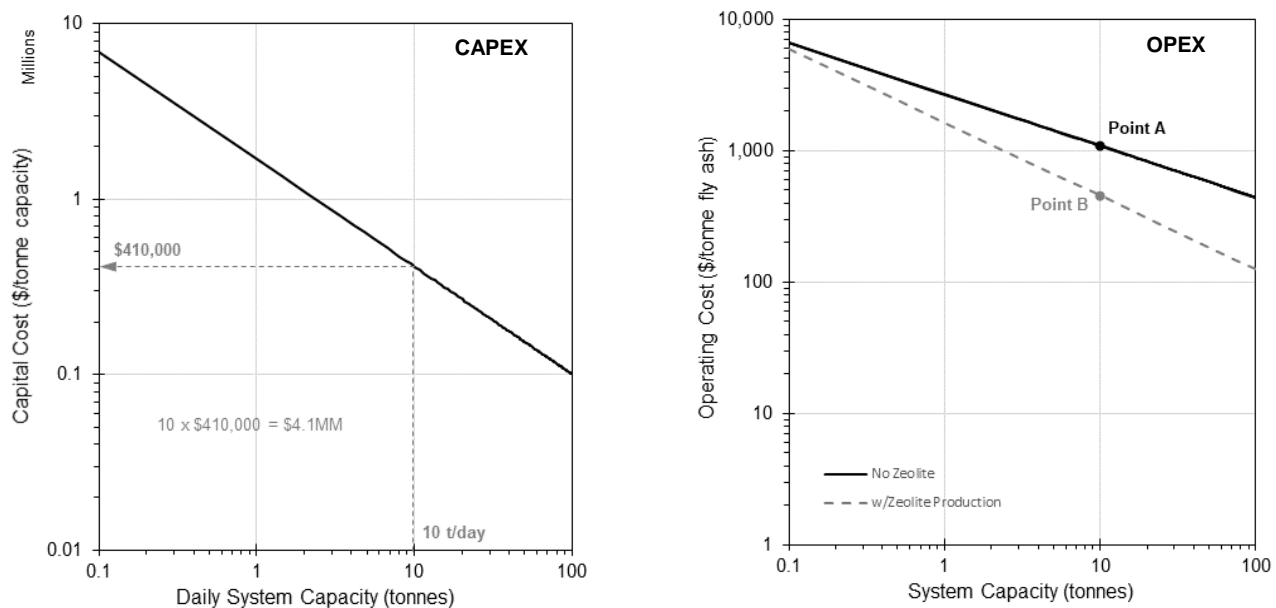


Figure B.5

Capital and operating costing model results for process system sizes between 100-kg/d to 100,000 kg/d

Cost estimate data shows a standard power-law relationship between capital and operating costs to system size, i.e. smaller systems cost more per tonne of fly ash processed than large system sizes. The figures allow for rapid estimation of CAPEX and OPEX for a given system capacity. If a 10 tonne/batch system size is targeted, the corresponding capital expenditure estimate is approximately \$4.1MM ($10 \times \$410,00$). If a simple amortization of capital at 4.5% interest for 10 years is used, the estimated capital cost for a 10 tonne/ day system is \$88/tonne of fly ash. Estimating the operating costs proceeds in the same manner, except there are two estimated values that can be used; one with zeolite revenues and one without zeolite revenues (although the revenue should not be technically included in operating costs, it allowed for two graphs to be used to determine a total cost estimate). Estimated zeolite revenue per tonne of fly ash processed was \$495 to \$500. Using this value, the estimated net operating cost with zeolite product revenues is \$450/tonne whereas without zeolite revenue the operating cost estimate is \$1,090/tonne. Therefore, the production of zeolites drops the net operating cost by 59%.

Although operating cost savings due to zeolite production is significant, the capital + operating cost for a 10 tonne system is still more expensive than the total dollar value of REEs present in the fly ash material. Specifically, the estimated cost per 1-tonne of fly ash treated (with a 10 tonne per batch system) is approximately \$540 while the estimated value of REEs in the fly ash is \$18-\$20/tonne. This is an excessive difference showing that the proposed process is not economically feasible strictly on the basis of REE revenue compared to extraction costs.

Further costing analysis showed that reducing chemical costs could dramatically decrease overall operating costs. If chemical costs could be decreased by 50%, then the overall operating costs would decrease by roughly \$460/tonne. Therefore, decreasing chemical costs by 50% would result in a total production cost of \$90/tonne of fly ash. Obviously, there are many factors that could change this conclusion, but it is interesting exercise to show that system costs could at the very least, begin to approach reasonable values.

Although the current proposed system does not produce sufficient quantities of REEs to offset operational and capital costs, additional factors including US strategic concerns, commercial demands, and defense department requirements must be factored. It is important to consider future implications of this technology that present a context for future impacts that cannot be ignored as one evaluates its significance.

The strategic implications of a technology capable of supplying a future need of a material, such as strategic REEs, with limited capital investment as compared to any ground -up technology alternative may be attractive. In this case of the current proposed system, operating cost penalties for example, should be weighed against relative capital and time investments from any other REE production alternative. New rare earth mines within the US for example, will be burdened with a long and complicated regulatory path including environmental permitting. They will also require massive initial capital investments likely to exceed \$billions.

The extraction technology for REEs found in this report can be implemented within a year at a fraction of the cost without new mine development or extensive permitting. Further, the raw material is well known at the available quantities. The resulting process can be designed within a short lifetime supported by known quantities of starting material (fly ash) at a modest cost. As a developing process, the potential for future improvements and cost savings is significant. This is particularly pertinent when the starting material, the fly ash, is consistent in composition, availability and physical form.

Section C

Task 2: Sampling and Characterization of Proposed Feedstocks

Task 2 activities focused on identification of suitable fly ash sources, obtainment of sample material, analysis and characterization of the different fly ash sources, selection of one fly ash material for the process development phase of the project, and resource estimation. Specific sub-tasks included:

- Sampling and Characterization Plan
- source material identification
- source material acquisition
- source material characterization
- Sampling and Characterization Report

The following sections summarize results obtained during Task 2 efforts.

C.1 Identification, Sampling, and Selection of Source Material

C.1.1 Identification of Source Materials

This project focused on the use of coal generated fly-ash as the source of REE feed-stock. Fly-ash typically consists of fine particulates (spherical – 0.5 μm to 300 μm) composed of mainly amorphous (some crystalline) silicon dioxide, aluminum oxide, and calcium oxide with trace amounts of other metals and rare earth elements (REEs). Pre-combustion coal sources are primarily bituminous leading to the production of primarily Class F fly ash (<20% CaO). Fly-ash was selected for this project due to the large amounts produced annually in the US (>55 million tonnes/yr) and the fact that it is a relatively easily accessible source material.

Initial efforts focused on identifying fly-ash sources that had high REE content exceeding 300 ppm along with high critical to excess REE ratios and high critical REE percentages. Candidate sources were identified by analyzing information provided on NETL's website¹. A thorough evaluation of over 700 potential fly ash sources from the website was completed with the eventual selection of six (6) targeted fly ash sources that had critical REE concentrations between 400-535 ppm and outlook ratios between 1.456 and 1.535. Geographically, the sources of coal that generated the selected fly-ash materials came from two regions; namely the Interior Region and Appalachian region. Within these regions, two distinct coal basins provided coal to the fly-ash generating facilities including the Illinois Basin and the Central Appalachian Basin. Figure C.1 illustrates the location of these basins within the United States.

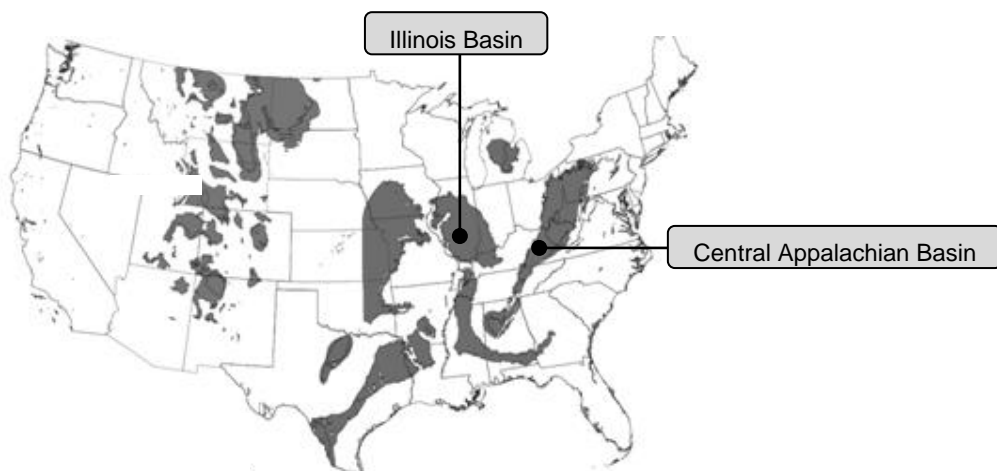


Figure C.1

Location of coal basins that provided coal to the power generating facilities that generated the fly-ash material for this project.

¹ DOE website: collected-samples-spreadsheet-v051515TLEdit7-16-15.xlsx

The locations of the selected fly-ash materials utilizing the coal from the basins shown in Figure C.1 came from power generating facilities located in the State of Kentucky. Figure C.2 shows the general locations of each fly-ash source.

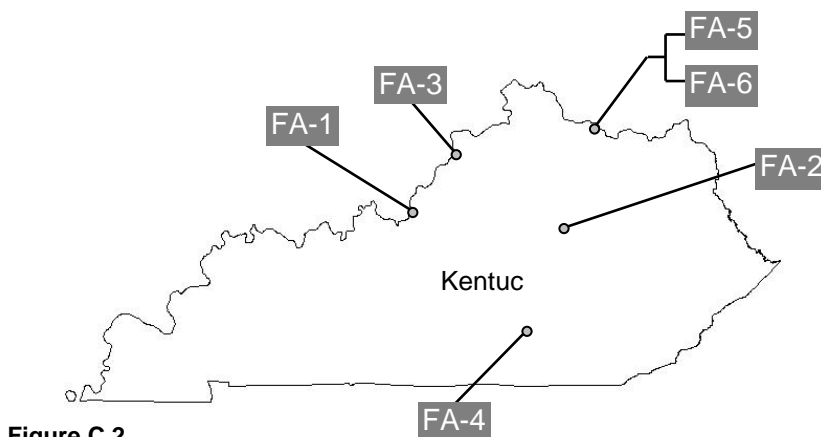


Figure C.2
Actual fly-ash generation locations for each fly-ash material sampled

Not surprisingly, fly-ash sources (FA-2, FA-4, FA-5, and FA-6) from the power generating facilities near the Central Appalachian Basin were produced from coal utilized from this basin. Conversely, power facilities that generated fly-ash sources FA-1 and FA-3 used coal primarily from the Illinois Basin. The Illinois Basin and the Central Appalachian Basin primarily consist of bituminous, high-sulfur coal seams. Differences in the overburden geology, rock chemistry, and weathering characteristics give rise to differences in REE content in the underlying coal leading ultimately to differences in REE content with fly-ash. Detailed location information and estimated reserves for each fly-ash source is summarized in Table C.1

Table C.1 General Data on Fly Ash Sources and Coal Information

Internal Sample ID	Fly-Ash Source	Fly-Ash Class	Primary Coal Basin	Estimated Recoverable Reserves ^A (bn tons)
FA-1	Mill Creek 4/11/2016	F	Illinois	67.2
FA-2	Dale 4/13/2016	F	Central Appalachian	50.1
FA-3	Trimble 4/12/2016	F	Illinois	67.2
FA-4	Cooper 4/15/2016	F/C	Central Appalachian	50.1
FA-5	Spurlock 4/14/2016	F	Central Appalachian	50.1
FA-6	Spurlock 4/14/2016	C	Central Appalachian	50.1

A – Milici, R.C., Flores, R.M., and Stricker, G.D., "Coal Reserves and Peak Coal Production in The United States", *International Journal of Coal Geology* 113 (2013) 109-115.

C.1.2 Sampling of Targeted Source Materials

Obtaining a representative fly-ash sample from each targeted source location (see Table C.1) was approached by balancing both probabilistic and judgmental sampling approaches. From a probabilistic perspective, multiple fractional samples at multiple locations would need to be acquired and then combined to form a final,

representative composite sample. There is no debate that probabilistic sampling gives a higher confidence level in representing the overall population (fly-ash material) over a judgmental sampling approach. Therefore, probabilistic sampling is the preferred approach if all aspects of sampling are equal between both approaches. However, there are difficulties in probabilistic onsite sampling (either from real-time fly-ash generation or from fly-ash storage) when practical issues such as required sample sizes, safety, transport, and financial constraints are factored.

A detailed discussion on the determination of the required sample size to obtain a representative sample based upon a standard error of 5% is summarized in Appendix A. In summary, the minimum required sample size based upon fly-ash particle size distribution, assumed REE dispersion within fly ash, compositional heterogeneity, and shape factor was estimated at approximately 160g for fly-ash lot sizes greater than 18-kg. This calculation assumes spatial and compositional heterogeneity throughout the entire lot sample. This is a very difficult to prove without many samples taken from multiple locations at different sampling times over time periods exceeding 1-month. This type of sampling program exceeded the scope of this project, so a practical hybrid approach was undertaken to merge both probabilistic and judgmental sampling into one single methodology. The methodology used was simply to sample fly-ash materials at each source location (see Table 2.1) at multiple locations (if possible) using a minimum sample volume of 20-kg. In some cases, a slip-stream of fly ash material was collected over time from a bulk flow of fly-ash. Since the intent was to collect over 15-kg of fly ash material, the minimum sample size was met assuming once again that the fly-ash material had consistent compositional and spatial heterogeneity.

Fly-ash samples from the six locations were immediately shipped to Tusaar's laboratory within plastic 5-gallon buckets. Table C.2 summarizes details of the as received fly-ash from each material source.

Table C.2 Fly-Ash Sampling Information

Sample	Power Plant Location	Container	Sample Location	Moist/Dry	Material Mass (kg)	Class C/F
FA-1	Mill Creek	5-gallon Poly Bucket	Silo A	Dry	25	F
FA-2	Dale		?	Moist	17.7	F
FA-3	Trimble		Precipitator	Dry	27.4	F
FA-4	Cooper		Truck	Moist	15	F/C
FA-5	Spurlock		Silo Units 1&2	Dry	22.1	F
FA-6			Silo Unit 3	Moist	8.2	C

The samples were inventoried upon arrival and stored in a designated area to avoid possible contamination and provide a secure area for archived storage. Fractional sampling of the received fly-ash materials was initiated in a two-step approach as illustrated in Figure A.3 in Appendix A. As Figure A.3 illustrates, the first step in acquiring a representative fractional sample from each bulk sample was the homogenization of the sample by rotating the 5-gallon bucket back-and-forth while periodically flipping the container. This action was conducted for a minimum of 10 minutes and was necessary since segregation of the fly-ash can occur during transport by a variety of mechanisms including movement of particles by vibration, rolling on the surface, and movement due to size and density differences.

The second-step was the actual fractional sampling of each 5-gallon bucket. A 16-cm³ sample thief was used to acquire samples at 8 different locations within each fly-ash bulk sample. The locations and depth of these

sampling locations are provided in Figure A.3. The spatial pattern and depth was selected to provide an optimal composite sample. The effective sampling volume (the volume each fractional sample represented) was assumed to be an ellipsoid within 1.25-cm around the sampling thief, resulting in an effective volume estimate of approximately of 50-cm³. Based upon 8 samples taken, this provided a total effective sampling volume of 2.3%. The actual total volume of all fractional samples for each fly-ash source was approximately 128-cm³. Using a measured bulk density of 1.58 g/cm³, the average composite sample mass from each fly-ash sample bucket was 200-g. This mass value is higher than the 160-g minimum calculated in Appendix A to obtain a representative sample with a 5% standard error. Therefore, the composite samples were assumed to be representative of the entire sample volume for each fly-ash source. Exactly 5-g of each composite sample from individual fly-ash sources were sent to external laboratory for lithium borate fusion analysis. The remaining composite samples were archived and stored for additional testing.

C.1.3 Characterization of Targeted Source Materials

The first step in the characterization of each fly-ash material was the pre-screening of samples based upon the total available REE content. Total REE content was determined by performing fusion analysis (lithium borate) on a 5-g sub-sample of the composite samples from each fly-ash source followed by REE quantification using ICP-MS. As a quality control check, REE quantification was conducted by an outside laboratory and compared to results obtained from in-house analysis. REE concentrations obtained from both analyses were within 1-2% of each other and were considered to be accurate REE quantification values. These concentrations from Li₂B₄O₇ fusion + ICP-MS analysis were used as the total available REE concentration within each fly-ash material for determination of percent recoveries and process efficiencies. Figures B.3 summarizes measured TREE+Y, Critical REE, and Excessive REE concentrations from each fly ash sample while Figure B.4 summarizes the calculated value of TREE+Y for each fly ash source in \$/tonne².

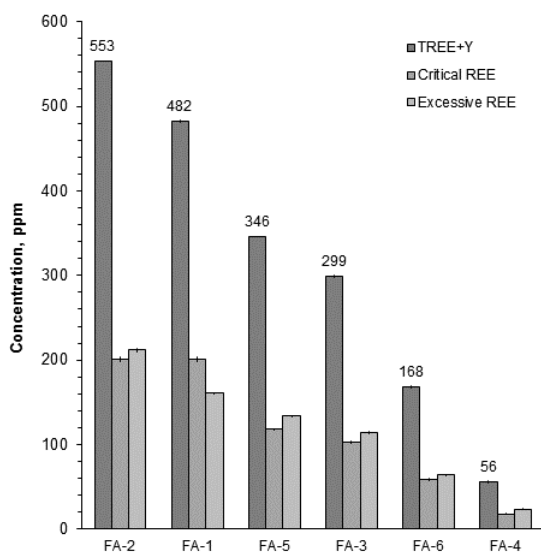


Figure C.3

REE characterization profiles for each fly ash material tested.

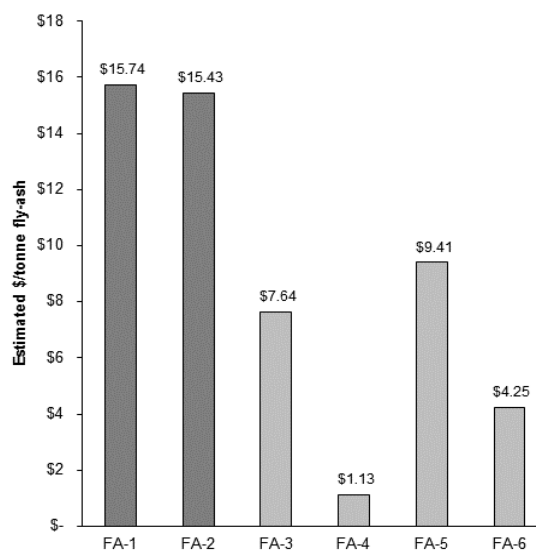


Figure C.4

Estimated value(US\$) of TREE+Y per tonne of fly-ash for each sample tested (see Table E.3 for estimated \$/kg for each REO)

Quantification results of the targeted fly-ash sources indicated that measured TREE+Y content had significant variability (55 – 550ppm) with four of the six samples having TREE+Y concentrations less-than 400 ppb (the lower end of the documented concentration range used to select samples). Only fly ash sample FA-1 had a TREE+Y concentration exceeding 450-ppm and an outlook ratio greater than 1.2. Further extension of the comparison by examining the estimated value of REOs in \$/tonne from each fly-ash lowered the number of

² Based upon 2017 prices

potential source materials to two, namely FA-1 and FA-2. These two fly-ash sources were extensively compared by investigating fly-ash availability, on-site sampling constraints, and long-term sourcing. Results are summarized in Table C.3.

Table C.3 Chemical Assay and Other Factored Differences between Sample FA-1 and FA-2

Chemical Assay (ppm and %)	FA-1	FA-2
TREE+Y	482	553
TREE	387	467
Critical REE	201	201
Excessive REE	161	212
La+Ce (% of TREE+Y)	44%	51%
\$.REE/tonne fly-ash ^A	\$15.74	\$15.43
Outlook Ratio	1.25	0.95
Other Factors		
Fly Ash Availability	yes	limited
In-place Sampling ³	yes	no
Long-Term Sourcing	yes	limited
Historical Information	yes	no

A – Assumed \$/kg-REO = La \$2, Ce \$2, Pr \$52, Nd \$42, Sm \$7, Eu \$250, Gd \$32, Tb \$400, Dy \$230, Ho \$55, Er \$34, Tm \$60, Yb \$62, Lu \$1258 (data from mineralprices.com)

C.1.4 Selection of Source Material

Based on the information in Table 3.3, both FA-1 and FA-2 have similar REE compositional make-ups. However, the fact that FA-1 is readily available and the generating station were FA-2 was collected is no longer in operation with limited access to fly-ash stock-piles, FA-1 from Louisville Gas & Electric’s Mill Creek power generation station in Louisville, KY was chosen as the fly-ash source for the project.

C.2 Characterization of Selected Fly-Ash

The selected fly ash (FA-1) was subjected to a variety of physical and chemical characterization tests to provide a baseline reference for project experiments and to determine detailed physical and chemical characteristics that assisted in the selection of pretreatment and acid digestion strategies investigated during the project. As discussed in Section E.1.3, lithium borate fusion followed by ICP-MS analysis was used to determine the total REE content of the selected fly ash. Additional characterization testing consisted of the following analytical assessments:

- Optical Evaluation
- QEMSCAN
- XRD
- Sieve Size Fractionation
- SEM
- PSA (particle size analysis)
- Chemical Assay

The following sections summarize the analysis results conducted on the fly-ash material used throughout the entire project.

³ Daily samples are pulled from the ash as the ash is transferred to trucks for transport to concrete companies.
 Final Project Report – Section C (Award No. DE-FE-0027155)
 Economical and Environmentally Benign Extraction of Rare Earth Elements (REES) from Coal & Coal Byproducts
 Tusaar Corp. – March 2018

C.2.1 Optical Evaluation

Samples of fly ash material were analyzed under an optical microscope (5X – 100X) to investigate differences in observable physical characteristics between fly-ash particles. Fly-ash precursors in the flu gas from a coal fired power facility solidify very rapidly producing particulates that are generally spherical in shape ranging in size from 0.5 μm to 300 μm . Rapid cooling does not provide enough time for crystalline formation, thereby leading to a material that is mainly amorphous. Since the majority of fly-ash contains significant amounts of silicon dioxide (SiO_2), the resulting material consists of small glass spherules. Figures C.5 and C.6 are images of fly-ash material obtained with an optical microscope at 40X.

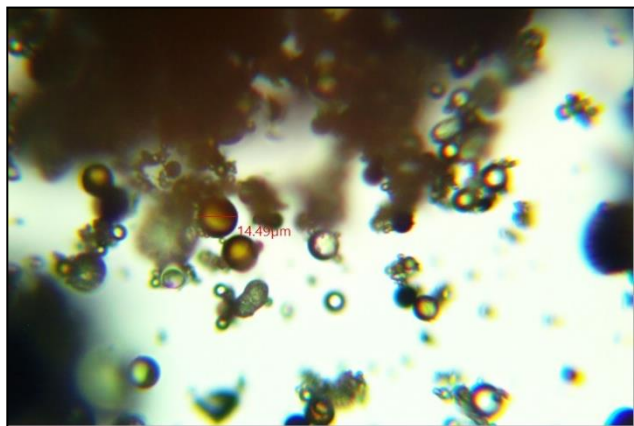


Figure C.5

40X image of untreated fly ash material showing diversity of particle sizes, color, and morphology.

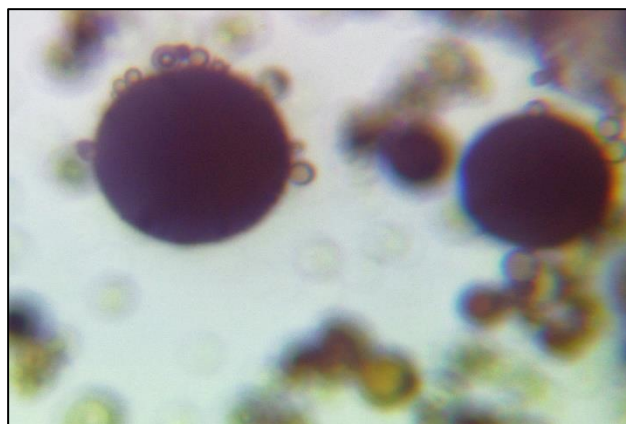


Figure C.6

40X image showing small fly-ash particles adhering to larger particles due to strong electrostatic interaction.

Images C.5 and C.6 show the predominance of glass spherules in the material composition. Figure C.5 clearly shows the diversity of particle sizes and color. The images clearly show that the majority of fly ash particles are spherical with particles as large as 15-20 μm and as small as 1 μm . Other images also show that the spherules can be hollow, with or without particles inside larger spherules, or solid. Figure C.6 illustrates the adherence of smaller fly ash particles (<3 μm) to larger particles due to the strong electrostatic interaction of the small particles. This is an important result since the material must be properly dispersed during chemical treatment. Also, the small size of the spherules indicates that grinding may not significantly alter the overall physical characteristics of the raw fly ash material prior to REE extraction.

C.2.2 QEMSCAN

QEMSCAN (Quantitative Evaluation of Minerals by SCANNing electron microscopy) is a method to determine the types of mineral phases present in a sample as well as provide quantitative mineral composition estimates. QEMSCAN was performed on a fly ash sample impregnated into a resin block. The analysis was able to generate an overall map of the elemental composition and mineral phases present in the fly ash sample. Figure C.7 is an image of QEMSCAN analysis on the selected fly ash showing the spherical nature of the fly ash particles along with a few particles with identified morphological phases. Table C.4 summarizes the semi-quantitative mineralogy estimates based upon the QEMSCAN analysis.

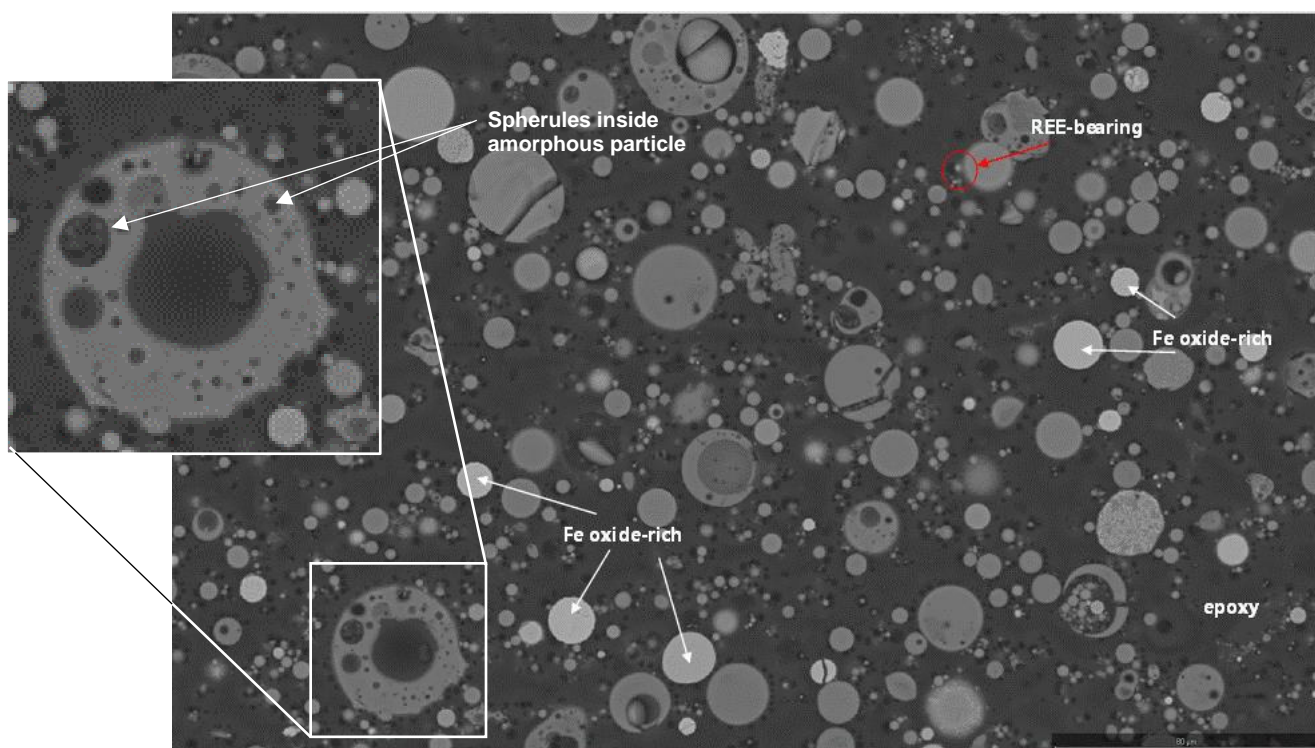


Figure C.7

Back-scatter electron brightness (BSE) image of fly ash material showing cross sections of different particle sizes and morphology of fly ash sample material.

Table C.4 Semi-quantitative mineralogy of fly ash based upon 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

Although a detailed evaluation of specific elemental concentrations was not targeted, the main elements identified by EDS within the siliceous glass component of the fly ash are summarized in Table C.4. Images and data show that the fly ash material has a heterogeneous composition both chemically and spatially with main crystalline phases identified as aluminum oxides, iron oxides, and possibly quartz. Not surprisingly, the main

chemical components of the selected fly ash material include silicon, aluminum, iron, potassium, and calcium. Close-up images of iron oxide and REE inclusions on/in glassy spherules are presented in Figure C.8 and Figure C.9 respectively.

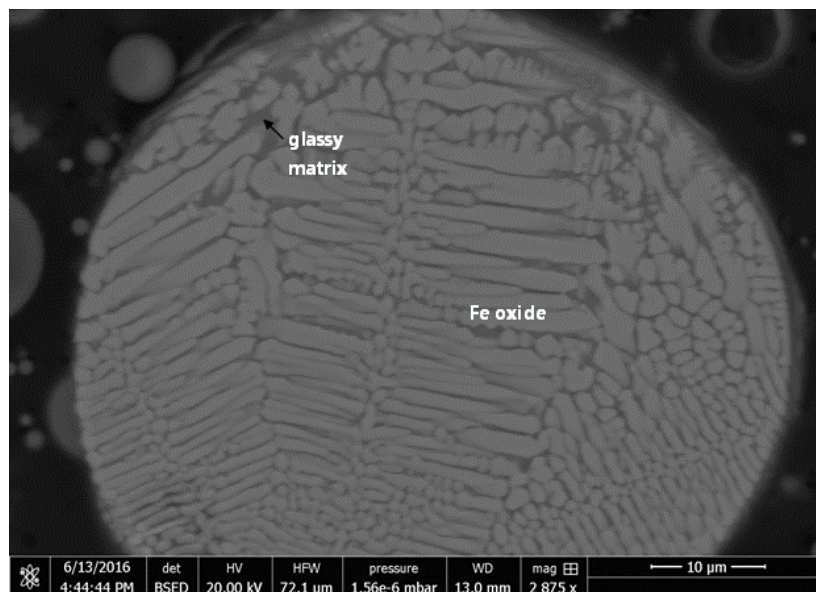


Figure C.8
Cross-section image of an iron-oxide bearing fly ash particle showing dendritic crystals in a glassy matrix.

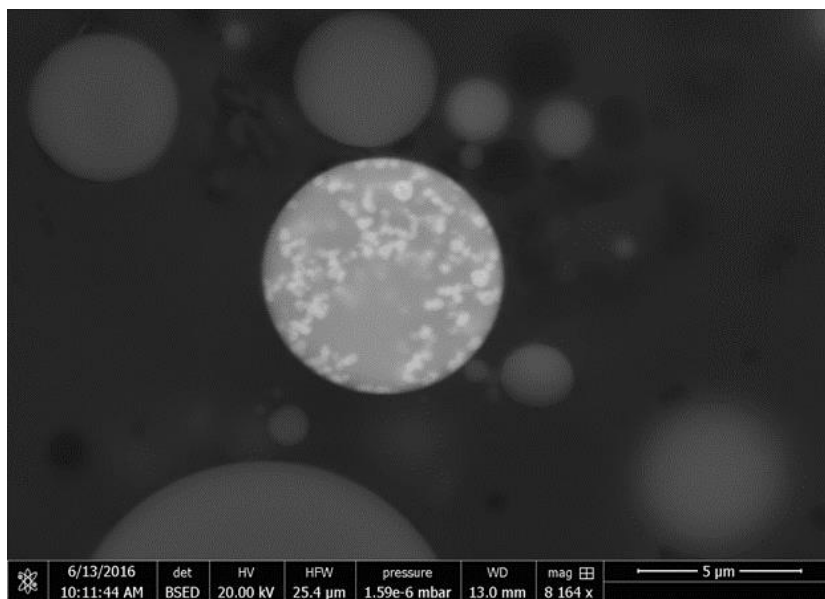


Figure C.9
Image of a small siliceous glass spherule with inclusions of rare earth oxides (REOs).

Overall, a limited number of REE-bearing phases were seen during QEMSCAN analysis which is not surprising considering the low concentration of REEs in the fly ash. Based upon observations, it is speculated that REEs occur as lanthanum-cerium-praseodymium-neodymium-thorium oxides or phosphates within the fly ash matrix. As an example, Figure C.9 shows very fine-grained inclusions (200 to 600 nanometers) of a lanthanum–cerium–praseodymium–neodymium–thorium oxide in a glassy spherule matrix.

C.2.3 X-ray Diffraction (XRD)

XRD is a method to determine the crystalline structure, if any, present in a material. XRD was used to verify the assumption that fly-ash materials have a large fraction of amorphous material. A fly ash sample was micronized in isopropyl alcohol, spiked with corundum (to aid in amorphous quantification), and analyzed by X-Ray Diffraction (XRD). Results of the XRD analysis are summarized in Figure C.10.

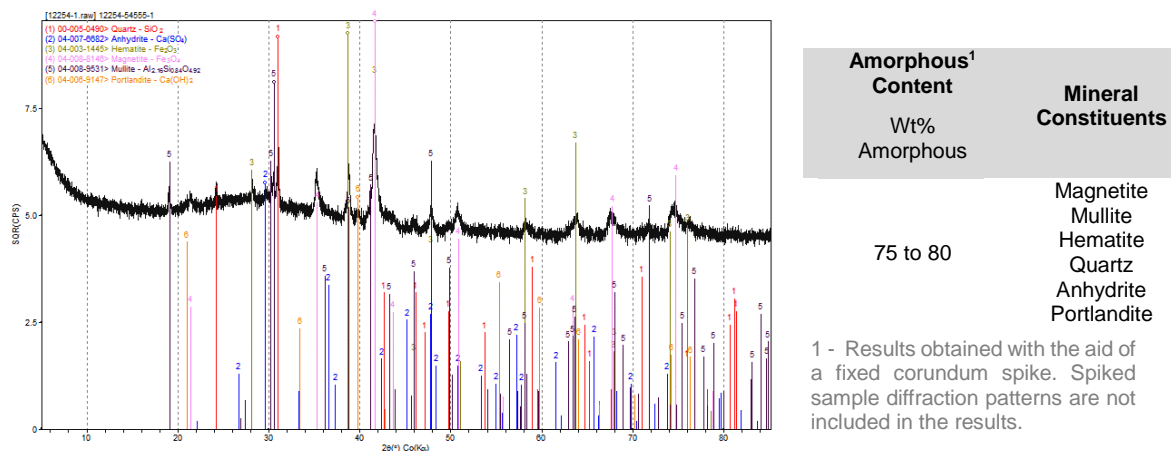


Figure C.10

XRD analysis results on fly ash material showing that the fly-ash is predominantly amorphous in structure.

XRD analysis shows that the fly ash material obtained for this project is mostly amorphous with quartz, magnetite, and hematite being the major identified phases.

C.2.4 Sieve Size Fractionation

The possibility that REEs are preferentially found in specific particle sizes was approached by conducting an experiment to separate the fly-ash by size and then determine the REE content within each fraction. In this section, results of the fly-ash fractionation are presented. A 150-g fly ash sample was sieved through a series of screens ranging from 20 to 325 mesh. The result of sieving analysis is summarized in Figure C.11.

It was found that the fly ash could be separated into 3 main fractions; +200 (>74μm), -200/+325 (74μm to 44μm), and -325 mesh (<44μm). The wt% of each fraction in these three size ranges was ~5, ~30, ~65% respectively. The results from sieving produced only 65% of the particles smaller than 44 μm. All results suggest that most fly ash particles are very small (<100 μm) and may tend to agglomerate which can affect the effectiveness of physical and chemical treatment methods. This speculation was verified by analysis of the three different size fractions which did not yield any alteration of the REE distribution.

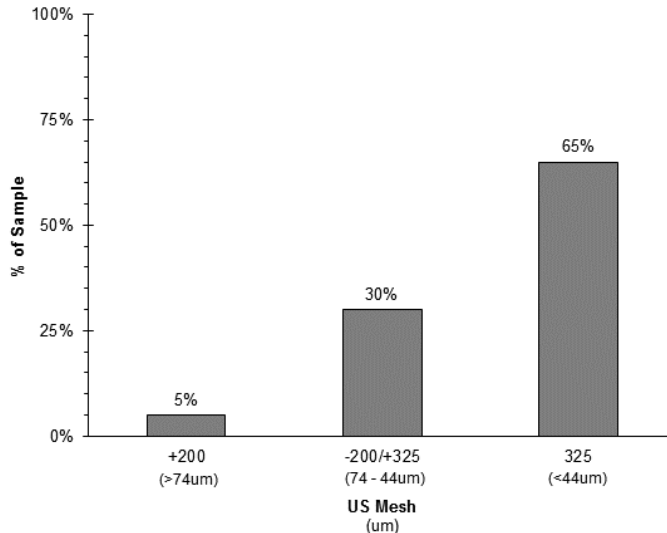


Figure C.11

Fly ash particle size based upon sieve analysis.

C.2.5 Scanning Electron Microscopy

Scanning electron microscopy (SEM) was used to obtain detailed images of fly ash particle to evaluate particle morphology and overall sample heterogeneity. Figure B.12 is a SEM image of raw, as received fly ash material.

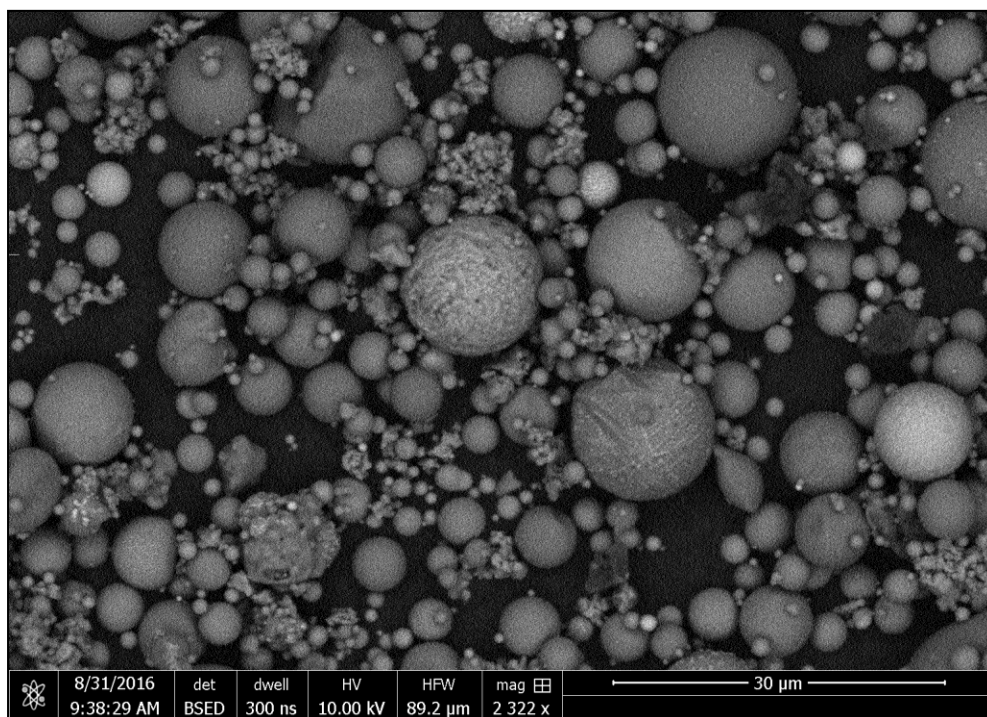


Figure C.12
SEM image of untreated fly ash material showing diversity of particle sizes and morphology.

It is clear from the image that the starting material is comprised of spherical particles with varied sizes and physical morphologies. The fly ash sample consists of spheres with different physical characteristics including; hollow spheres (cenospheres), solid spherical particles filled with smaller particles (plerospheres), and some spheroid particles with irregular shapes.

C.2.6 Particle Size Analysis (PSA)

The fly ash selected for this project was analyzed by sieve fractionation and by a laser diffraction particle size analyzer. The combined results are graphically summarized in Figure C.13.

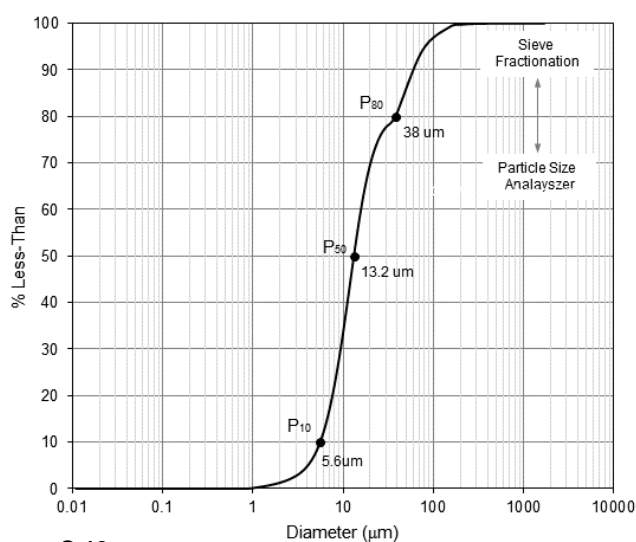


Figure C.13
Particle size distribution of selected fly ash. (>38μm determined by sieve fractionation, < 38 μm determined by laser diffraction analyzer)

The particle size distribution of the fly ash showed a P₈₀ of 38 µm with a minimum of ~0.8 µm and a maximum of ~425µm. Based upon results, approximately 10% of the fly ash was smaller than 6 µm with a P₅₀ of 13.2 µm.

C.2.7 Chemical Assay

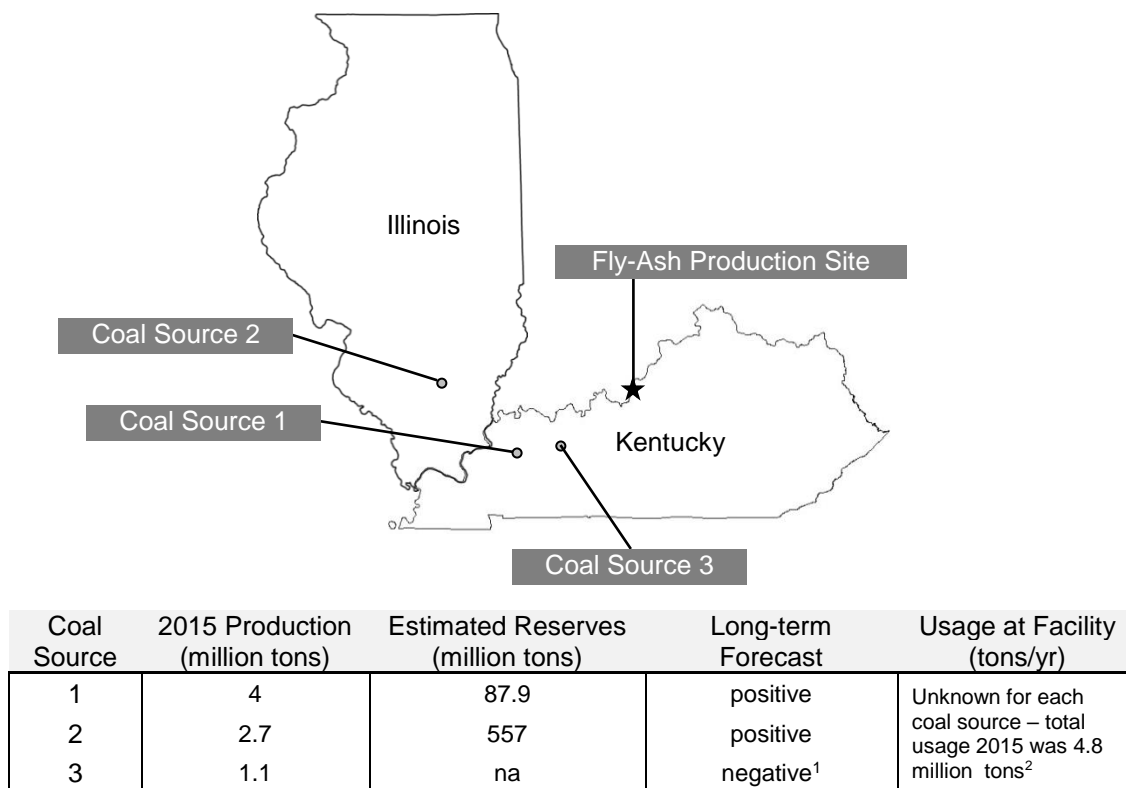
Lithium borate (Li₂B₄O₇) fusion analysis was completed to determine total REE content and the concentration of 48 other elements within the fly ash material. Fusion analysis was completed on a 5-g sub-sample followed by ion quantification using ICP-MS. A detailed 61 metal chemical assay of the selected fly ash was completed. Iron had the highest wt% in the fly ash sample at approximately 18% while silica was measured at 14 to 15% of the total mass of constituents measured. Aluminum was also significant with a 10 to 11 wt% concentration. The most predominant element on fly ash is oxygen which is not shown in the table.

C.3 Material Resource Estimate

Estimating the fly ash resource quantity and dollar value of REEs from the selected fly-ash (see Section C.1.4) required determination of the amount of coal utilized the basin source that produced the fly-ash material, i.e. the material resource estimate must include both fly-ash and coal information that can be consolidated into one material resource estimate. The following sections summarize the size of the estimated size of actual in-ground coal reserves, estimated fly-ash production quantities, and REE reserves based upon the extraction efficiency of the developed extraction process (see Section E).

C.3.1 Estimation of Coal Reserves

The first step completed to estimate overall REE resource reserved was to estimate the size of the coal reserves that supply coal to the Mill Creek power generation facility. The coal sources that were utilized by the power generating facility are summarized in Figure C.14



1 - possible closure in Jan. 2017

2 - coal mixed from each source to maximize BTU generation, coal stored on-site with varied blending throughout the year.

Figure C.14

Coal source locations for the power generation facility that produced the selected fly-ash for this project used to estimate coal reserves and resource estimates.

All of the coal sources illustrated in Figure C.14 are from the Illinois Coal Basin. The coal from this basin is bituminous with high sulfur content. The estimated total recoverable coal reserve in the Illinois Basin is 67.2 bn tons, while the total estimated coal reserve at the mines servicing the Mill Creek power generating facility is approximately 645 million tons (excluding source 3) representing roughly 1% of the total available coal in the Illinois Basin.

Given the estimated yearly usage of 4.8 million tons of coal at the Mill Creek power generating facility, estimated total coal reserve at the source mines would last nearly 135 years. This estimate is based on the assumption that the coal sources listed will only provide coal to the discussed power generation facility; the power generation facility will not switch coal sources, and that the REE concentration and actual distribution throughout the coal beds at the sources (mines) listed will be relatively uniform. Given these constraints and limitations, it must be noted that any estimate as to the resource amount and timeline is obviously not absolute. However, even with these limitations, the total material resource estimate in the following sections was based off the assumption that all of the coal in the Illinois Basin will converted into fly ash and it has the same chemical characteristics measured in the fly ash tested.

C.3.2 Estimation of Fly-Ash “Reserves”

Concentrations of individual rare earth elements and TREE+Y in the selected fly-ash source are summarized in Table C.5. These values were used along with an annual fly ash production rate of 920,000 tonnes at the Mill Creek power generation site to calculate annual mass and revenue generation rates. Illinois Basin reserve estimates were used to determine total material resource estimates.

C.3.3 Material Resource Summary

A main goal of project activities was to provide a material resource estimate that could be used to judge the applicability of the selected material as a long-term source for REE materials. In this project, the material is fly-ash produced from a power generating facility (Mill Creek, Louisville, KY) that using specific sources (Illinois Basin) of coal for operations. Estimation of the “material resource” involved the following stepwise progression summarized in Figure C.15.

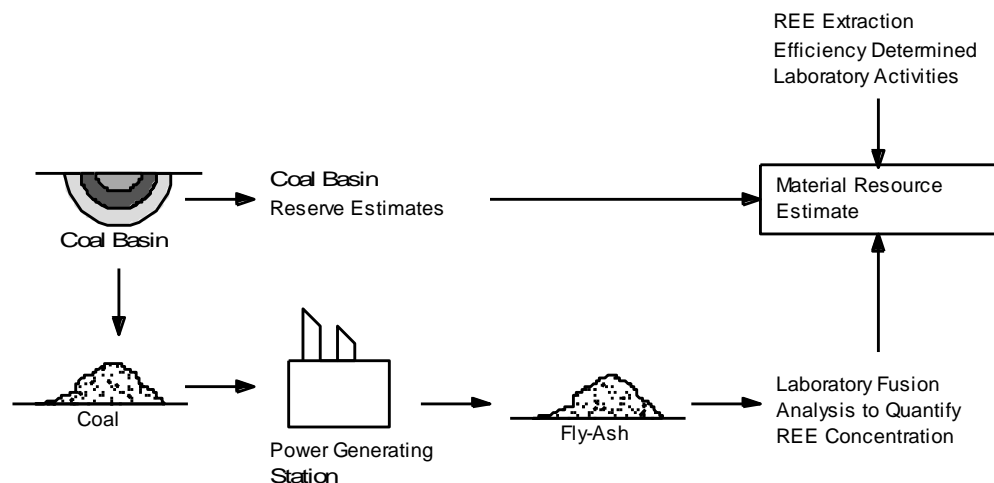


Figure C.16
Approach used to calculate Material Resource Estimate

Table C.5 Total Resource Estimates of Individual REEs and TREE+Y

REE	Concentration in Fly-Ash (g/t)	Production ^A (t/yr)	Est. REO Price ^B (\$/kg)	REE Value (\$MM/yr)	Total REE Resource Value within Illinois Basin ^C	
					Mass Basis ^C (kt)	Value (\$MM)
Light REEs						
La	79.7	39.5	1.4	0.051	55.2	77.2
Ce	198.1	98	1.4	0.127	137.1	192
Pr	20.5	10	36.4	0.342	14.2	516.5
Nd	80.2	40	29.4	1.080	55.5	1632
Sm	18.2	9	1.4	0.012	12.6	17.6
Sub-total	396.7	196.5		1.61	274.6 kt	≈ \$2,435MM
Heavy REEs						
Eu	3.8	2.0	105	0.183	2.6	276.2
Gd	22.7	11	22.4	0.233	15.7	351.9
Tb	3	1.5	280	0.385	2.1	581.4
Dy	23	11.5	161	1.695	15.9	2563.1
Ho	3.7	2.0	38.5	0.065	2.6	98.6
Er	12.9	6.5	23.8	0.141	8.9	212.5
Tm	1.3	1	42	0.025	0.9	37.8
Yb	11.6	6	43.4	0.231	8.0	348.5
Lu	1.1	0.5	880	0.443	0.8	670
Sub-total	83.1	74.1		3.700	57.5 kt	≈ \$5,140MM
Other						
Y	121.1	60	4.2	0.233	83.8	352.1
	(g/t)	(t/yr)		(\$MM/yr)	(kt)	(approx. \$MM)
TREE	480	427		5.01	332	7,575
TREE+Y	601	535		5.24	416	7,927
Excessive REE	216	192		0.89	149	1,347
Critical REE	244	217		3.72	169	5,617

A – Based on a coal consumption rate of 9.8 million short tons per year with an average fly-ash to coal ratio of 0.103 (American Coal Ash Association 2013 Coal Combustion Product Production & Use Survey Report - survey results 516.2 million tonnes of coal consumed per year produced 53.4 million tons of fly-ash). Values rounded to nearest 0.5 tonne/yr.

B – Using September 2015 spot prices for each REO with a 30% discount of each price due to mixed-metal composition

C – Based upon total Estimated Resource Reserves of 6.72 bn tonnes of coal converted into 0.69 bn tonnes of fly-ash

Material resource estimates using the approach outlined in Figure C.16 with an average REE recovery rate of 42% (discussed in Sections D and E) and the fly-ash production estimates in Table C.5 suggests that the adjusted maximum TREE+Y material source and total potential revenue (based on current prices) would be approximately 175,000 tonnes and \$3.33 billion. A breakdown of these resource estimates into critical REEs/excessive REEs for both mass and potential revenue is provided in Figure C.16.

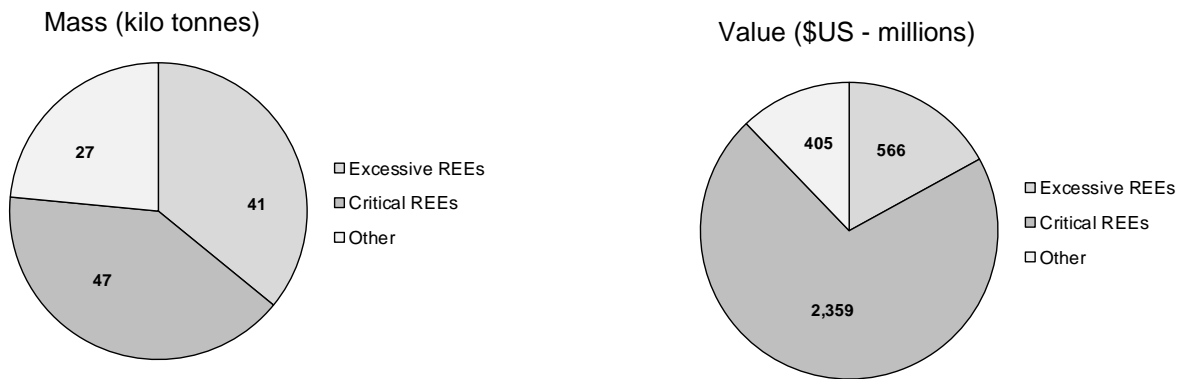


Figure C.16
Total adjusted REE resource estimates for total mass and estimated value (based upon current REO prices).

It must be emphasized that these estimates are based upon multiple assumptions, one being that the concentration of REEs in the source fly-ash is consistent. At this time, there is no way of confirming this assumption. Additional testing would be required to sample the basins and determine the distribution and average REE concentration in the coal source for the facility. This is a very difficult task. The best alternative was to assume that RE E concentration will fluctuate, but on average will be near the calculated resource estimate.

D.1 Evaluation of Pretreatment Strategies

It has been observed by numerous investigators that typical hydrometallurgical treatment of fly ash materials only produces TREE recovery rates of approximately 20-30%. A targeted effort was initiated to develop a process methodology including various pretreatment techniques followed by subsequent acid digestion optimization to enhance REE recovery rates. The validity of each tested technique was based primarily on the percentage of REEs extracted after each pre-treatment followed by standardized acid digestion utilizing 2M HCl at reflux temperature for 4 hours and a 10% solids loading. Utilizing this approach allowed for a direct comparison between each pretreatment technique. Pretreatment techniques investigated included (both chemical and physical):

- Physical Pretreatment
 - Thermal shock
 - Grinding
 - Magnetic Separation
- Chemical Pretreatment
 - Type of Caustic Solution
 - Concentration of Caustic Solution
 - Solid wt% Slurry
 - Temperature
 - Reaction Time

A brief summary for each pretreatment technique along with major results are given in the following sections.

D.1.1 Physical Pretreatment – Thermal Shock

Thermal shock pretreatment simply consisted of heating a small amount of fly ash material (5g) to two different temperatures of 200°C and 400°C in a muffle furnace for 30 to 60 minutes to ensure uniform temperatures throughout the sample. Samples were removed from the furnace and immediately poured into 20°C water. Subsequent standard acid digestion at 2M HCL at reflux for four hours produced an 18% TREEs recovery. The relative amount of TREEs extracted from non-pretreated fly ash samples using the standard digestion procedure range between 18-22%. Comparing this range of extraction efficiencies to the obtained recovery of 18%, it is clear that the thermal shocking method of the fly ash did not enhance REE recovery. This is most likely due to the fact that fly ash characterization results (Section C) showed the particles to be highly spherical and relatively small resulting in very strong particles that are resistant to thermal/mechanical stresses.

D.1.2 Physical Pretreatment – Grinding

A ground sample of fly ash was produced by placing approximately 5g in a mortar-and-pestle with subsequent grinding by hand. Follow-on standard acid digestion using 2M HCL at reflux for 4 hours of the treated solid resulted in a 17% extraction efficiency of REEs. Compared to the 18% REE extraction efficiency from standard acid digestion without pretreatment, physically grinding the fly ash did improve REE extraction. As was a similar situation during thermal treatment, fly ash particles are highly spherical and relatively small resulting in very strong particles that are resistant to mechanical stresses. It may be possible that with a ball mill, particles can be reduced in size and broken apart to enhance REE extraction efficiency. However, a reduction in particle sizes increases filtration time of the pretreated and acid digested solids thereby reducing daily throughput.

D.1.3 Physical Pretreatment – Magnetic Separation

Separation of the magnetic (mag) fraction from the non-magnetic (non-mag) fraction within the fly-ash material was accomplished by attaching neodymium magnets to the outside of an Erlenmeyer flask with subsequent mixing of a fly ash slurry followed by removal of the magnetic fraction. Mass analysis shows that approximately 56% of the fly ash material was magnetic while the remaining 44% was not magnetic. These fractions were then

subjected to a standardized acid digestion using 2M HCl at reflux temperature for 4 hours with a solids concentration of 10%. Results of ICP-MS analysis of the filtered solutions are summarized in Figure D.1.

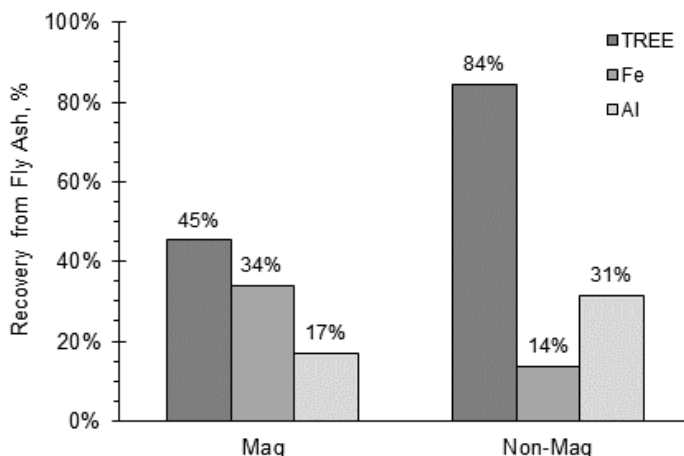


Figure D.1

Total rare earth element (TREE), Fe, and Al recovery from magnetic (mag) and non-magnetic (non-mag) fractions after standardized acid digestion (2 M, 10wt% solids, reflux temp., 4 hours).

Figure D.1 shows that TREE recovery was almost 2X higher in the non-mag fraction compared to the mag fraction. Not surprisingly, the amount of iron extracted from the mag fraction was significantly higher than that witnessed in the non-mag fraction, 34% to 14% respectively. Conversely, the amount of aluminum extracted was higher in the non-mag fraction compared to the mag fraction, 31% to 17% respectively. Analysis of the data from the viewpoint of the mass ratio of iron and aluminum to TREE indicated that the ratio of Fe to TREE in the magnetic fraction is approximately 4.5X higher than in the non-magnetic fraction while the Al to TREE ratio in both fractions is the same. Although this observed difference in the Fe/TREE ratios may have influenced TREE removal performance and operation during media sequestration and element concentration, this pretreatment strategy was abandoned because losing 30% of available TREE in the fly ash material was not acceptable.

D.1.4 Chemical Pretreatment – Type of Caustic Solution

Four different caustic chemicals of various concentrations were used to etch the silicate shell for increased recovery of the REEs. Sodium bicarbonate, sodium carbonate, sodium hydroxide, and potassium hydroxide (examination of counter-ion) solutions were tested. Comparisons between the various caustic pretreatments were based upon TREE concentration in solution after standard acid digestion utilizing 2M HCl at reflux temperature for 4 hours. Overall results are summarized in Figure D.2.

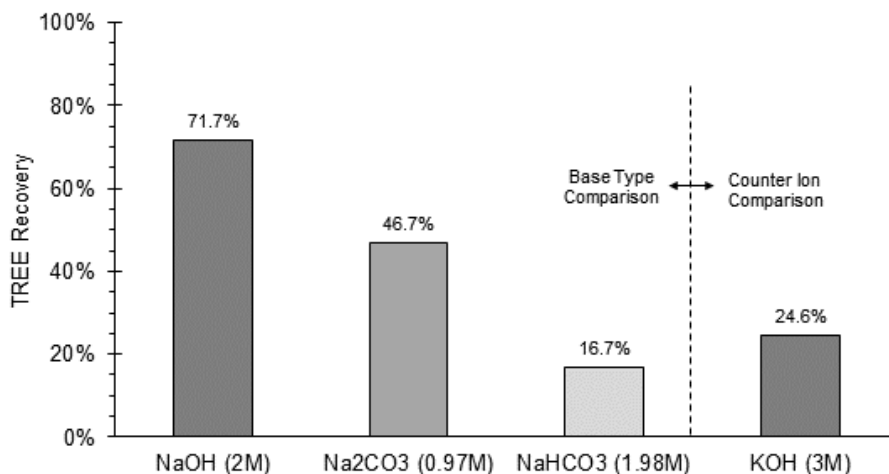


Figure D.2

Total rare earth element recovery based upon the type of caustic chemical showing the influence of chemical species and type of counter ion based upon caustic pretreatment for 4 hours at reflux temperature followed by standardized acid digestion (2 M, 10wt% solids, reflux temp., 4 hours).

Figure D.2 shows the effect of decreasing caustic base strength (at similar concentrations) on TREE recovery with a proportional decrease in recovery rate versus base strength. Sodium hydroxide recovered almost 2X more TREES compared to sodium carbonate and over 4X the TREES compared to sodium bicarbonate. It is interesting that potassium hydroxide at 3-molar concentration only achieved a maximum TREE recovery of approximately 25% even though the hydroxide mass to fly-ash mass ratio was slightly higher-than that of NaOH (0.65 to 0.53 g-OH/g-fly-ash respectively).

When the results of the various caustic pretreatments are compared to acid digestions without pretreatment, there was no improvement of the recovery of REEs utilizing sodium bicarbonate, 18-22% TREE recovery with acid digestion alone compared to approximately 17% for NaHCO_3 . Potassium hydroxide showed only a minimal improvement in TREE recovery enhancement, 25% compared to 18-22%. Both sodium hydroxide and sodium carbonate pretreatment enhanced TREE recovery compared to no caustic pretreatment by a factor of 4X and 2X respectively. Therefore, caustic pretreatment utilizing these specific caustic sources significantly enhances TREE extraction efficiency. Based upon these observations, sodium hydroxide pretreatment was a clear choice of the four caustic chemicals tested to maximize TREE extraction efficiency.

D.1.5 Chemical Pretreatment – Concentration of NaOH

The concentration of caustic (NaOH) pretreatment was varied to determine the optimal solution concentration needed to produce the greatest TREE recovery. Fly ash solids were contacted with 2, 3, 4, and 5 molar NaOH solutions at the same solids loading of 10%wt. Based upon the solution volumes used and the mass of fly-ash present, the corresponding hydroxide mass to fly-ash mass ratios varied between 0.33 to 0.87 g-OH/g fly-ash. A summary of the results is provided in Figure D.3.

Figure D.3 shows an improvement in recovery when the concentration of NaOH increased up to 0.40 g-OH/g fly-ash. Although increasing hydroxide concentration resulted in higher hydroxide to fly-ash mass ratios after this point, observed TREE recovery decreased from approximately 82% to 68%. Based upon this result, caustic pretreatment concentration was targeted within a narrow range to achieve g-OH/g fly ash ratios between 0.38 to 0.42 to optimize TREE recovery during the course of the project.

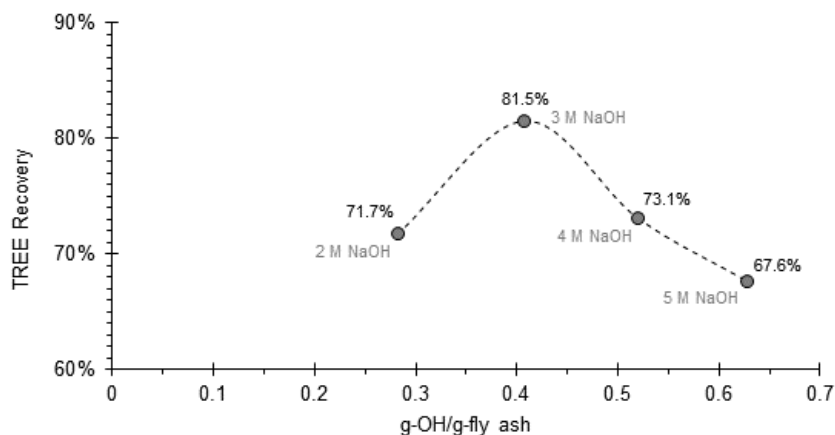


Figure D.3

Impact of hydroxide to fly-ash mass ratio on total rare earth element recovery utilizing NaOH pretreatment at reflux temperature for 4 hours followed by standard acid digestion (2M, 10% wt solids, reflux temp., 4 hours).

Once the NaOH concentration had been determined, a series of experiments were completed to determine if there was preferential extraction of specific REEs. Accurate determination of each REE concentration by ICP-MS analysis provided comparison data. The recovery of each rare earth element on the basis of total mass extracted per mass of fly ash and the relationship between individual REE concentration in the fly-ash material to observed extraction values are summarized in Figure D.4 and Figure D.5.

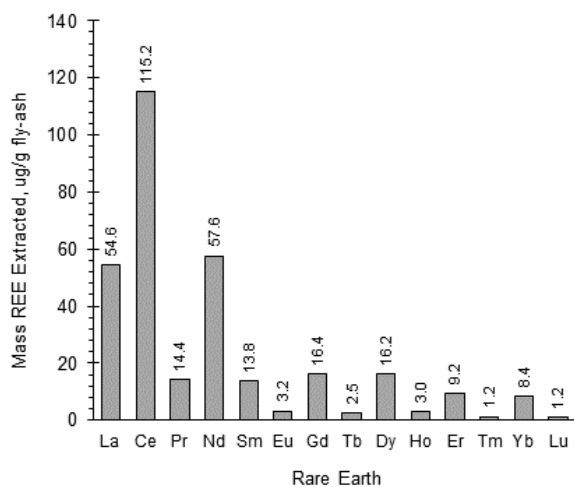


Figure D.4

Individual rare earth element recovery utilizing NaOH pretreatment at reflux temperature for 4 hours followed by standard acid digestion (2M, reflux temp., 4 hours).

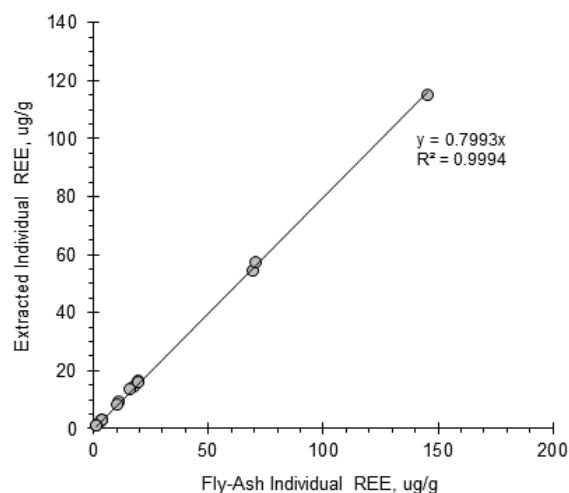


Figure D.5

The amount of each REE extracted to total amount of each REE in the fly-ash material

The figures show that although the amount of each REE removed is different, the amount of each REE extracted is approximately 80% as shown in Figure D.5. This linear proportion between the concentration of each REE in the untreated fly ash to the amount extracted indicated that there was no preferential removal of any one REE. This was positive result since the goal of the pretreatment process was to maximize REE extraction by acid digestion (see next section), not limit extraction any one REE.

D.1.6 Chemical Pretreatment – Solids wt% in Pretreatment Slurry

An important design element in the scale-up of the treatment process developed during this project was the maximization of treatment efficiencies/economics through optimization of unit processes. One such optimization was to determine the highest solids concentration that could be pretreated with NaOH while maintaining REE extraction performance. The impact of solids concentration during caustic pretreatment was evaluated by contacting fly-ash with various volumes of 4M NaOH to obtain 10, 20, and 30 wt% solids in solution. Higher solids loadings up to 40% were attempted but proved to be too thick to stir using magnetic stirring or overhead stirring. The various solutions were heated to reflux temperature (approx. 100°C) for 4 hours with subsequent filtering and rinsing of the pretreated fly-ash. The fly ash was dried and then contacted with 2M HCl at reflux temperature for 4 hours at a solids concentration of 10%. Experimental results are summarized in Figure D.6.

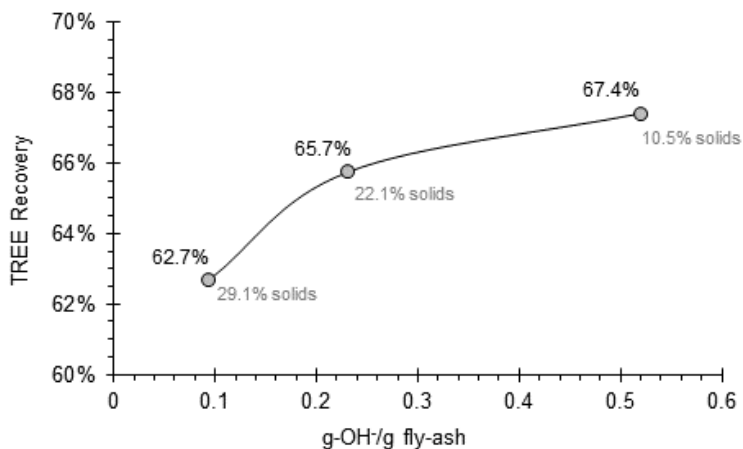


Figure D.6

Relationship between TREE recovery and the ratio of g-OH/g fly-ash for various wt% solids concentrations contacted with 4M NaOH at reflux temperature for 4 hours followed by standard acid digestion (2M, reflux temp., 4 hours).

Decreasing recovery with increasing percent solids is clearly evident in Figure D.6. This result is consistent with the fact that as the ratio of g-OH/g fly ash decreases, so does the observed TREE recovery (see Figure D.3). Although these tests were performed using 4M NaOH rather than the optimized 3M NaOH (see Figure D.3), additional results also indicate that up to a 30 wt% can be used with approximately 5-7% reduction in TREE recovery. This decreased recovery is, however, eclipsed by the economics of 3x relative production throughput at 30% vs 10% so higher mass loadings were used throughout the project.

D.1.7 Chemical Pretreatment – Temperature

Obtaining and maintaining high temperatures can be operationally cost prohibitive and safety concerns with refluxing caustic solutions cannot be dismissed. Therefore, an investigation into the determination of optimal caustic pretreatment temperature was completed. Caustic pretreatment was investigated at 40, 60, 80 and 100°C utilizing a g-OH/g fly-ash ratio of approximately 0.1, 30wt% at a 4 hour reaction time (chosen as a functional operational limit for future large-scale system). Test results are summarized in Figure D.7.

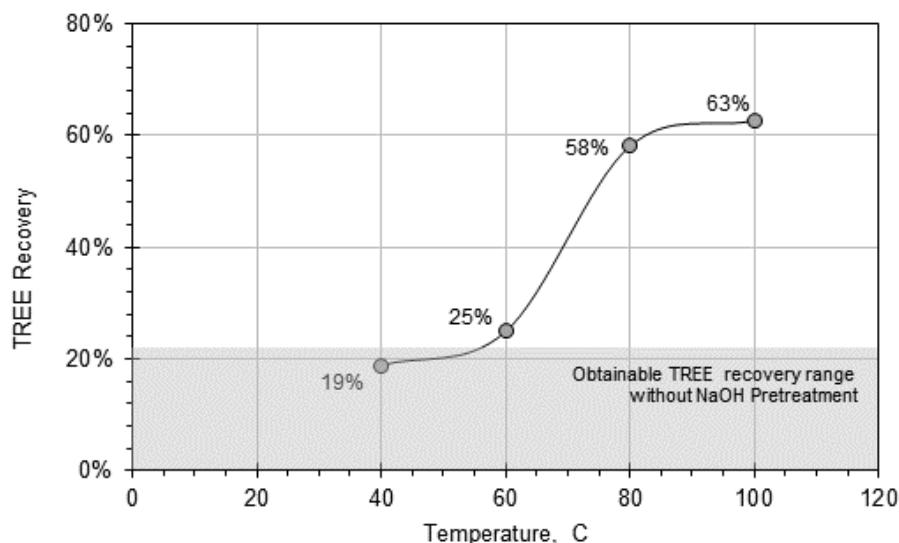


Figure D.7

Effect of pretreatment temperature on rare earth element recovery from fly ash utilizing NaOH pretreatment at reflux temperature for 4 hours followed by standard acid digestion (2M, reflux temp., 4 hours).

It is clear that pretreating fly-ash material at 40°C for 4 hours did not result in any TREE recovery improvement. Results at 60°C also do not show any significant improvement in recovery. At 80°C recovery was only slightly less than the maximum recovery of 63% obtained at 100°C (reflux). Although experiments were completed at approximately 0.1 g-OH/g fly-ash rather than the optimal ratio of 0.4 g-OH/g fly-ash (see Figure D.3), follow-on testing results indicated that pretreatment at reflux (100°C) produced consistent, high recovery efficiencies.

D.1.8 Chemical Pretreatment – Time

The impact of the reaction time on observed TREE extraction efficiency (recovery) was determined by investigating TREE recovery after 1, 2, 4, and 8 hours of caustic pretreatment. Experiments were conducted using a g-OH/g fly-ash ratio of 0.11, 33 wt% solids, and at reflux temperature (100°C). After the treatment, the fly ash samples were washed then dried with follow-on acid digestion using 2M HCl at 100°C for 4 hours. The amount of TREE removed compared to the total present (available) in the fly-ash material with results presented in Figure D.8.

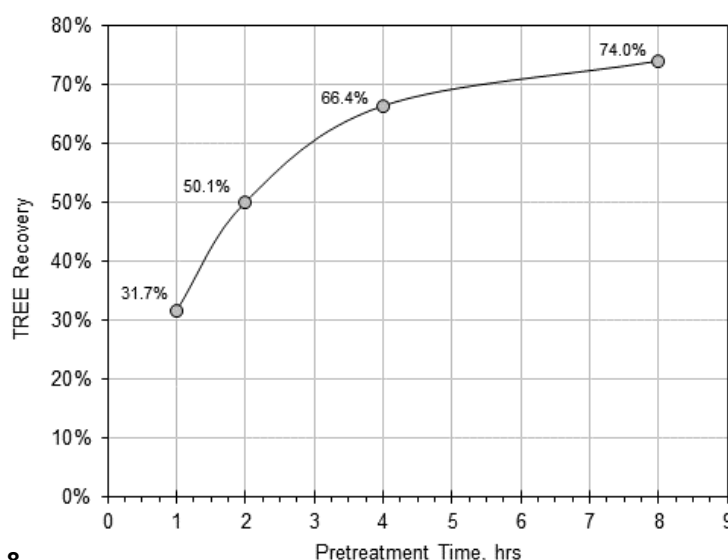


Figure D.8
Evaluation of NaOH pretreatment reaction kinetics at reflux temperature, 0.11 g-OH/g- fly-ash, and 30% solids loading followed by standard acid digestion (2M, reflux temp., 4 hours).

Results indicated that TREE recovery increased proportionally in relation to pretreatment reaction time with decreasing improvement after 4 hours. TREE recovery increased 34% from 1 to 4 hours, but only increased by an additional 8% from 4 to 8 hours. Based upon this result, 4 hours was chosen as the targeted reaction time that maximizes extraction efficiency will simultaneously balancing processing limitations.

D.1.9 Chemical Pretreatment – Optimization

During multiple experiments using different batch volumes during NaOH pretreatment it was observed that significant variability in TREE recovery rates occurred. Figure D.9 shows the variability in TREE recovery from solutions produced from small-volume batches compared to larger-volume batches based upon g-OH/g-fly-ash applied during pretreatment.

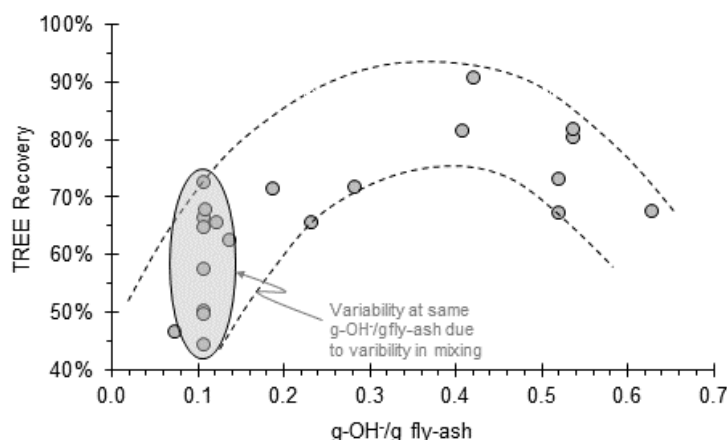


Figure D.9
TREE recovery at varied NaOH concentrations (g-OH/g-fly ash) at reflux temperature and 30% solids loading followed by standard acid digestion (2M, reflux temp., 4 hours).

A portion of the results in Figure D.9 could be explained by the inherent variability in the data, but a portion of the data points could not be readily explained. Therefore, additional testing was initiated to understand and solve this issue since the difference in overall economics of a full-scale installation is very sensitive to TREE recovery rates. Figure D.10 summarizes the results of tests investigating the impact of pretreatment solution volume on TREE recovery.

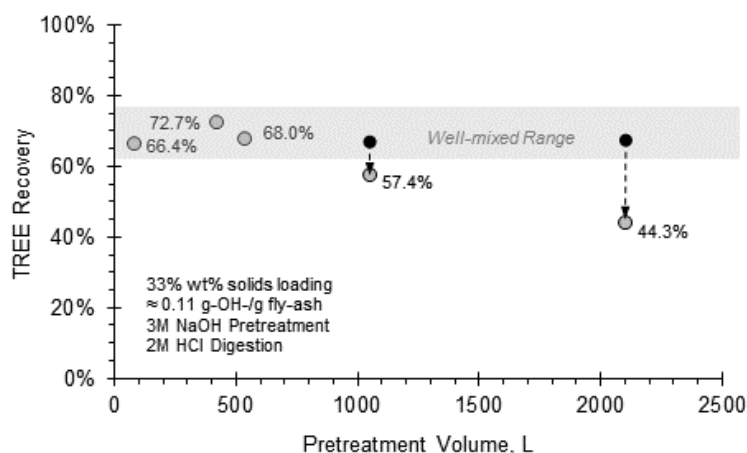


Figure D.10

Impact of NaOH pretreatment reactor volume on TREE recovery at reflux temperature and 30% solids loading followed by standard acid digestion (2M, reflux temp., 4 hours).

Figure D.10 shows that as the pretreatment sample size is increased past 1-L, recovery efficiency decreased. Follow-on digestion optimization revealed that the formation of silicic acid at high HCl concentrations above 80°C severely impacted mixing and recovery of filtrate from the digestion slurry. A more detailed discussion is provided in Section D.2.6. Based upon understanding both pretreatment and acid digestion processes together resulted in a change in operating strategy, namely the use of 10wt% solids during both treatment steps.

D.2 Evaluation of Digestion Strategies

It was decided in the proposal phase of this project that acid digestion would be used as the main treatment method to extract REEs from coal fly ash. This acid digestion stage is preceded by the NaOH pretreatment stage and followed by applying Tusaar's proprietary sorption media to remove U/Th and concentrate REEs. Based upon this general treatment strategy, a focused effort was placed on maximizing REE extraction efficiency as a necessary result to develop an economically viable process.

The extension of the experimental approach after finalization of the pretreatment process (section D.1) was the evaluation and optimization of acid digestion. A targeted effort was initiated to develop a process methodology including various acid digestion techniques to enhance REE recovery rates. The validity of each tested acid digestion technique was based primarily on the percentage of REEs extracted. Utilizing this approach allowed for a direct comparison between each acid digestion technique since the same pretreatment technique was used throughout experimentation. Acid digestion parameters investigated included:

- Type of Acid Solution
- Concentration of HCl
- Solid wt% in Digestion Slurry
- Digestion Reaction Temperature
- Digestion Reaction Time

A brief summary of each acid digestion technique along with major results are given in the following sections.

D.2.1 Type of Acid Solution

Three mineral acids; HCl, HNO₃, and H₂SO₄ were chosen for testing recovery rates of REEs from pretreated fly-ash. Two different concentrations of each acid were used, 1M and 2M, at a solids concentration of 10 wt%. Results for each acid type and concentration are summarized in Table D.1.

Table D.1 TREE+Y recovery utilizing different acids at 1M and 2M concentration.

Acid Concentration	Acid Type	TREE+Y Recovery ¹ %
1M	HCl	50.0%
	HNO ₃	52.2%
	H ₂ SO ₄	22.3%
2M	HCl	68.6%
	HNO ₃	59.2%
	H ₂ SO ₄	41.2%

1 – Recovery defined as mass of TREE+Y measured after pretreatment + digestion compared to mass of TREE+Y determined from lithium borate fusion analysis of untreated fly-ash material.

Results indicate that an increase in acid concentration from 1M to 2M increased REE recovery for all acids tested. The increase in REE extraction efficiency from concentration 1M to 2M was greatest for HCl, approximately 19%. Results also show that HCl at a 2M concentration extracted approximately 10% more TREE+Y than the next best acid tested, HNO₃. This significant improvement in REE extraction efficiency using acid HCl at a 2M concentration coupled with the greater difficulty in disposal of spent nitric acid solutions lead to the decision that HCl was the best choice for all future testing efforts.

For comparison purposes, highlighting the importance of pretreatment before acid digestion, the highest REE extraction efficiency obtained without NaOH pretreatment (see Section D.1) was approximately 20%. Using this baseline value, pretreatment followed by proper acid selection and concentration increased removal by over 3X. Therefore, the NaOH pretreatment process developed during this project was essential to achieving high REE recovery rates.

D.2.2 Concentration of HCl

The impact of HCl concentration on REE recovery rates at a solids (fly-ash) concentration of 10wt% was investigated using HCl at different acid concentrations. Specific tests were completed at acid concentrations of 1.5, 2, 2.5, 3, and 4M with results summarized in Figure D.11.

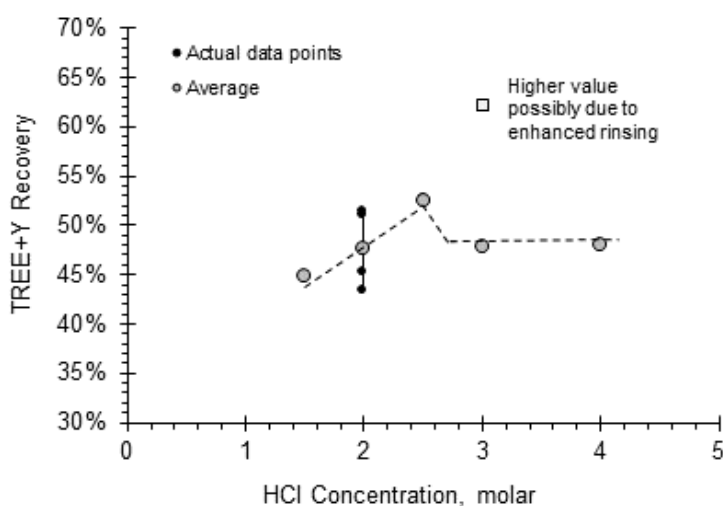


Figure D.11

Impact of concentration of selected digestions using HCl on total rare earth element (TREE+Y) recovery at a solids concentration of 10wt%.

Figure D.11 shows a general increase in TREE+Y recovery as HCl concentration was increased from 1.5 to 2.5 molar, with a relatively stable recovery after concentration 2.5 molar. The highest observed recovery of 62% at concentration 3 molar was due to more efficient rinsing of the sample. Recovery rate from enhanced rinsing was investigated by conducting an experiment at a HCl concentration of 2.5M. During this experiment, the concentration of TREE+Y in the primary filtrate (PF) from the digestion liquor and the filtrate after rinsing was quantified. Results are summarized in Figure D.12.

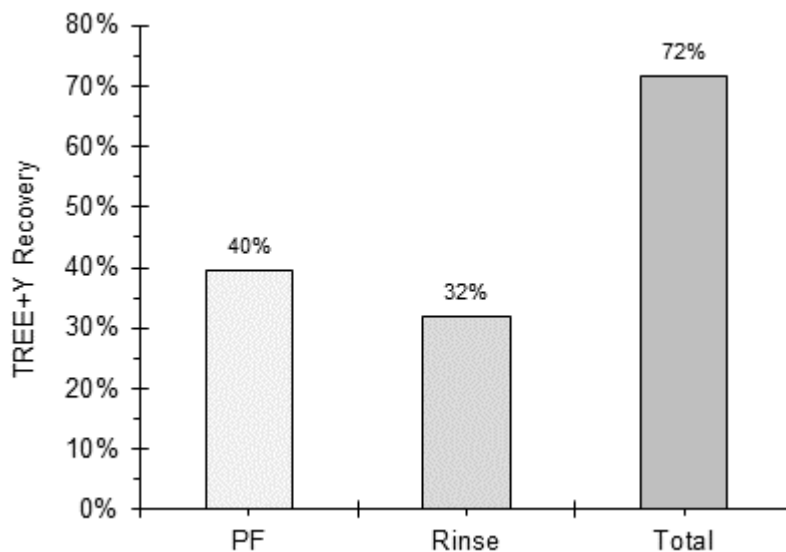


Figure D.12
Enhancement of TREE+Y recovery using 2.5M HCl at a solids concentration of 10wt%.

Results in Figure D.12 show that rinsing during post-digestion processing increased the average TREE+Y recovery by over 30% when 2.5M HCl is used during digestion. This indicated that proper rinsing of the digestion fly ash solids was very important to maximize REE extraction efficiency.

D.2.3 Solids wt% in Digestion Slurry

The solids weight percent of fly-ash in digestion solutions was varied to determine the minimum required acid dosage (HCl) for a given unit of fly-ash. Slurries at three different solids concentrations of 10, 20, and 30wt% were tested using HCl at a concentration of 2.5M. Not surprisingly, at a constant acid concentration, the extraction of REEs decreased with increasing solids concentration. This is indicative from the decreasing acid concentration to solids concentration ratio as the solids concentration increases. A reduction in REE recovery of approximately 13% was observed when the solids concentration increased from 10wt% to 30wt%. In an effort to achieve a similar REE recovery efficiency at solids concentration 30wt% to that achieved at solids concentration 10wt%, the concentration of HCl was increased to enhance REE extraction efficiency. Results indicated that increasing HCl concentration from concentration 2M to 2.67M increased REE extraction efficiency from 58% to 76%. Therefore, an acid concentration of 2.67M and a solids loading of 30wt% was targeted for the remainder of the project.

D.2.4 Digestion Reaction Temperature

Temperature is very important operating consideration of a full-scale facility since the cost of heating reaction solutions can be high. To investigate a possibility of reducing costs of fly-ash digestion, experiments were conducted at three different temperatures of 100, 80, and 60°C to determine the minimum digestion temperature that still maintains a high recovery level of REE s. Results of REE recovery at the three different temperatures using HCl at 2.67M with a solids concentration of 30wt% are summarized in Figure D.13.

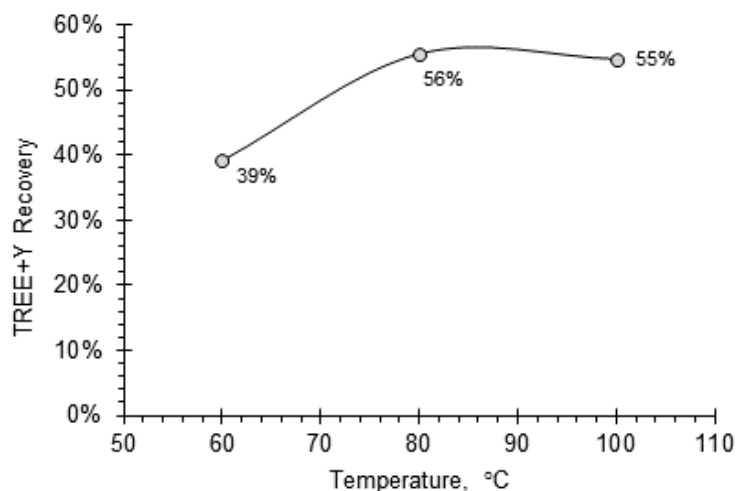


Figure D.13

Impact of temperature on TREE+Y recovery using HCl at a concentration of 2.67M and a solids concentration of 30wt%.

Results showed that REE recoveries at 100°C and 80°C were virtually identical at approximately 55%. As temperature is decreased from 80°C to 60°C, a significant decrease in REE extraction efficiency occurs (55% to 39%). It was not determined if temperatures between 60°C and 80°C would result in similar extraction efficiencies as that witnessed at 80°C to 100°C. Based upon experimental results, 80°C was chosen as the targeted digestion process temperature for large-scale experiments.

D.2.5 Digestion Reaction Time

An important consideration in development of the full-scale process was the required size of digestion reaction vessels. Obviously, vessel size is directly proportional to the time required for reactions to occur. Therefore, a series of experiments using reaction times of 2, 4, 6, and 8-hrs were completed to determine the optimal required reaction time. Results from these experiments are summarized in Figure D.14.

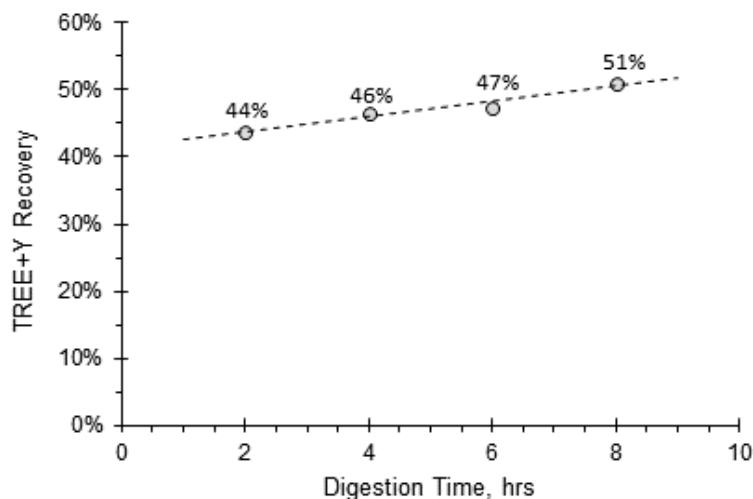


Figure D.14

Impact of digestion time on TREE+Y recovery using HCl at 2.67M with a solids concentration of 30wt%.

Results showed a linear increase in REE recovery as the digestion time increased. For every additional hour of processing time, an additional 1.2% of REE recovery was obtained. This was a marginal increase that

translated into slight recovery gains from significant increases in equipment sizing and processing costs. For example, increasing digestion time from 4 to 8-hrs (i.e. doubling tankage size or decreasing system capacity by 50%) only increases REE recovery by 5%. This increase was not enough to justify the additional process equipment and energy requirements. Therefore, 4-hrs was selected as the required time necessary for digestion. It should be noted that the overall low recovery rates shown in Figure D.14 are believed to be due to inefficient rinsing of the digested fly-ash sample.

D.2.6 Digestion Optimization

It was discussed in Section C.1.9 the effect of NaOH pretreatment solids loading on TREE recovery. Over 50 laboratory tests processing different lots of fly-ash material with influent mass ranging from 15-g up to 1-kg were analyzed for REE extraction efficiency based upon pretreatment conditions (%solids, temperature, base concentration, time) and digestion treatment factors including; acid type and concentration, solids loading, temperature, and reaction time.

REE digestion data was analyzed based upon the molarity of acid used with solids loading between 10 and 20wt% at 80°C at a 4-hr reaction time. Figure D.15 summarizes the analysis of the data with regards to solution molarity and the impact of the mass of fly ash treated per batch.

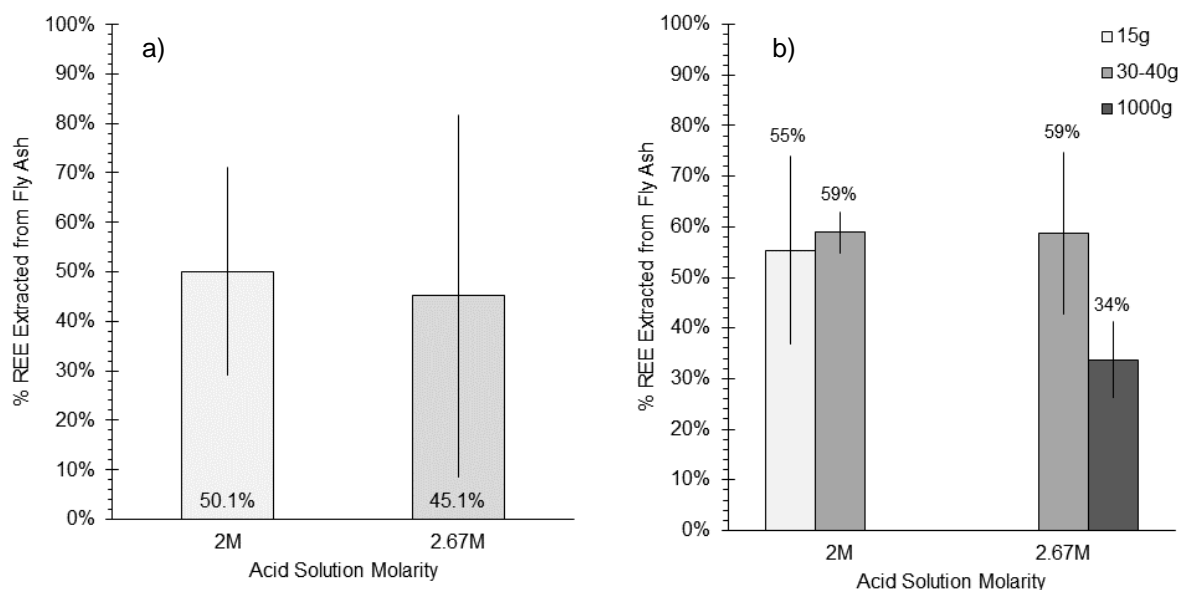


Figure D.15

Summary of % REE extracted from all experiments (a) versus digestion solution molarity and b) REE%

Results in Figure D.15 indicate that there was not a significant difference in extraction efficiencies between the 2M and 2.67M digestion solutions. However, the variability in the 2.67M solution extraction efficiency was large. Although a small portion of this variability can be accounted for by differences in fly-ash pretreatment and digestion factors such as solids loading, further scrutiny of the results was warranted to understand this variability. The %REE extraction efficiency was separated based upon the mass of fly-ash treated per batch. Results suggest that the biggest subset that impacts overall REE extraction efficiency was the 1-kg digestion batches.

It was observed that the solids produced from the digestion process, when large quantities of fly ash were used per batch, did not readily filter with the filtration system that was available in the laboratory. Based upon this observation, the average amount of digestion liquid retained within the solids was compared at each of the three reactor mass loadings; 15g, 30 g, and 1,000g. The mass of liquid in the fly ash solids was determined from a loss-on-dry analysis. Results of the analysis are summarized in Figure D.16

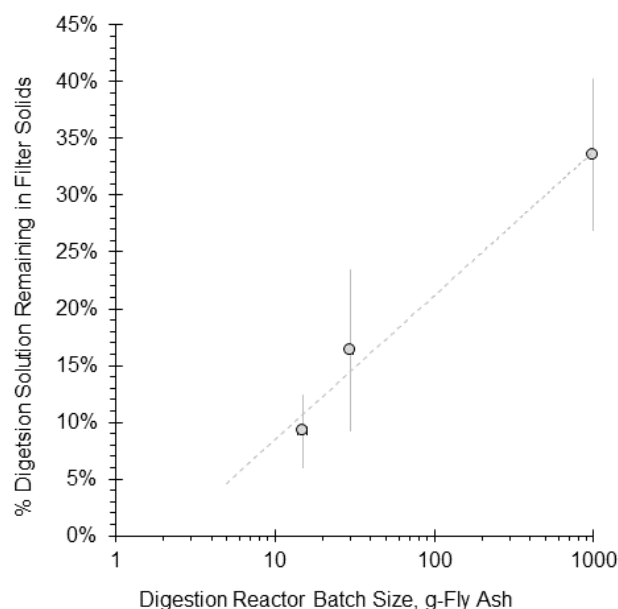


Figure D.16

Resulting percentage of digestion solution remaining in filter solids versus the size (g-fly ash) of the digestion **batch**.

Figure D.16 shows a strong relationship between the amount of digestion liquid retained in the solids versus batch size with increasing retained digestion solution due to the increase in digestion batch size. This has significant ramifications since an increase in digestion solution retained in the solids decreases the recovered amount of REEs from the process as witness in Figure 2.4. The data also shows that improving filtration efficiencies for larger batch sizes is achievable since with proper filtration at the lower batch sizes less-than 10% of the digestion solution remained within the solids.

Two additional observations provided information that was helpful in formulating an explanation and a strategy to solve REE recovery variance. The first observation was that during digestion of pretreated fly-ash solids, if the solution temperature exceeded 85°C the solution would thicken to a point resembling “pudding” and not mix well. The second observation was that if the digestion solution was maintained at 80°C then filtered to separate residual fly-ash solids from the liquor containing extracted REEs, the solid – liquid matrix would thicken to the point that the solution appeared to be “gelatinous”. These changes to the solution and solids did not occur during fly-ash digestion if the ash was not subjected to pretreatment. Therefore, linking pretreatment conditions to the conditions during digestion gave insight into the possibility of silicic acid formation during processing.

During digestion if the temperature exceeded 85°C, it was likely that short-chain silicic acids condensed to form complex polymeric structures that interacted with one another resulting in a “gelatinous” fluid. The hypothesis that silicic acid caused filtration issues also holds true when explaining filtration of digestion solutions below 85°C. In these instances, during filtration as water is removed from the digestion liquor, short-chain silicic acids weakly interact with one another to form a “gelatinous” mass. Based upon observations and the proposed hypothesis of silicic acid being generated during processing, three methods were targeted to manage silicic acid, 1) large water volume rinsing, 2) separation of silicic acid solution prior to rinsing, and 3) decrease solids loading (wt% solids) during NaOH pretreatment and acid digestion.

Large volumes of water were used to rinse the acid digested fly ash. In simplistic terms, small amounts of fly-ash after digestion were mixed with large volumes of water and then filtered. The impact of this approach is summarized in Figure C.17 which shows an average REE extraction efficiency of 48% ($\pm 4\%$) with low-volume water rinses compared to a high-volume rinse which resulted in a total recovery of 72%.

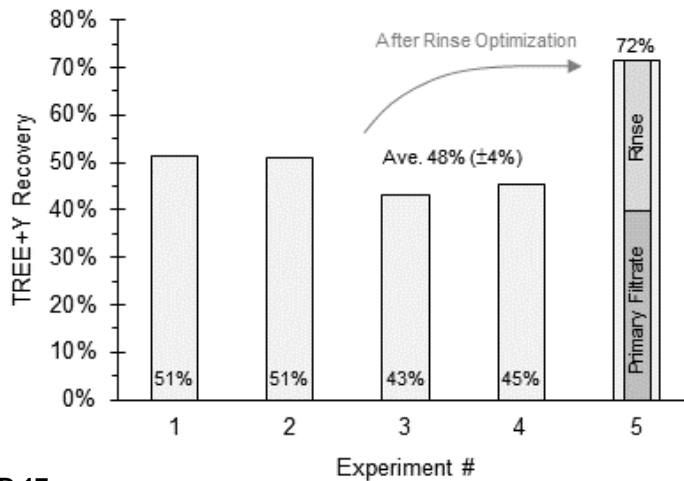


Figure D.17
Improvement in REE recovery by implementing a large-water volume rinsing process.

Although the high-volume rinse methodology improved REE recovery, the practical implementation of this approach in a large full-scale system is problematic. Required water volumes and subsequent volumes of waste solutions from the rinsing process are not attractive from an equipment/space requirement and from a residuals management perspective.

Separation of fly-ash materials from the digestion liquors prior to media rinsing was investigated with the addition of chemical flocculants followed by fly-ash settling, decanting of the supernatant high in silicic acid, re-suspension of the remaining solids, and repeated rinsing/filtration of treated fly-ash solids. It was found that this process sequence did not entirely eliminate the formation of “gelatinous” material, resulting in continued problems with filtration after digestion. The process technique that worked well in limiting the formation of silicic acid while maximizing TREE recovery was the use of low, 10wt% solids loading during NaOH pretreatment and HCl digestion. The strategy produced solid slurry that could be reasonably filtered with TREE recoveries over 60%.

D.3 Uranium and Thorium Removal

To understand the development of uranium (U) and thorium (Th) removal unit within the context of the proposed REE extraction/purification process, it is beneficial to examine the proposed treatment system strategy during early stages of the project. Figure D.18 is a simplified illustration of the main unit processes within the proposed treatment system.

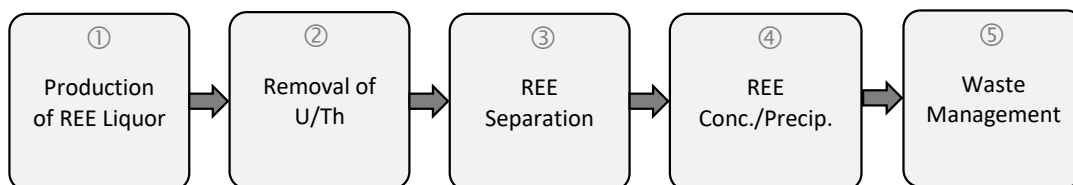


Figure D.18
Main unit process groups in the initial proposed REE production system.

This diagram shows five main areas of processing; 1) production of REE liquor (pretreatment and digestion), 2) removal of U/Th, 3) REE separation, 4) REE concentration/precipitation, and 5) waste management. The U/TH processing step was the next processing step after pretreatment and digestion activities. The U/Th removal process uses an adsorptive bed (proprietary media manufactured by the Recipient) to bind U and Th while allowing REEs and other ions in solution to pass through for downstream processing. The adsorptive bed required the influent solution from the production of REE liquor (pretreatment + digestion) to be particle free and at a

targeted pH to eliminate media bed clogging and to maximize U and Th sequestration. This general processing concept is illustrated in Figure D.19.

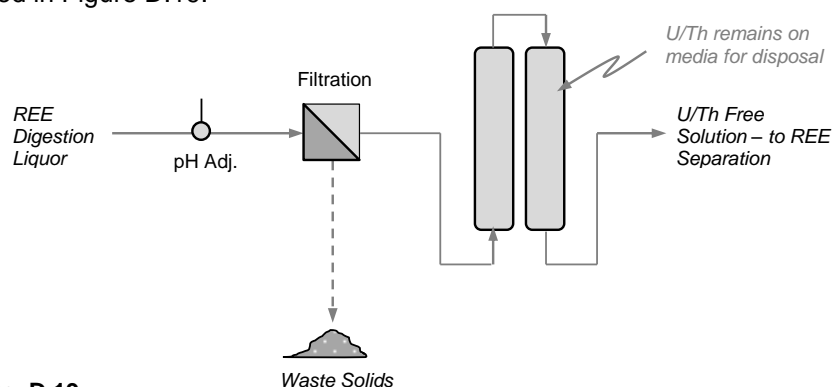


Figure D.19

Schematic of treatment unit to remove uranium (U) and thorium (Th) from digestion process effluent.

Based upon the general process scheme in Figure D.14, the overall tasks to understand and optimize the sequestration of U/Th from digestion solutions was separated into three focus areas:

- Operating pH for U/Th Sequestration
- Evaluation and Selection of Adsorptive Media
- U/Th Empty Bed Contact Time (EBCT)

Each focus area is discussed in the following sections.

D.3.1 Operating pH for U/Th Sequestration

It was known that metals removal by Tusaar's proprietary sorption media is dependent on the pH of the solution contacted with the media, i.e. a pH >3.5 is needed for cation adsorption to occur. Therefore, a series of experiments were targeted to find the pH value that maximized U/Th sequestration efficiency by the adsorptive media. However, before this optimal pH could be determined, the operational pH range needed to be determined since uranium or thorium precipitation within the adsorption columns would be problematic. A series of experiment were completed using a digestion liquor adjusted to a series of pH values to determine the maximum pH before rare earth metal precipitation occurred. An example of one experimental result (all were similar) is summarized in Figure D.20.

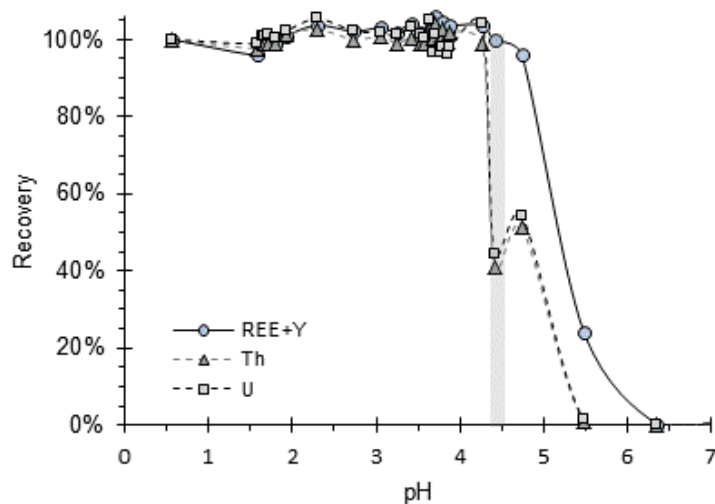


Figure D.20

Impact of pH on selective precipitation of uranium, thorium, and TREE+Y from actual digestion liquor from fly-ash.

It is clear from Figure D.15 that digestion solution pH could be adjusted to approximately 4 to 4.5 before precipitation of the rare earth elements occurred. It is interesting to note that uranium and thorium started precipitating from solution at approximately the same pH as the TREES. Based upon these observations, the available operational pH range for uranium and thorium sequestration was between 0 and 4. Although U/Th and REEs were not precipitated within this pH range, a significant amount of other dissolved constituents did precipitate from solution requiring an additional filtration step prior to column adsorption.

Precipitate formation during pH adjustment after digestion and prior to U/Th column adsorption was anticipated. However, the difficulty in removing these solids from the process stream was not expected. The challenge with the pH adjusted solution is the fact that flocculation (particle agglomeration) does not readily occur within the pH range of 0 to 4. This constraint resulted in solutions that contained small precipitates that are difficult to remove from solution. Solution pH after acid digestion was adjusted to 4.

D.3.2 Evaluation and Selection of Adsorptive Media

A major step in the development of the U/Th sequestration process was the evaluation and selection of an optimal adsorptive media that could effectively remove U/Th while allowing REEs to pass through. The specific steps required to find the best media were; 1) the production of various adsorptive medias, 2) single element tests to obtain U/Th uptake kinetics, and 3) determine U/Th capacity on chosen media.

Various Tusaar proprietary adsorptive materials were produced with differing surface functionalities, ligand addition, and particle size. A diverse group of media types were produced to find a material that maximized kinetic removal and overall adsorptive capacity of uranium and thorium. Table D.2 below lists selected media materials produced during the project:

Table D.2 Selected adsorptive media materials tested for U/Th removal.

Media	Surface Functionality	Particle Size
AM1	low	large
AM2	low	medium
AM3	medium	small
AM4	v. high	small
AM5	high	small

The adsorptive materials produced were activated carbon based that were subjected to different chemical pre- and post-treatments. The details of production, and the resulting specific chemical properties of each media are confidential, however, adsorbent materials AM3 and AM4 were targeted as the best available adsorptive materials based upon prior knowledge.

Adsorptive media materials AM1, AM2, AM3, and AM4 were each contacted with a 500 ppb uranium solution and a 1,000 ppb thorium solution at various pH values. Solution pH was varied between 1 to 2.5 because at pH 3, REEs started to load onto each adsorptive media (determined by investigating europium removal). Samples were taken at specific time intervals to obtain information related to sorption kinetics. A typical test result is shown in Figure D.21.

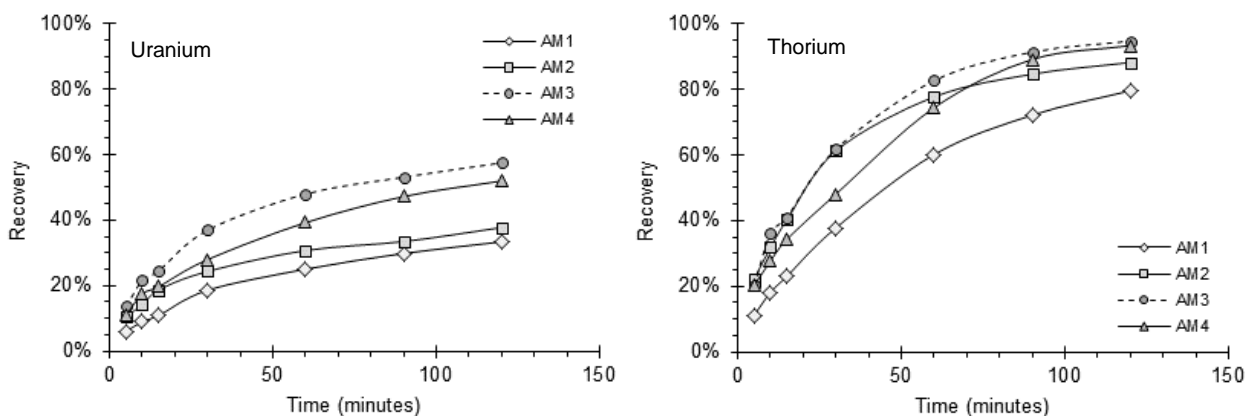


Figure D.21

Sorption removal kinetics of uranium (U) and thorium (Th) onto four selected sorptive materials, AM1, AM2, AM3, and AM4 with varied surface functionality.

From shaker kinetics in Figure D.21, it is evident that adsorbent media AM3 performed slightly better than adsorptive media AM4 for uranium removal and equally as well for thorium removal. It was also observed that adsorptive media AM1, although surface treated with a specific organic ligand, did not perform well compared to the all other media materials. Based upon these results, adsorptive media AM3 was chosen as the best media and was used for the entire project duration.

With the specific adsorptive media identified and selected, a series of tests were completed to determine the adsorptive capacity of U and Th onto the media. The media was contacted with various solution concentrations of U and Th at different mass values. Figure D.22 summarizes adsorption isotherm information.

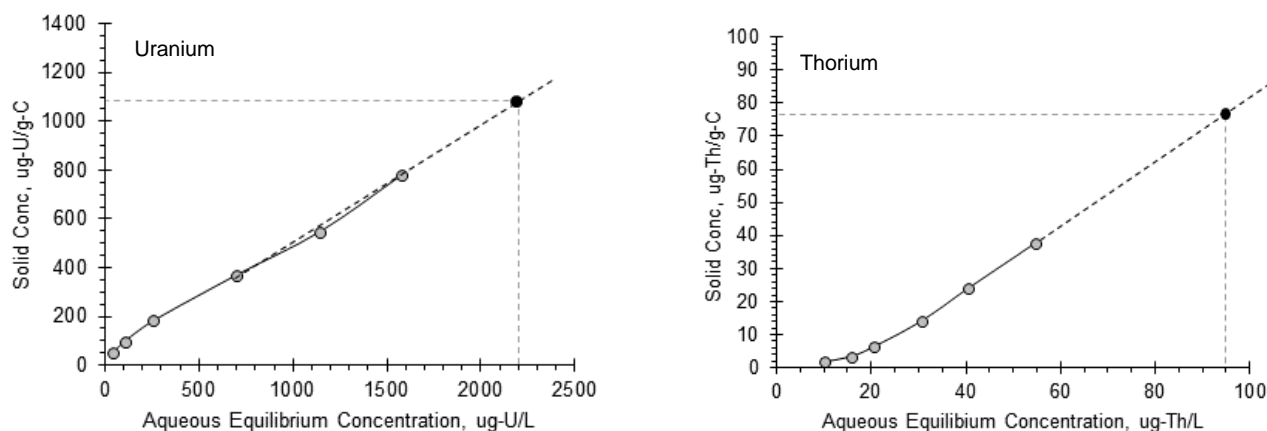


Figure D.22

Adsorption isotherms for uranium and thorium onto selected adsorptive media AM3

The data shows that uranium follows a linear isotherm model while thorium follows linear adsorption behavior at equilibrium concentrations exceeding 20 ppb. Based upon a typical digestion liquor influent of 2,200 ppb-U and 95 ppb-Th, the projected adsorptive media capacities were approximately 1,100 $\mu\text{g-U/g-C}$ and 75 $\mu\text{g-Th/g-C}$ for uranium and thorium respectively. These capacity values for uranium and thorium sequestration were used to size the adsorption columns used in all experiments.

D.3.3 U/Th Column Empty-Bed-Contact Time

The removal of uranium and thorium within adsorptive columns filled with media AM3 was initiated to assess kinetic properties and to verify bed capacities. Uranium removal was investigated at three different column retention (empty-bed contact) times of 2.3, 5.5, and 8 minutes by varying the flow rate through a column. A solution with only uranium and thorium was used to determine the required adsorption bed retention time.

Influent concentrations of uranium and thorium were 2,700 ppb-U and 95 ppb-Th respectively. Figure D.23 illustrates the impact of empty bed contact time on uranium removal (thorium data not shown because thorium was not detected in effluent samples from the column).

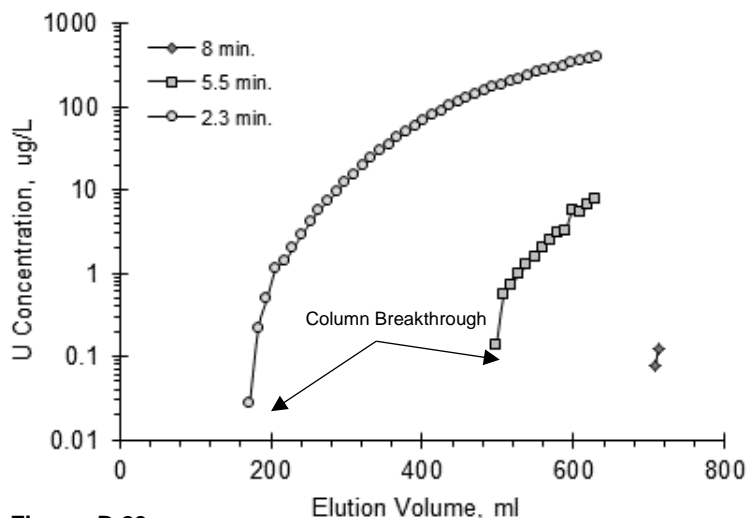


Figure D.23

Influence of column retention time on effluent uranium concentration in adsorption column effluent using adsorptive media AM3.

Figure D.23 shows that an increase in empty bed contact time (EBCT) increased adsorptive capacity, i.e. the volume of liquid treated before uranium breakthrough occurs. For example, at an EBCT of 2.3 min, uranium broke through the column after 180 ml of fluid passed through the adsorptive media. For comparison at an EBCT of 5.5, uranium broke through the column after 500 ml of fluid passed through the column. Thus, a 2.2X increase in EBCT resulted in an increase in volume treated (point of uranium breakthrough) by 2.8X. This is illustrative of the influence of EBCT on adsorption kinetics within the adsorption column. Although an increase in EBCT from 5.5 to 8 min. increased the volume of liquid that could be treated before uranium breakthrough, the additional 30% decrease in applied flow rate was not attractive from a scale-up perspective. Therefore, an initial EBCT of 5 minutes was chosen to balance removal performance and equipment requirements.

A series of final experiments were completed to determine the quantity of adsorptive media required to meet a uranium discharge target of 15 ppb (1/2 the EPA MCL for U). Since thorium appears to be >99% removed by the media, uranium adsorption capacity was the main design constraint. Adsorptive columns were operated at a 5 min. EBCT and an influent pH of 2. A typical removal curve is provided in Figure D.24.

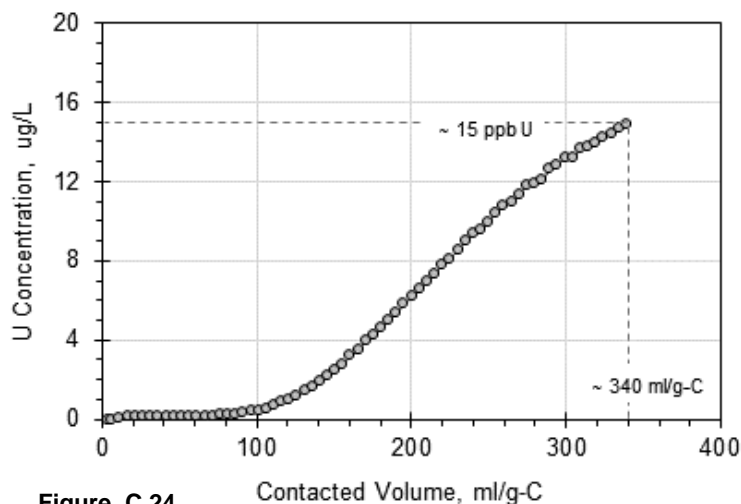


Figure C.24

Uranium adsorption effluent curve showing breakthrough profile.

Figure D.24 shows an effluent profile in which uranium in the column effluent is consistent with a mass transfer zone within an adsorptive bed. At termination of the experiment when the effluent uranium concentration of 15 ppb was reached, approximately 350 ml of the digestion liquor was processed. Based upon the mass of carbon used during the experiment, it was determined that 8.5 kg of carbon was required to treat 3,000 L of digestion liquor (volume produced from 1,000 kg of fly-ash).

D.4 Evaluation of Chromatographic Separation of REEs

A series of experiments were devised to investigate the proof of concept for the chromatographic separation of REEs from non-REE metals within the digest liquor. Experiments were separated into five main groupings:

- Column Hydraulic Loading Rate
- Bolus Strength
- Bolus Volume
- Column Aspect Ratio
- Carbon Media Particle Size

The following sections summarize the results for each experimental grouping.

D.4.1 Column Hydraulic Loading Rate

It is well known in chromatography that the rate at which a chemical constituent flows through a chromatographic column can significantly affect peak separation and overall elution shape for each constituent. This chromatographic dependence can be critical in determining whether separation can be achieved. To test this possible dependence, two different flow rates of 0.79 and 3.85 ml/min were investigated. These flow rates translated into an approximate hydraulic loading rate (HLR) of 1.00 and 4.9 cm³/cm²/min respectively. Based upon test flow rates and a column working volume of approximately 8 cm³, the estimated empty bed contact time (EBCT) for each test was 10.15 and 2.1 minutes respectively.

Each test consisted of passing through a known quantity of pH adjusted digestion liquor the media column, followed by an injection of acid to remove adsorbed metal species including REES from the media into a low volume acid volume. All tests were performed at an influent pH 2 with a 2 ml “strip” bolus of 10M HCl. Results of both tests are summarized in Figure D.25.

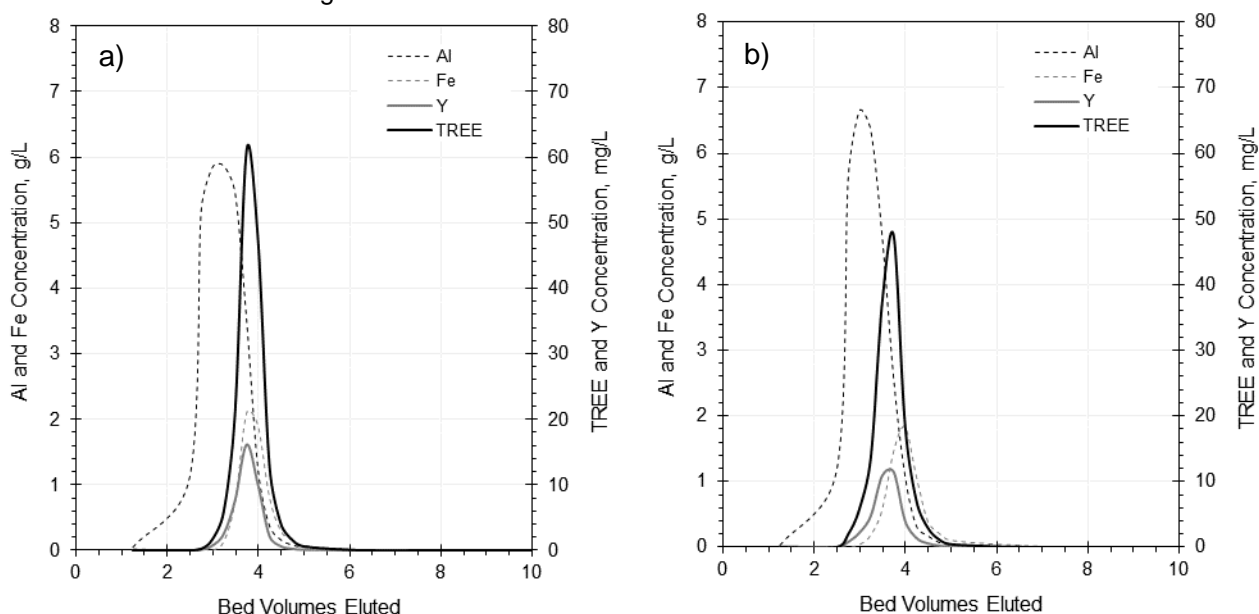


Figure D.25

Chromatographic separation of Al, Fe, Y, and TREE from pH adjusted digest liquor (pH 2) through a 1cm Ø x 10.2 cm length adsorption column (8 cm³ working volume) at a HLR of a) 1.00 cm³/cm²/min and b) 4.9 cm³/cm²/min.

Figure D.25 shows that, in general, both HLRs produced approximately the same extent of separation and peak shape for Al, Fe, Y, and TREEs. There is a clear separation of Al from the remaining constituents, i.e. the majority of the Al in solution elutes before the remaining constituents. This is significant because aluminum accounts for most of metal cations in the digest liquor, approximately 75% of major cations present. Therefore, isolation and selective removal of Al provided a method to isolate and increase REE content. This separation of REEs from aluminum is further illustrated in Figure D.26 which shows the mass percentage of REEs versus the mass percentage of Al collected in the column effluent.

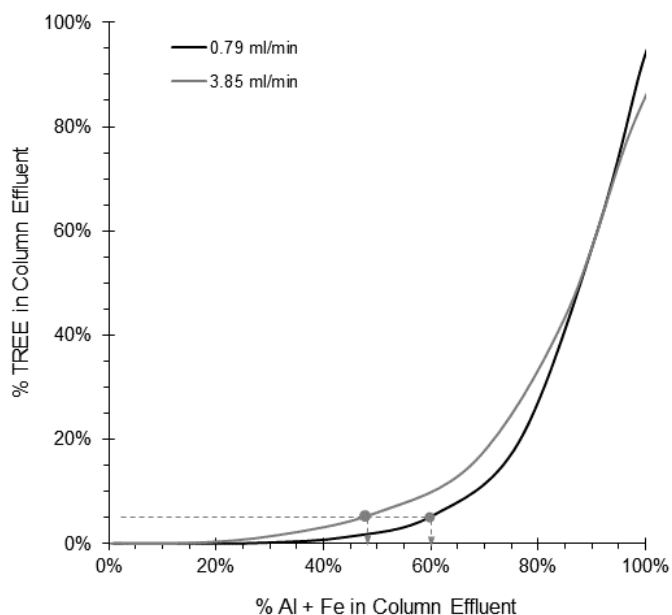


Figure D.26

Relationship between % mass of applied TREE versus % mass of applied aluminum and iron collected in column effluent showing retardation of TREE in column effluent.

The results in Figure D.26 indicate that, if the column effluent is separated and discarded prior to the point where 5% of the loaded TREEs, then the remaining 95% of TREEs will be collected along with roughly 40 to 60% of aluminum in the original digestion solution therein resulting in TREE isolation and concentration. Additional experiments revealed that there was an improvement from 50% to 60% aluminum removal when the flow rate was decreased. Therefore, initial large-scale experiments targeted a HLR of 1.00 cm³/cm²/sec with an empty bed contact time (EBCT) of approximately 10 minutes.

D.4.2 Bolus Volume

Chromatographic separation of cationic species using Tusaar's proprietary media is based upon proton displacement and ion affinity chromatography. Although test conditions were chosen to minimize the affinity for loading metals on the column, a few metals with a very high affinity for the activated carbon surface such as Fe will still load onto the media. Therefore, protons introduced into the column in a highly acidic solution, provide the displacement or "push" to remove loaded metals from the media. The size and strength of this "push" bolus needed to optimize chromatographic separation and recovery was investigated. The first step was to determine the size of the "push" bolus which consisted of testing three different volumes; 2.5 mL, 5mL, and 10mL. Figure D.27 summarizes the experimental results for the 2.5 and 10 ml "push" bolus volume (the 5 ml volume bolus was similar to the 2 ml volume bolus).

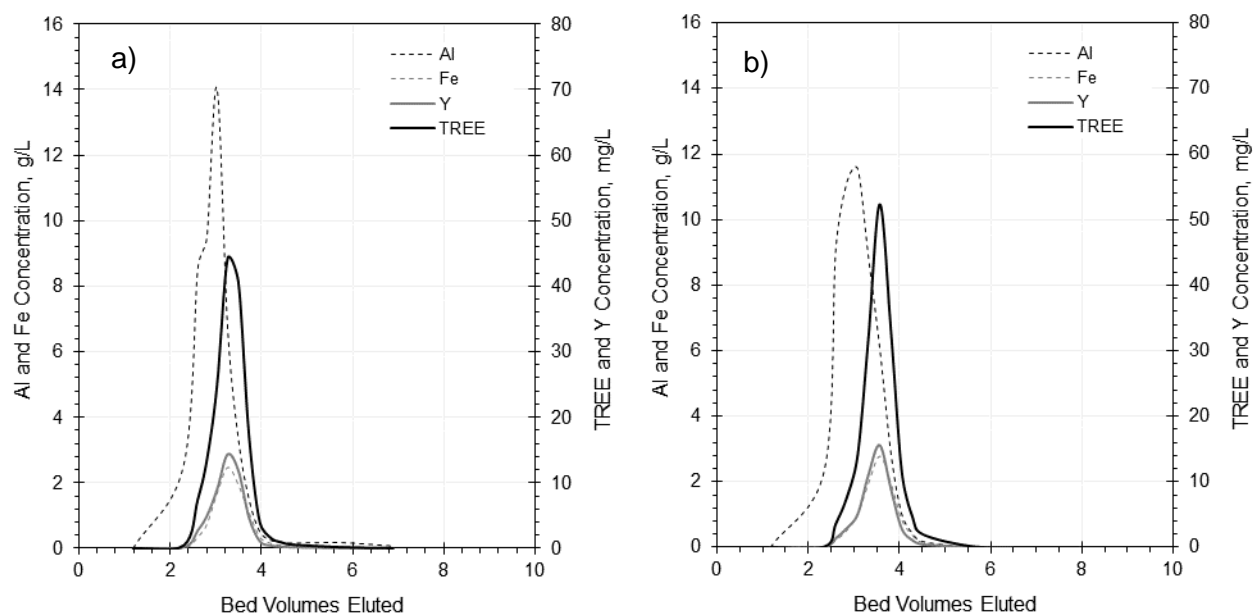


Figure D.27

Chromatographic separation of Al, Fe, Y, and TREE from pH adjusted digest liquor (pH 2) through a 1 cm Øx 10.2 cm L adsorption column (8 cm³ working volume) using a “push” bolus volume of a) 2.5 ml and b) 10 ml.

Figure D.27 indicates that the “push” volume of bolus did not significantly change the time for each component to elute from the column, nor did the volume appreciably change the shape of the elution peaks. Further analysis of the data was conducted to find subtle differences in performance. The data was analyzed by comparing the % recovery of each component from the column after elution. This simply consisted of comparing the mass of each constituent collected in the column effluent compared to the applied mass. Values less than 100% represent the fraction that is bound to the column media. Graph a) in Figure D.28 summarizes recoveries versus “push” bolus volume.

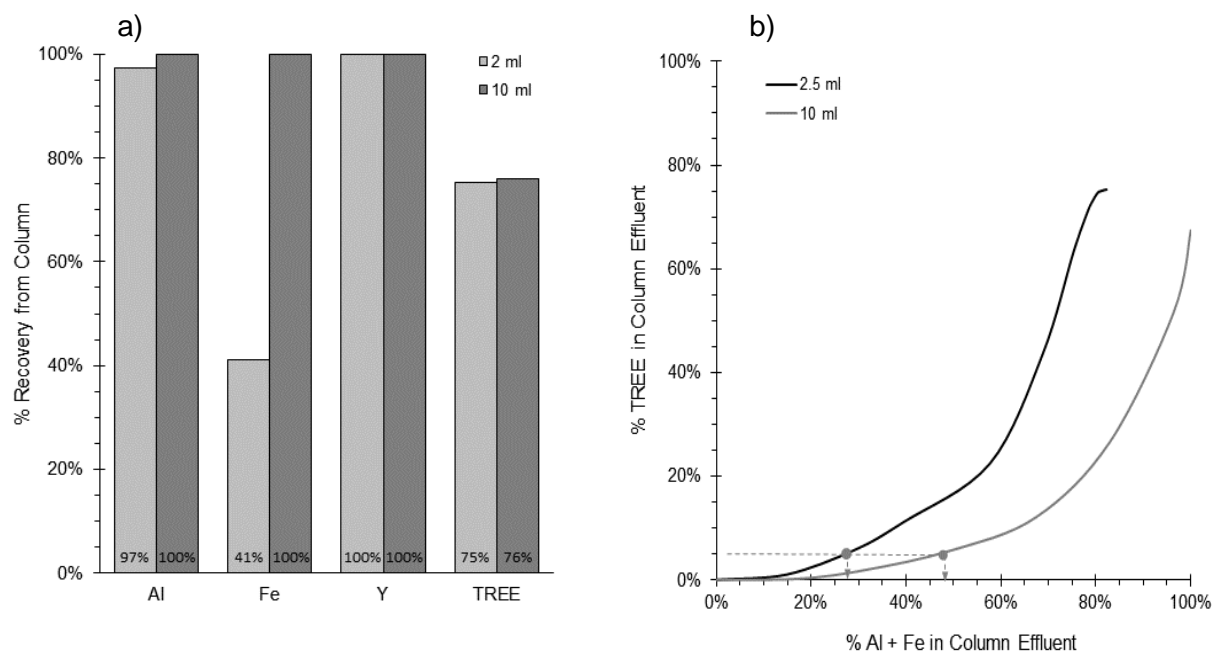


Figure D.28

A) Percent recovery of Al, Fe, Y, and TREE through chromatographic column using two different “push” bolus volumes and b) relationship between % mass of TREE applied versus % mas of aluminum and iron applied that is collected in column effluents showing improved performance in 10 ml “push” volume.

Results in graph a) show that increasing the “push” volume from 2.5 ml to 10 ml did not affect TREE removal. However, increasing the “push” volume did increase iron (Fe) removal from approximately 41% to 100% and slightly improved aluminum (Al) recovery. Using the collected fraction data, it was possible to calculate the mass-% of TREE in the column effluent compared to the mass-% for aluminum + iron. Results of this analysis are given in graph b) in Figure D.28.

Results in graph b) show that, for both the 2.5ml and 10ml “push” bolus, the mass-% of aluminum + iron in the column effluent (mass of Al and Fe collected compared to the mass of Al and Fe applied to the column) is greater than that witnessed for TREE. This simply means that a greater amount of Al and Fe applied to the column elutes more quickly from the column compared to TREE. This allows for fractional collection of the column effluent such that initial fractions contain primarily aluminum with minimal TREE, resulting in isolation and wt% increase of TREE in the bolus solution. Graph b) also shows that increasing the “push” bolus size from 2.5 ml to 10 ml increased the amount of aluminum + iron that could be isolated from the TREE fraction. For example, if 5% TREE is collected in a column effluent fraction, then approximately 28% and 48% of the aluminum and iron would also be collected in the fraction for a “push” volume of 2.5ml and 10ml respectively. Therefore, if this fraction is discarded and the remaining column eluent is collected, then 95% of the TREE applied to column and 52% to 72% of the aluminum and iron applied to column will be in the final solution. Although the 10ml “push” volume resulted in slightly better performance, the small “push” volume was chosen due to experimental constraints at the scale being tested.

D.4.3 Bolus Concentration

Optimal concentration of HCl in the “push” bolus to maximize REE separation and removal of (aluminum and iron) was investigated. The primary goal during this experimental phase was to determine the acid strength required to resolve the elution peaks of each constituent in the column effluent. Experiments investigate HCl “push” bolus strengths of 1, 2, 2.5, and 3 molar.

Experimental data showed, in general, the elution peaks for TREE and Y are at approximately 4 bed volumes. Interestingly, the iron elution peaks also coincide at 4 bed volumes while the aluminum elution peaks are centered around 3 to 3.5 bed volumes. This result was consistent with all previous column testing where aluminum always eluted before REEs and iron. To elucidate the differences between bolus acid strength, data was evaluated by plotting the percentage of TREE applied to the column compared to the percentage of aluminum applied to column. This relationship simply shows that for a given percentage of aluminum recovered in the column effluent, the corresponding amount of TREE in that same collected fraction can be estimated. This relationship for each “push” bolus HCl concentration tested is summarized in Figure D.29.

	% Recovery from Column			
	1M	2M	2.5M	3M
Al	100	100	100	95
Fe	100	100	100	92
Y	88	100	100	96
TREE	87	75.9	100	94

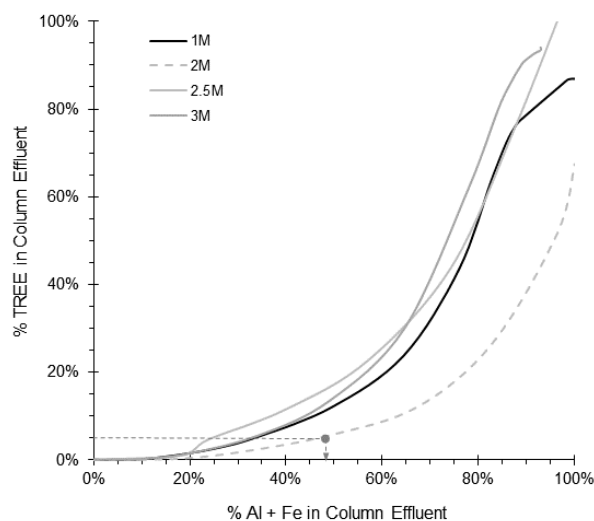


Figure D.29

Percent recovery of Al, Fe, Y, and TREE through chromatographic column using four different “push” bolus HCl concentrations and the relationship between % mass of TREE versus % mas of aluminum and iron collected in column effluents.

Figure D.29 indicates that all HCl concentrations tested resulted in the same relationship except for the 2.5M concentration curve. All curves show the same consistent trend that more aluminum is eluted in the early column effluent fractions than TREEs resulting in isolation and removal of aluminum from the digest liquor. When recovery of TREE and Y are compared for each acid concentration tested (see table in Figure D.29), the 2.5M solution resulted in virtually 100% recovery of TREE, which did not occur at lower acid concentrations. Given the importance of TREE recovery and the better isolation and higher removal of aluminum from TREE fraction in the column effluent, a “push” bolus concentration of 2.5M was used for all follow-on experiments.

D.4.4 Column Aspect Ratio

Another important consideration in development and understanding of column chromatography was the impact of column aspect ratio since the linear velocity of the concentration front through the column affects the separation of individual components. An experimental matrix was evaluated using three different column sizes with varied length and width. Column aspect ratios of 14x1, 28x1, and 6.25x1.5 (cm) were investigated. The impact of aspect ratio on separation efficiency was determined by the amount of aluminum that could be separated from the TREE stream. The percentage of aluminum in the column effluent in relation to the percentage of TREE in the column effluent for all three column sizes tested is illustrated in Figure D.30.

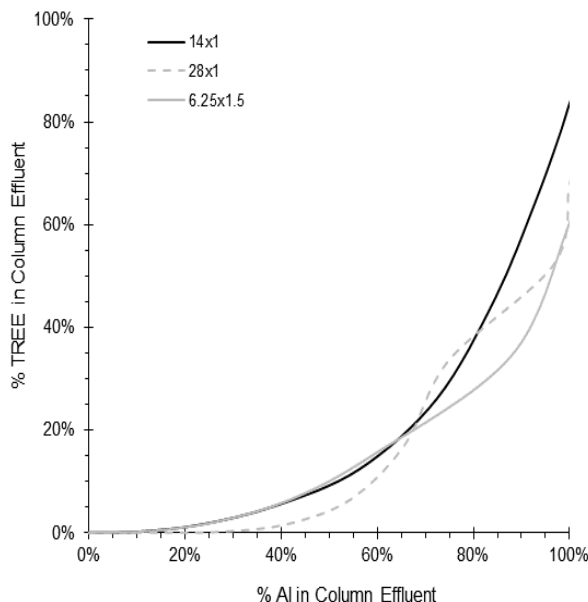


Figure D.30

Relationship between % mass of applied TREE versus % mass of applied aluminum and iron collected in column effluent showing retardation of TREE in column effluent.

The results in Figure D.30 indicate that there was no significant difference in the separation of aluminum from the TREES in the column effluent at the three column sizes tested. It is clear that doubling the length, and therefore mass of the column, or widening the column produced similar results. This observation is consistent given a plug of liquid flowing through the column with separation occurring from the front to the tail of the plug. In a smaller diameter column, the distance from the concentration front to the tail is increased, increasing the length necessary for transfer/separation. Based upon this result, the selection of column aspect ratio was dependent on the type of experiment being conducted.

D.4.5 Carbon Media Particle Size

The final variable investigated in the development of chromatographic separation was media particle size. Since constituent interaction and subsequent retardation of the chemical constituent occurs at the surface of the media particle, it was assumed that increasing the available surface area would improve performance. To investigate this, carbon media used was fractionated into particle ranges. The unfractionated media had 85% of

particles > 50 mesh and was used as the baseline value. Two other particle fractionations of 60/100 US mesh and 100/200 US mesh were produced. The smallest mesh size of 100/200 produced too much back pressure for the pump and was not tested. The 60/100 mesh fraction did produce a better aluminum separation from the TREE fractions, but still did not provide a true separation. Therefore, a media particle size of >50 was used since it produced similar results and produced less hydraulic back-pressure during operation.

D.5 Conventional Load/Strip Separation of REEs

A series of experiments were performed to determine the best operation conditions required for loading and stripping of REEs from an adsorptive media. These experiments differed from those described in Section C.4 because the , although similar, by viewing performance strictly from a “load and strip” perspective. Variables such as load flow rate, aspect ratio, strip bolus size and concentration, repeatability and scaling factors were investigated. Experiments were separated into Five main groupings:

- Column Hydraulic Operation
- Column Aspect Ratio
- Strip Bolus Size
- Strip Bolus Concentration
- Repeated Cycle Loading

The following sections summarize the results for each experimental grouping.

D.5.1 Column Hydraulic Operation

Empty bed contact time (EBCT) time was varied through the a packed media column at 1.5, 3, and 6 min by using flow rates of 0.8, 0.4, and 0.2 ml/min respectively. Fractional samples were collected in the column effluent and analyzed for TREE concentration to determine when REE breakthrough occurred. All three flow rates produced a breakthrough result in the same fraction collected, i.e TREE was measured in the same column fraction sample for all three flow rates. The lowest flow rate of 0.2 mL/min produced a TREE breakthrough concentration of 27 ppb (0.3% of the influent value) while TREE breakthrough concentrations at 0.4mL/min and 0.8 ml/min were 235 ppb and 693 ppb, 2.6% and 7.7% of the influent TREE concentration. In addition, the recovery of the TREES and working capacity increased with decreased influent flow rate as summarized in Table D.3.

Table D.3 Impact of influent column flow rate on TREE+Y recovery and column working capacity

Flow, mL/min	TREE+Y % recovery	Working Capacity, wt%
0.2	51%	0.18%
0.4	47%	0.17%
0.8	41%	0.15%

The results summarized in Table D.3 are logical from an intuitive perspective since a lower flow rate allows for more reaction time and mass transfer to the media surface therein increasing overall loading, therein resulting an increased amount of recovered REEs in the strip solution, i.e. the working capacity of the column. Although the lowest flow rate of 0.2 ml/min had a slightly higher working capacity (0.18% compared to 0.15% at 0.8 ml/min), it was decided that this small loss in recovery was acceptable for the purposes of fitting the experiments into single daily shifts rather than extended or double shifts.

D.5.2 Column Aspect Ratio

Column aspect ratios were varied to determine the effect of changing linear fluid velocity on the sequestration and isolation of TREEs in the influent digest liquor. Three different column aspect ratios were investigated; 1) 1.5 cm Ø x 2.8 cm L, b) 1cm Ø x 6.8cm L, and c) 1cm Ø x 3.5 cm L. Therefore, both the length and width of the columns tested varied allowing for evaluation of the impact of length for a constant diameter and width based upon a similar column height. All experiments were conducted at a pH of 4 with an influent flow rate of 0.2 ml/min. This flow rate corresponds to linear velocities of 6.8 cm/hr for the 1.5 cm diameter column and 15.27 cm/hr for the 1 cm diameter columns. The estimated EBCT for each column were 24.7, 26.7, and 13.8 minutes respectively. Results of the experiments are summarized in Figure D.31

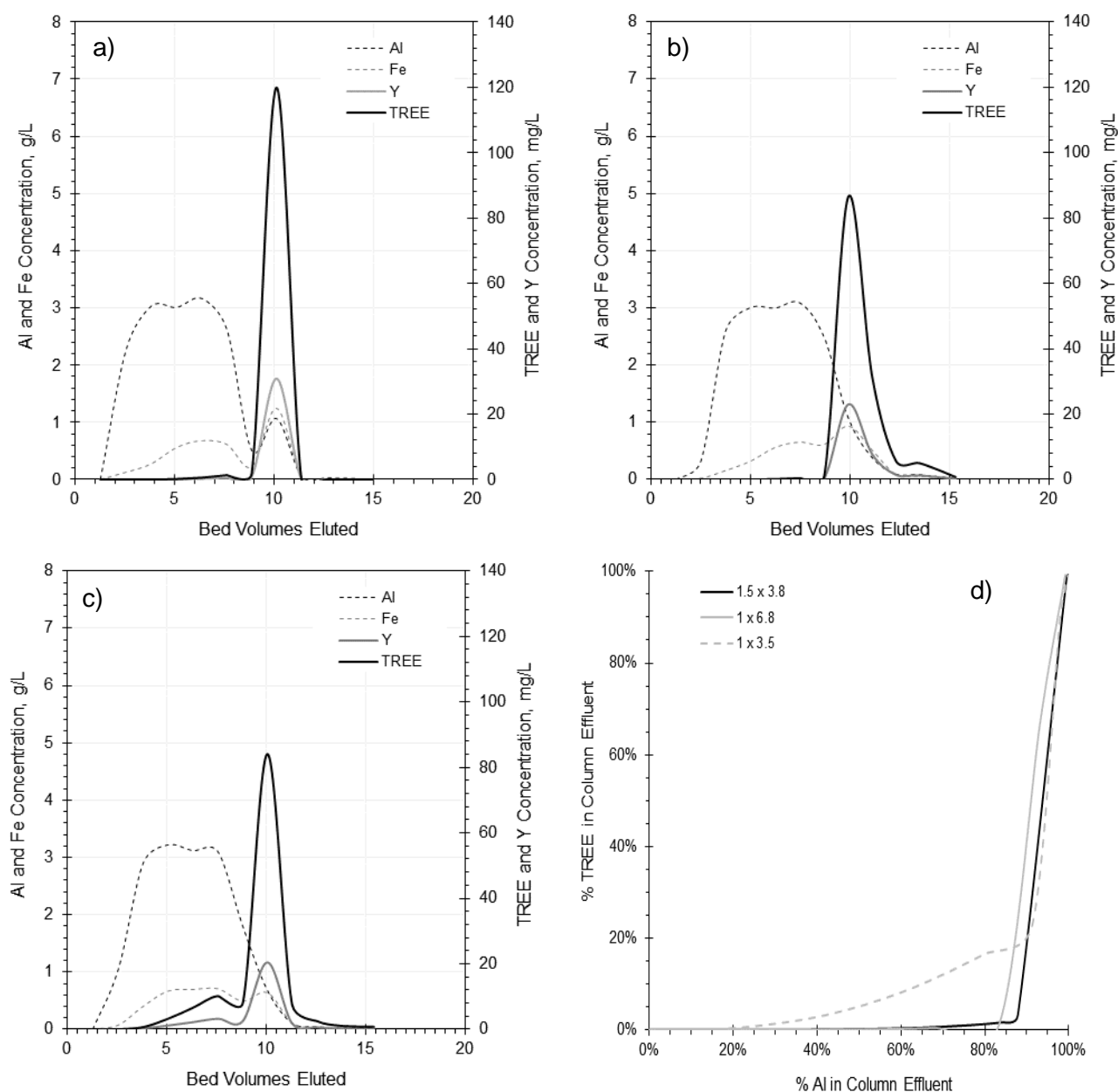


Figure D.31

Separation of Al, Fe, Y, and TREE from pH adjusted digest liquor (pH 4) through three different column sizes of a) 1.5cm Ø x 2.8cm L, b) 1cm Ø x 6.8 cm L, and c) 1cm Ø x 3.5cm L at an applied flow rate of 0.2 ml/min. Graph d) summarizes the relationship between % mass of TREE versus % mas of aluminum and iron collected in column effluents

Results in Figure D.30 show that all columns produced a similar elution trend with peak TREE concentration occurring around 10 bed volumes. In addition, most of the aluminum eluted from the columns before the bulk of TREES allowing for aluminum fractional removal. Although all columns performed similarly, the 1.5cm Ø x 2.8cm L column appeared to have the sharpest TREE elution peak. When the percentage of aluminum versus the percentage of TREE in the column effluent were compared for each column size, the two larger columns worked better than the small 1cm Ø x 3.5 cm column. The results suggested that over 80% of the aluminum in the digest liquor could be selectively removed from the TREE in solution if the proper operational conditions were used.

D.5.3 Strip Bolus Size

The volume of the HCl “strip” bolus used to remove adsorbed constituents on the activated carbon media was varied between ~4 BV (bed volumes) to ~21 BV to investigate the impact on overall TREE removal and separation of the aluminum and iron fractions in the digest liquor. The recovery of TREE versus the “strip” bolus volume is provided in Figure C.32.

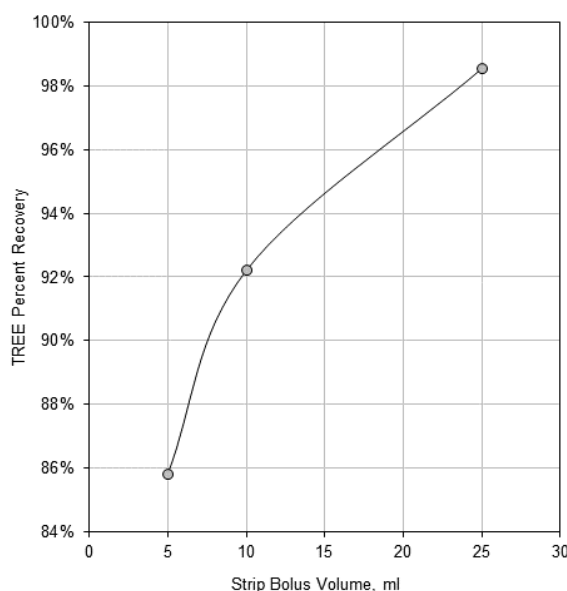


Figure D.32

Percent TREE recovery from adsorption columns versus HCl “strip” bolus size

Figure D.32 shows that TREE recovery increased with larger “strip” bolus volume. The increase in recovered TREES from a “strip” volume of 25 BV compared to 10 BV was approximately 6%. Since a 6% increase in recovered TREES required 25x the amount of “strip” bolus, it was decided that a 10 BV strip would be used since larger volumes did not appreciably increase TREE recovery.

D.5.4 Strip Bolus Concentration

The concentration of the “strip” bolus was varied to optimize the efficiency of removing adsorbed metals on the media surface and to determine if differing affinities for metals and the media would allow for selective separation of the metals. A series of experiments were completed with the HCl “strip” bolus concentration varied between 0.01M and 3M. The concentration of TREES along with Al, Fe, Y, U, and Th were measured in the column effluent before and after HCl stripping. These values were used to calculate the mass of each constituent that was loaded onto and subsequently stripped from the media column. The ratio of these values was simply converted into a recovery percentage. Results for aluminum, iron, yttrium, and TREES for each strip molarity tested are summarized in Figure D.33.

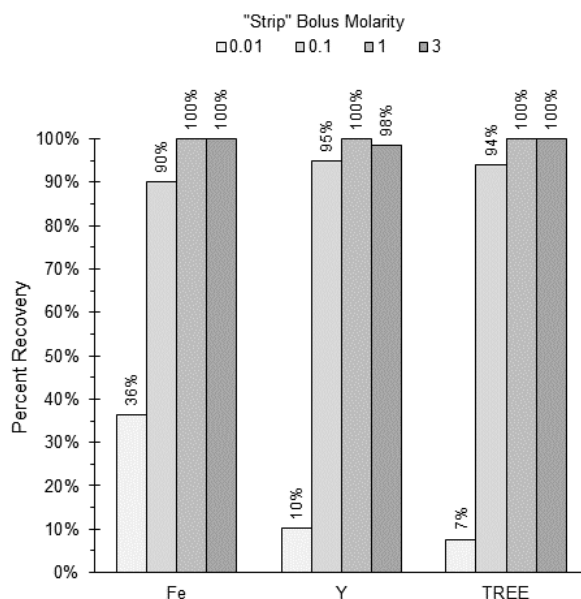


Figure D.33

Percent TREE recovery from adsorption columns versus HCl "strip" bolus concentration.

Results show, that at a strip bolus concentration of 0.01M HCl, only 7% of the TREES were recovered from the media column whereas there was 10% recovery of yttrium and 36% recovery of the iron. Aluminum data (not provided) showed that 100% recovery was obtained at all HCL bolus concentrations tested. It is clear that as the bolus strength increased, virtually 100% of the metals were removed from the media at a 1M strip bolus concentration. Based upon these results, a step gradient experiment, from 0.01M to 1M, was completed to examine if separation of Al and Fe from the remaining REEs could be achieved. Results of the test produced a fractional "cut" of the stripped metals that contained +15% REE concentration by weight with a recovery of 25%. It was clear that the step acid concentration gradient did not improve separation of aluminum and iron from REEs in solution, therefore a constant concentration strip solution of 1 molar was used during follow-on experiments.

D.5.5 Repeated Cycle Loading

An experiment consisting of repeated, multiple load and acid strip sequence was conducted to evaluate the repeatability of the load-strip process. Four cycles of loading followed by stripping with a pH equilibrating mobile phase between the acid strip solutions is shown in Figure D.34. Data showed that the TREE recovery was similar for each dual set of loads and strips. The lower concentrations witnessed in the strip during the second load-strip cycle was due to the fact that two loading and two column strips were performed with a slight variation in the influent applied to column. The data reveals that performance is repeatable and similar for each load/strip operation. A small percentage of metal that is loaded is not removed in normal stripping conditions on the first cycle. A higher recovery 97.7% was experienced in the second and fourth cycles. The mass balance TREES through the four load/strip procedures was 99.9% with a 95.3% average TREE recovery. This sequence verified that repeated column separation and concentrating of REEs was possible with the recipient's proprietary media.

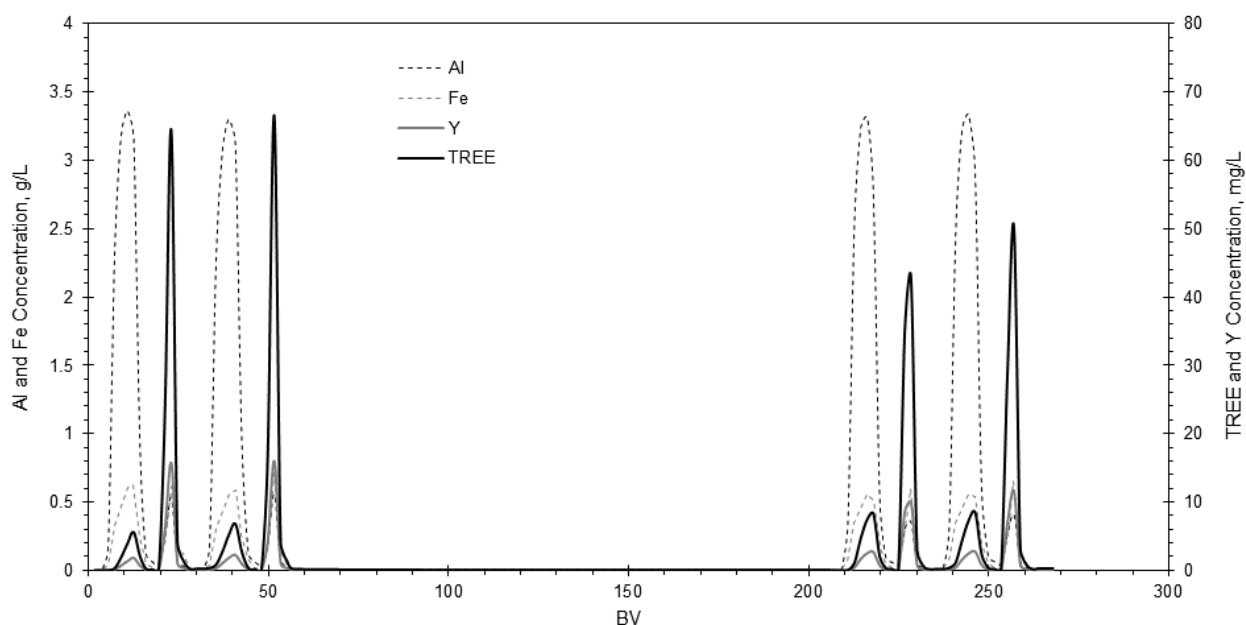


Figure D.34

Repeated load (adsorption) and strip cycles through a 1cm Ø x 3.5cm L media column showing the separation and elution consistency of Al, Fe, Y, and TREE from pH adjusted digest liquor (pH 4).

D.6 Wastewater Treatment

To demonstrate that the liquid effluent discharged from the proposed treatment process meets RCRA discharge limits, an experiment was initiated by subjecting an actual produced discharge stream (in the laboratory) to waste treatment process consisting of chemical precipitation flowed by pressure filtration. An effluent solution from the U/Th Adsorption Column that was contacted with filtered digest solution - representing the most challenging waste stream possible from the treatment process - was treated. This test simulated the highest possible concentrations of contaminants that the waste treatment system could feasibly witness. The solution pH was adjusted to 10, then filtered, pH adjusted to 3, followed by carbon adsorption and pH adjustment to 6.5 simulating a complete treated effluent solution. This process sequence provided an accurate test regarding the quality of liquid discharged from the system and whether the effluent water quality could meet RCRA standards. Table D.4 below summarizes a list of RCRA metals, allowable discharge concentrations, and the measured concentration of each metal in the discharge liquid from the waste treatment process.

Table D.4 Concentrations of RCRA metals in the process system effluent.

Metal	Discharge Limit (ppm)	Measured Conc. (ppm)	Detection Limit (ppm)	Pass (Y/N)
Arsenic (As)	5	0.0	0.000025	Y
Barium (Ba)	100	25.9	0.000020	Y
Cadmium (Cd)	1	0.0	0.000010	Y
Chromium (Cr)	5	0.0	0.00025	Y
Lead (Pb)	5	0.0	0.000005	Y
Mercury (Hg)	0.2	0.0	0.000010	Y
Selenium (Se)	1	0.0	0.000250	Y
Silver (Ag)	5	0.0		Y

Results show that the designed waste treatment sequence produces a liquid discharge that meets RCRA discharge standards. Additional metals analysis of the waste stream showed that the discharge liquid met the recipient's laboratory discharge standards to the local POTW which are more stringent than RCRA. Given this result, the designed wastewater treatment process produced water discharges that can be discharged directly to the local POTW.

D.7 Zeolite Production

Current REE market prices are low, with an average REO selling price between \$15-\$20/kg (individual REEs can be much higher). REO prices have slightly increased over the past couple of years, but still remain much lower than the high prices witnessed in 2011. Given this historical and anticipated slow market recovery, a focused effort on the investigation and development of value-added products from the production system was undertaken. Through the analysis of the process streams and residuals from the proposed treatment system, two potential products were identified; 1) the production of zeolite materials and 2) the synthesis of iron impregnated fly-ash residuals for arsenic removal. This later product was abandoned early due to experimental difficulties; however, the production of zeolite materials was performed utilizing residual process streams from the treatment system.

D.7.1 Zeolite Production Process

The zeolite production process consisted of a mixed reactor that was be heated utilizing two main process streams from the solids/liquid filtration system (pretreatment liquor and filtrate rinses) and the concentrated aluminum stream from the U/Th unit process. Under certain circumstances, inclusion of the digestion treated fly-ash and supplemental addition of aluminum was integrated into the production system. Figure D.35 provides a simplified process diagram for zeolite production.

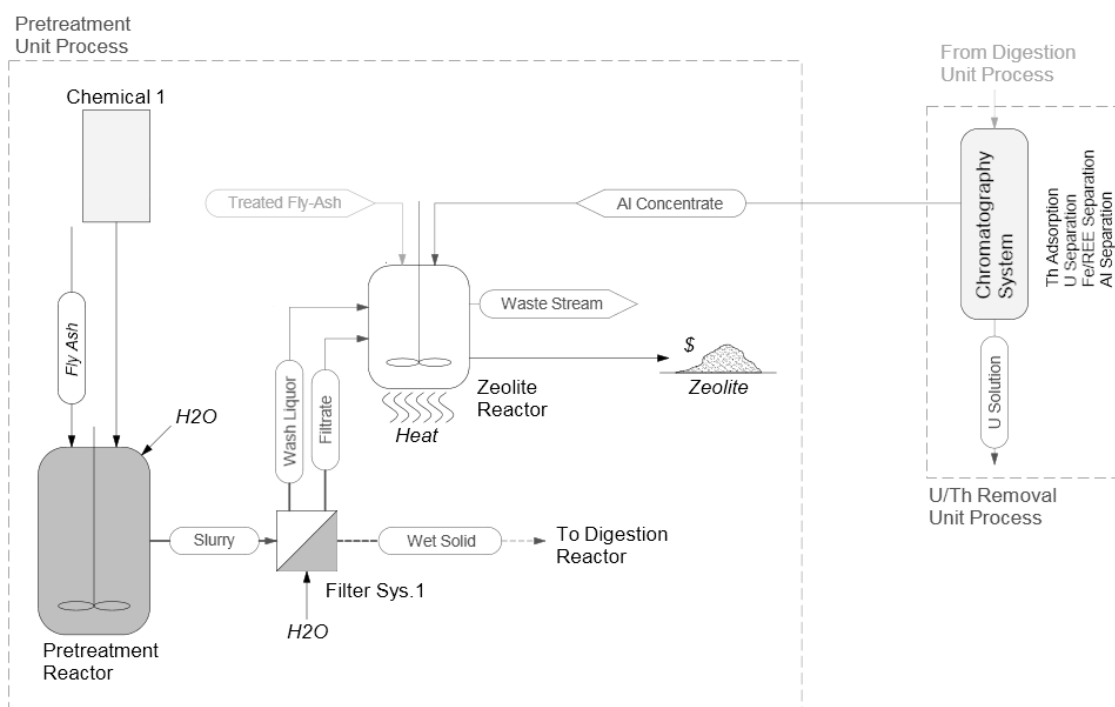


Figure D.35

Zeolite production process utilizing liquor from Pretreatment reactor, aluminum concentrate stream from the U/Th removal unit process, and post-digestion fly-ash (optional).

The process steps to produce the zeolite material were simple and straightforward. The source of the high concentration of silica is from the pretreatment reactor effluent liquor while the source of aluminum is variable

derived from either acid digested fly-ash material, the external addition of Al_2O_3 or Al^{3+} , or recycling of high concentration aluminum solutions from the U/Th unit process, or a combination thereof. The high concentration aluminum fraction from the U/Th removal process was produced by the chromatographic separation and isolation of aluminum from filtered acid digest liquor. To better understand the effects and ultimately the best combination of process solutions and substrate additives, a series of experiments were completed. Concentrations of Si and alumina in the repurposed process streams were quantified to provide a baseline to determine if additional amounts of either Al or Si were required. Based upon measured Si and Al concentrations, a series of experiments were conducted to investigate the impacts of no chemical addition, the use of aluminum oxide, the addition of aluminum, the reuse of digested fly-ash, and combinations thereof on zeolite formation from the pretreatment liquor.

- Liquor from pretreatment reactor (PL)
- Liquor from pretreatment reactor + Al_2O_3 (PL+ Al_2O_3)
- Liquor from pretreatment reactor + Al^{3+} (PL+ Al_3)
- Liquor from pretreatment reactor + acid digested fly-ash (PL+TFA)
- Liquor from pretreatment reactor + acid digested fly-ash + Al_2O_3 (PL+TFA+ Al_2O_3)

The solutions were heated to 100°C and maintained at that temperature for minimum of 96 hours. The mass of the inputs for each test (i.e. Al_2O_3 , Al^{3+} , and/or TFA) were subtracted from the measured zeolite mass at the end of the experiment to determine the mass of zeolite “produced”. The ratio of the mass of zeolite produced to the mass input of the additives was also calculated to evaluate which combination of solutions produced the highest mass of product compared to chemical inputs. Figure D.36 summarizes the results.

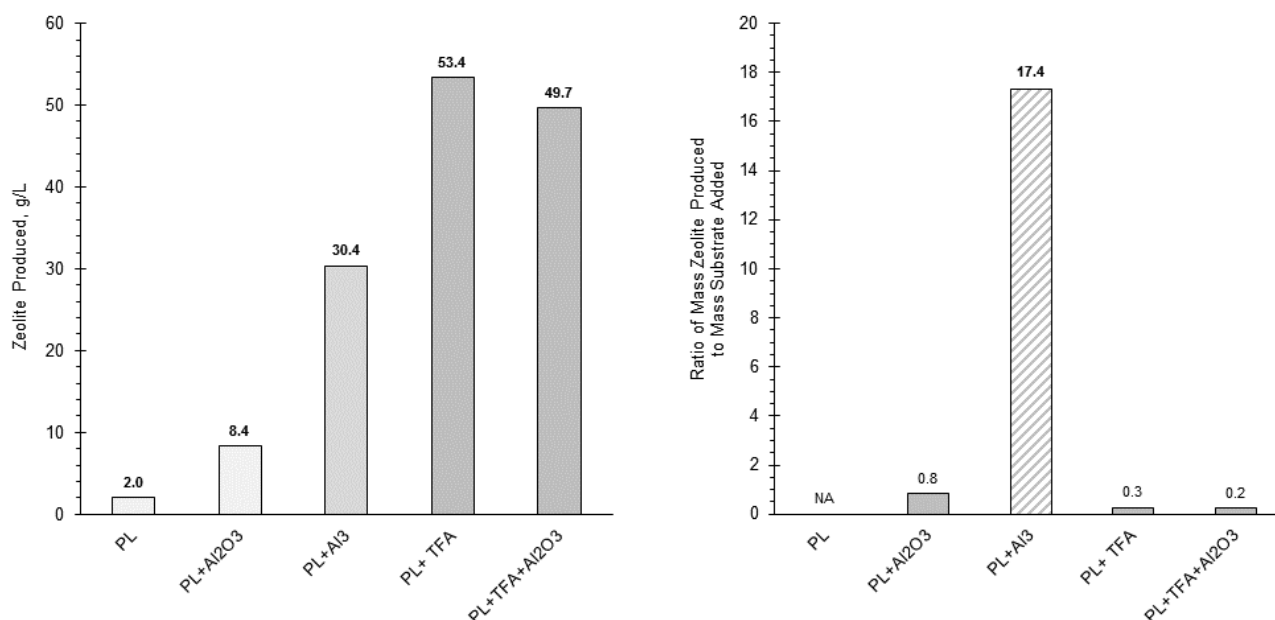


Figure D.36

Amount of zeolite produced for each test solution (PL = pretreatment liquor, Al_2O_3 = aluminum oxide, Al_3 = aluminum added, TFA = treated fly-ash) and mass ratio of zeolite produced to mass of substrate added (Al_2O_3 , TFA, and Al_3).

The results summarized in Figure D.36 show that the use of heat only on the pretreatment liquor did not produce an appreciable quantity of zeolites. The addition of aluminum oxide resulted in 4x the production of the raw pretreatment liquor while the addition of aluminum resulted in 15x the production. It is important to note that the aluminum used in the experiment was the high-purity aluminum fraction stream from the chromatography system used to separate U/Th from the acid digest liquor. The solutions in which fly-ash was

added produced the highest production values; however, this was primarily due to the fly-ash mass. When the amount of zeolite produced is compared to the mass of external inputs into the zeolite production unit, it is clear that the pretreatment liquor with the recycled aluminum stream produces a much higher product ratio, 17.4 compared to 0.2 to 0.8 for the other solutions. This is an exciting result considering the fact that by simply combining two waste streams and heating the solution can produce approximately 30 g/L of product. To put this into perspective, this translates into roughly 59-kg zeolite produced from 1-tonne of fly-ash compared to 0.2 kg-REO extracted per 1-tonne fly-ash.

D.7.2 Type of Zeolite Produced

A solid sample of zeolite produced (PL+Al3) was analyzed by X-ray diffraction (XRD) to determine the chemical and structural composition. Results of the analysis are provided in Figure C.37.

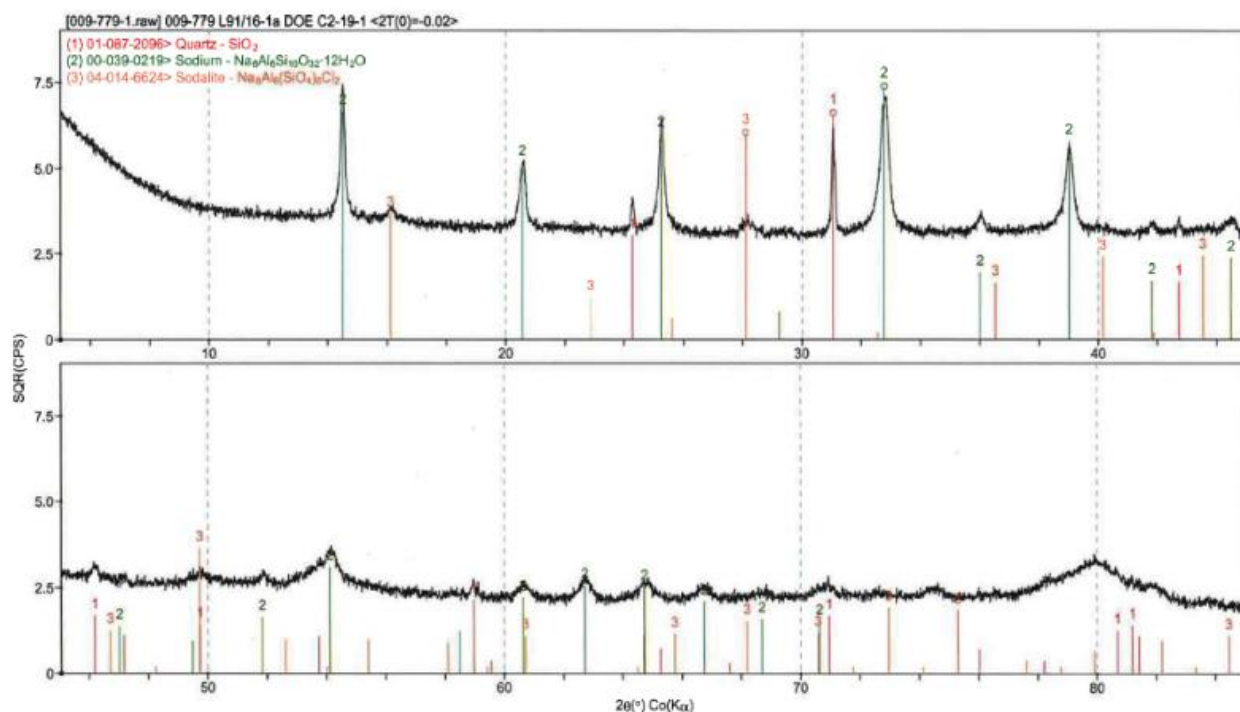


Figure D.37

XRD analysis of zeolite produced by combining the pretreatment liquor and recycled aluminum stream followed by heating to 100°C for 96 hours. Data indicates a P1 type zeolite was most likely produced.

XRD results indicated that the zeolite produced was most likely a hydrated sodium aluminum silicate (Na-P1) with a generalized formula of $\text{Na}_6\text{Al}_6\text{Si}_{10}\text{O}_{32} \cdot 12\text{H}_2\text{O}$. Zeolite Na-P1 is a common product of zeolitization and has a GIS (Gismondine) structural frame work with an approximate pore size opening of 5Å. The cation exchange capacity (CEC) is relatively high between 2.6 and 2.8 meq/g. This high CEC lends its use in a wide variety of applications including the removal of heavy metals from drinking water, removal of radium isotopes, adsorption of acid compounds from used transfer oil in refining operations, fertilizer and water adsorption for agricultural, etc. This flexibility of zeolite P1 into multiple market sectors provides an opportunity to produce a value-added product that has existing marketing chains. Therefore, the production of this zeolite and the ability to modify the zeolite produced with simple dopants may provide significant revenue generation.

E.1 Proposed Process Design

The REE extraction and production process developed during Task 3 (see Section D) project utilizes six fundamental unit operations; 1) fly-ash pretreatment to enhance REE extraction, 2) REE extraction by acid digestion, 3) U/Th removal, 4) REE separation and concentration by carbon adsorption and column chromatography, 5) REE oxide production, and 6) residuals treatment and discharge. Secondary processing steps to manage process residuals and additional processing techniques to produce value-added products were integrated into the final overall process approach. These secondary steps were not only necessary to manage residuals, but also provided potential additional revenue streams. A generalized process approach is summarized in Figure E.1.

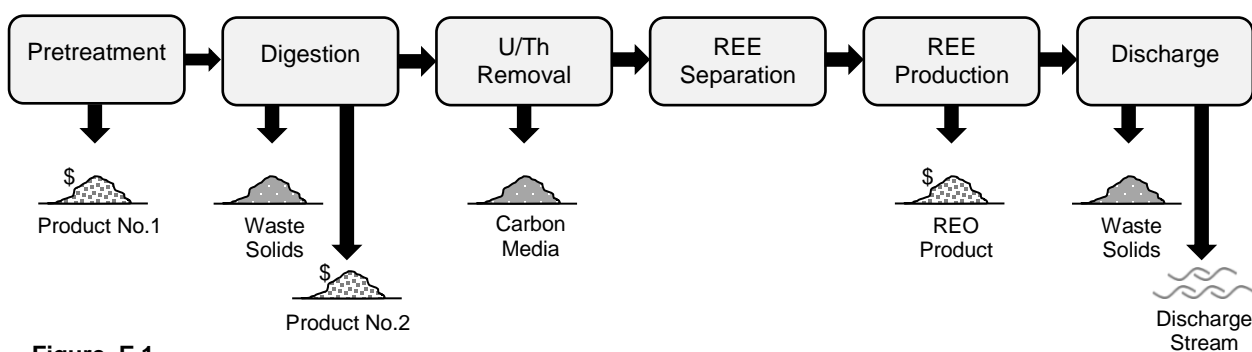


Figure E.1

Generalized REE extraction process summarizing the six (6) main unit operations highlighting operations that produce value products and/or waste residuals.

The main inputs into the process system other than fly-ash material include acid solutions, base solution, water, carbon adsorbent, and energy (both electrical and natural gas). The process produces three value product streams, two solids waste streams, one carbon media discharge (U/TH loaded), and one liquid discharge stream that meets requirements for discharge into a receiving water body. A mass balance of input materials and the quantities of products produced, waste solids generated, and liquid waste discharged from the system was quantified. The system was designed to minimize residuals exiting the system incorporating recycling of process streams for reuse and conversion of residual process streams into value-added materials.

Detailed process design allowed for accurate evaluation of material mass balances and estimation of operating costs of each operational unit and for the overall system. In an effort to simplify process design and evaluation of operational costs, a target system size of 1,000-kg of fly-ash per day was selected as a base-line design constraint. Using this system size, detailed mass inputs and outputs as well as estimated operating costs for the proposed treatment system were calculated.

The following sections summarize the proposed process and a preliminary economic evaluation of the technology.

E.1.1 Final Process Design

Although the main objective of the process was the production of REOs, the main goal of the workable process design was to produce a product or group of products that could generate a positive revenue stream, or at least minimize overall costs. Given current REO market prices, there were additional economic pressures placed on the system design to generate additional revenue streams. This critical requirement guided the development of the entire process system to utilize residual streams that otherwise may have been discarded and to reuse as many process effluents as possible. A final process that met these design constraints is presented in Figure E.2.

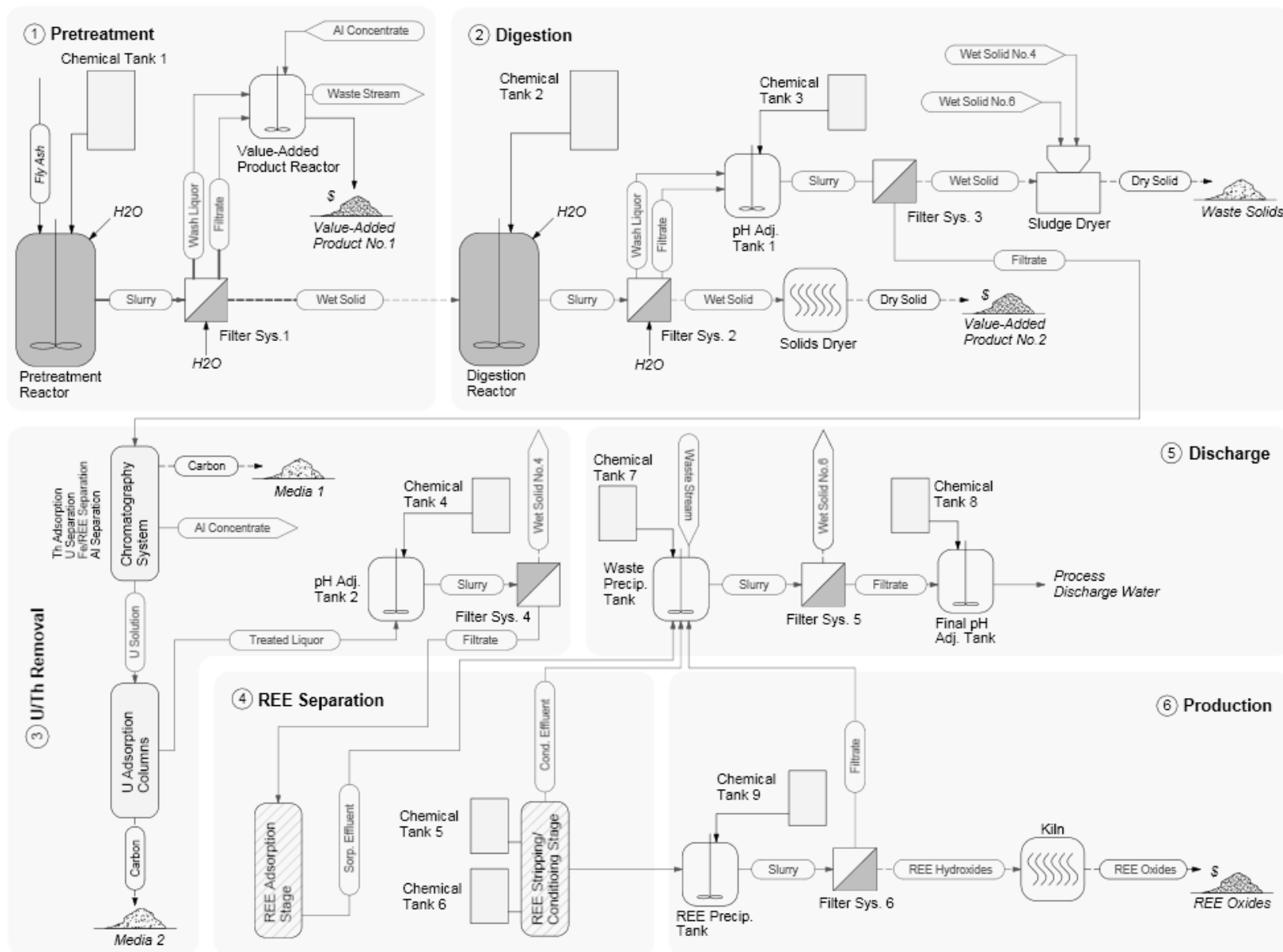


Figure E.2

Detailed process design of the REE extraction process developed during this project.

E.1.2 Final Process Mass Balance

Detailed process design shown in Figure E.2 allowed for accurate evaluation of material mass balances and estimation of operating costs of each operational unit and for the overall system. In an effort to simplify process design and evaluation of operational costs, a target system size of 1,000-kg of fly-ash per day was selected as a base-line design constraint. Using this system size, detailed mass inputs and outputs as well as estimated operating costs for the proposed treatment system were calculated. Actual consumable usage, product generation rates, and required processing times that were witnessed during laboratory operations were used within all design calculations therein providing the most accurate design possible. Using this detailed analysis, a system mass balance was performed with regards to all inputs and outputs. Results are summarized in Figure E.3.

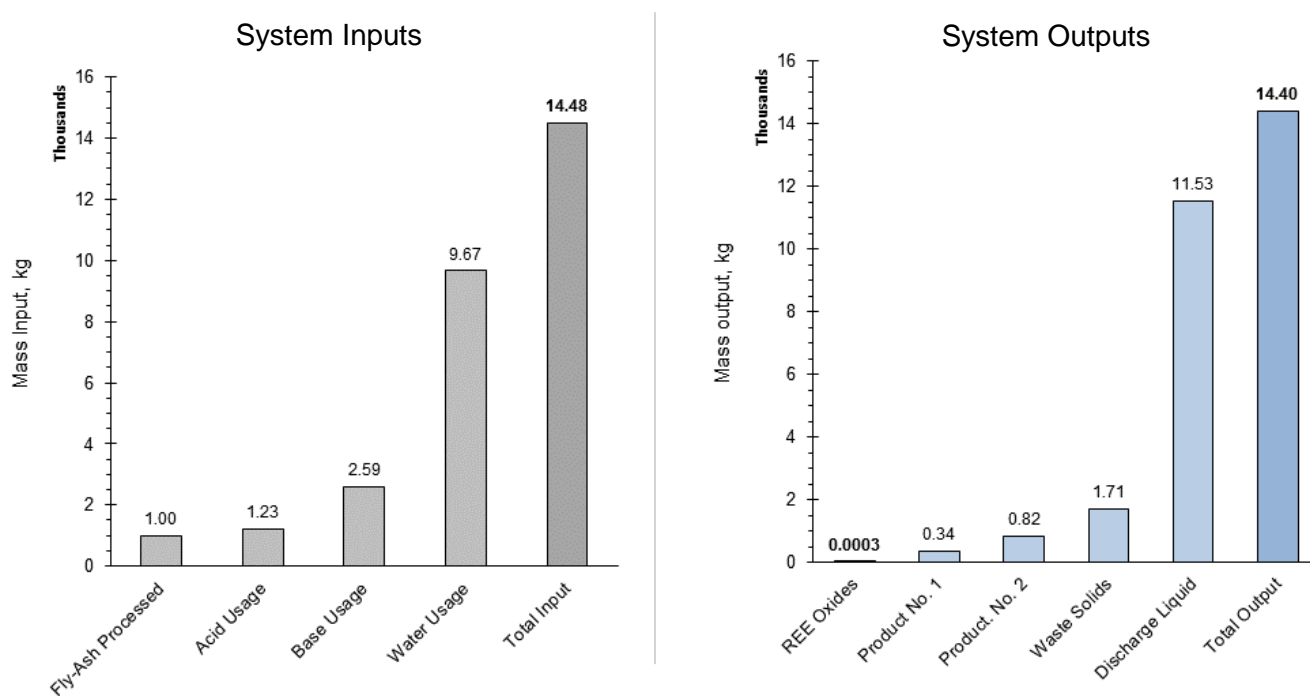


Figure E.3

Summary of mass inputs and outputs from the proposed treatment system for a 1,000-kg per day fly-ash treatment system capacity.

Results provided in Figure E.3 indicate that for a 1,000 kg fly-ash processing system, the estimated total mass input and output from the system are within 0.5%, indicating that the design calculations summarized in Appendix B provide an accurate mass balance accounting. This was critical first step in analysis and optimization of the system design. Based on mass balance analysis, the two major inputs into the system are base chemical usage and water consumption (18% and 67% of total mass inputs respectively).

From an overall perspective, the mass ratios of fly-ash to consumable usage for acid, base, and water (without consideration for recycling and reuse) are approximately 1:1.2, 1:2.6, and 1:9.7 respectively. The Excel process design spreadsheet that provided the information in Figure E.3 was used to calculate system mass balances up to a system size of 200 tonnes/day. Results showed that the mass ratios above are relatively consistent throughout the scale-up process. Therefore, these ratios were used to estimate consumable usage for a variety of system sizes used in economic analysis.

E.2 Process Recovery and Yield

The project target for REE recovery efficiency through the entire treatment process was >25%. This value is simply calculated as the mass of recovered TREE in the process product compared to the amount of TREE that was present in the original fly-ash material. During the course of the project, over 100 experiments were completed to determine the overall REE extraction efficiency in the pretreatment and digestion unit operations at small-scale and to determine REE loss through subsequent unit operations until the final product was produced. Follow-on large-scale tests (up to 1-kg fly ash batch sizes) were completed to ascertain scalability of each unit operation and to further refine design and operational parameters. The following sections summarize the REE extraction and recovery efficiencies for each unit operation within the proposed process.

E.2.1 REE Extraction – NaOH Pretreatment

Two, 200-g fly-ash samples were pretreated with base solution (designated as Test 1 and Test 2). Test 1 material was used in Test 1.1 and Test 1.2 while Test 2 material was used in Test 2.1 and Test 2.2. For both test materials, pretreatment consisted of a 3M base solution at a 30wt% solids loading heated to a temperature of 85°C for 4 hours. After pretreatment operations, the filtered liquid was analyzed by ICP-MS to determine what metals were leaching from the fly-ash during base pretreatment. Table E.1 below summarizes the results.

Table E.1 Pretreatment – Effluent Liquor Characteristics

Effluent Concentration (mg/L)	Test 1	Test 2
Mg	298.2	136.5
Al	310.3	493.5
Si	6,351	8,722
P	3.21	0
Ca	1,313	241.1
V	42.4	44.6
Mn	0	14.1
Fe	0	0
Ni	0	0.68
Zn	0	66.5
Ge	6.1	8.27
As	11.4	15.7
Mo	7.7	8.24
Pb	0.3	2.98
U	0.2	0
Th	0	0
TREE+Y	0	0

Results summarized in Table E.1 indicated that the primary constituents leached from fly ash during base chemical pretreatment are silica, aluminum, and calcium. No extraction of TREES was witnessed during this treatment step.

E.2.2 REE Extraction – HCl Digestion

As stated in the previous section, two 200-g fly-ash samples were pretreated with base solution, designated as Test 1 and Test 2. Test 1 material was subsequently used in Test 1.1 and Test 1.2 while Test 2 material was used in Test 2.1 and Test 2.2. For both test materials, acid digestion used a 2.67M acid solution at a 20wt% solids loading heated to a temperature of 85°C for 4 hours. After acid digestion, the filtered liquid was analyzed

by ICP-MS to determine what metals were extracted from the fly-ash during treatment. Table E.2 below summarizes the results.

Table E.2 Acid Digestion – Effluent Liquor Characteristics

Influent Concentration (mg/L)	Test 1.1	Test 1.2	Test 2.1/2.2
Mg	140	175	230
Al	2,835	2,998	4,414
Si	279	440	98
P	6.6	9.0	14.4
Ca	319	338	473
V	6.4	7.9	12.4
Mn	6.1	10.4	22.8
Fe	2,721	3,114	5,513
Ni	3.7	18.3	63.2
Zn	8.2	9.4	13.1
Ge	0.9	1.5	1.4
As	0.3	0.4	0.7
Mo	0.1	0.8	2.4
Pb	3.2	3.3	4.8
U	1.3	1.2	1.8
Th	0.8	0.7	1.1
TREE+Y	15.4	16.6	23.2

Results summarized in Table E.2 indicate that significant amounts of aluminum and iron were extracted from the fly ash source during acid digestion. Not surprisingly, moderate amounts of calcium, magnesium, and silica were also extracted. The critical result shown in Table E.2 is the extraction of TREEs from the pretreated fly-ash. Based upon lithium borate fusion analysis of the selected fly-ash material, digestion results from each experiment listed in Table E.2 corresponds to TREE extraction efficiencies of approximately 33, 36, and 25% (Figure E.4).

Results shown in Figure E.4 indicate low TREE+Y recovery rates, i.e. lower than previous attained values that were between 50 to 75%. It was determined that the lower than anticipated extractions efficiencies from the digestion process were due to higher solids loading (soln. wt%) utilized in the pretreatment process. When the solids loading was maintained around 10wt% during pretreatment, the TREE recovery rates increase to greater-than 50%.

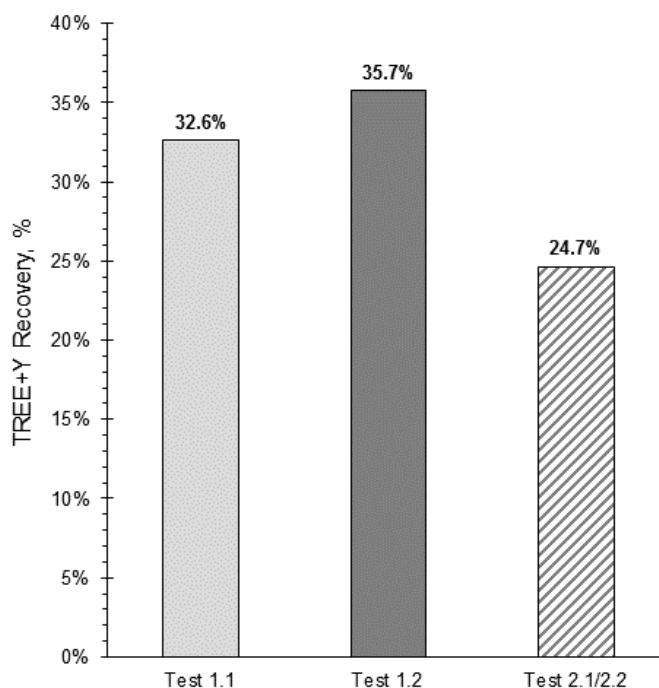


Figure E.4
Extraction efficiency of TREE+Y from fly ash material for all three large-scale digestion experiments.

E.2.3 REE Extraction – U/Th Removal

The removal of uranium and thorium (U/Th) from the digestion liquors was necessary to produce a REE solutions that could be treated to produce an REE product that had little to no radionuclide material. The strategy for removing U/Th from the digestion liquor was to pH adjust the liquor to pH 2.5, filter the solution, and then contact the solution with an adsorption bed to remove U/Th. The pH adjustment was to maximize U/Th sorption onto a stationary media while simultaneously limiting the adsorption of REE species.

As stated previously, two 200-g fly-ash batches were pretreated and designated as Test 1 and Test 2. Test 1 material was separated into two equal fractions of 100g each and were digested to produce liquor volumes of 560-ml each. These experimental samples were designated Test 1.1 and Test 1.2. The Test 2 digested liquor sample (600-ml) was separated into two equal volume fractions of 300-ml, designated 2.1 and 2.2 respectively. Test 1 and Test 2 experimental adsorption columns used the same dimensions, type and quantity of adsorptive material, but differed in applied flow rate. Test 1 column utilized and high flow rate of 6.9 ml/min while Test 2 used a low flow rate of approximately 0.9 ml/min. Column operational parameters are summarized in Table E.3:

Table E.3 U/Th Sorption Columns – Operational Parameters

	Test 1.1	Test 1.2	Test 2.1	Test 2.2
diameter (cm)	1.5	1.0	1.5	1.0
length (cm)	17	15	17	15
media (g)	11.2	5.6	11.2	1.01
media height (cm)	17	15	16	3.5
L/D ratio	11.3	15	10.7	3.5
flow rate (ml/min)	2.15	0.95	2.15	0.956
velocity ^A (cm/min)	1.21	1.21	1.21	1.22
EBCT (min.)	14.0	12.4	13.1	2.9

A – Based upon column diameter and flow rate

All experiments were conducted with the same fluid velocity (approximately 1.21 cm/min) with variable L/D aspect ratios for Test 1.1 and Test 2.1 at approximately 11:1, Test 1.2 at 15:1, and Test 2.2 at a ratio of 3.5:1. Tests 1.1 and 2.1 were designed to provide excess adsorptive media to virtually guarantee 100% removal of U/Th while tests 1.2 and 2.2 were designed to use low amounts of adsorptive media to ascertain adsorptive capacities for uranium and thorium.

All tests were conducted in a “load-strip” mode in which a mobile phase is introduced into the column followed by a specific volume of pH adjusted digest liquor (loading), then a small volume of mobile phase followed by a small volume of concentrated acid (strip - 3M HCl), and finally a small amount of mobile phase. For Tests 1.1, 1.2, and 2.1, only a bulk sample was obtained after acid stripping while during Test 2.2, fractions were collected for analysis. Influent solution characteristics for each test are summarized in Table E.4.

Table E.4 U/Th Sorption Columns – Influent Liquor Characteristics

Influent Concentration (mg/L)	Test 1.1 ^A	Test 1.2 ^A	Test 2.1 ^B	Test 2.2 ^B
Al	2,470	1,975	5,028	5,875
Fe	495	836	3,370	3,845
U	0.71	0.79	1.39	1.54
Th	0.002	0.010	0.002	0.009
TREE+Y	14.1	13.8	28.7	29.5

A- Pretreatment: 30wt%, 3M base; Digestion: 20wt%, 2.67M acid

B- Pretreatment: 30wt%, 3M base; Digestion: 30wt% solids, 3M acid

It is evident from Table E.4 there was a +130% difference in aluminum concentration, a +440% difference in Fe, and a +110% increase in TREE+Y concentrations between Test 1.1, 1.2 and Test 2.1, 2.2. These differences in separation performance was due to alterations in the digestion procedure in which the acid concentration was increased from 2.87M to 3M and the solids concentrations was increased from 20wt% to 30wt%.

Table E.5 below summarizes U/Th mass balances through the adsorption columns for all large-scale tests.

Table E.5 U/Th Sorption Columns – Removal Performance

	U Inf. (ug)	U Eff. (ug)	U Removal	Th Inf. (ug)	Th Eff. (ug)	Th Removal
Test 1.1	708	0	100%	1.7	0	100%
Test 1.2	796	1.2	99.8%	10	3.6	64%
Test 2.1	418	0	100%	0.6	0	100%
Test 2.2	461	389	16%	2.7	2.1	22%

The data in Table E.5 shows that virtually 100% of the uranium contacted with the sorption columns in Tests 1.1, 1.2, and 2.1 was removed. Only 16% of the uranium was removed in Test 2.2 - the test with the lowest amount of adsorptive media used to determine adsorptive capacity. Thorium followed a similar trend with 100% of thorium removed in the columns designed to remove all of the U/Th, while the other columns with lower amounts of adsorptive media did not achieve 100% thorium removal. It was clear that Test 2.2 required closer scrutiny to investigate operational parameters that could explain the poor witnessed performance. Figure E.5 illustrates the adsorptive response of uranium through the column in Test 2.2.

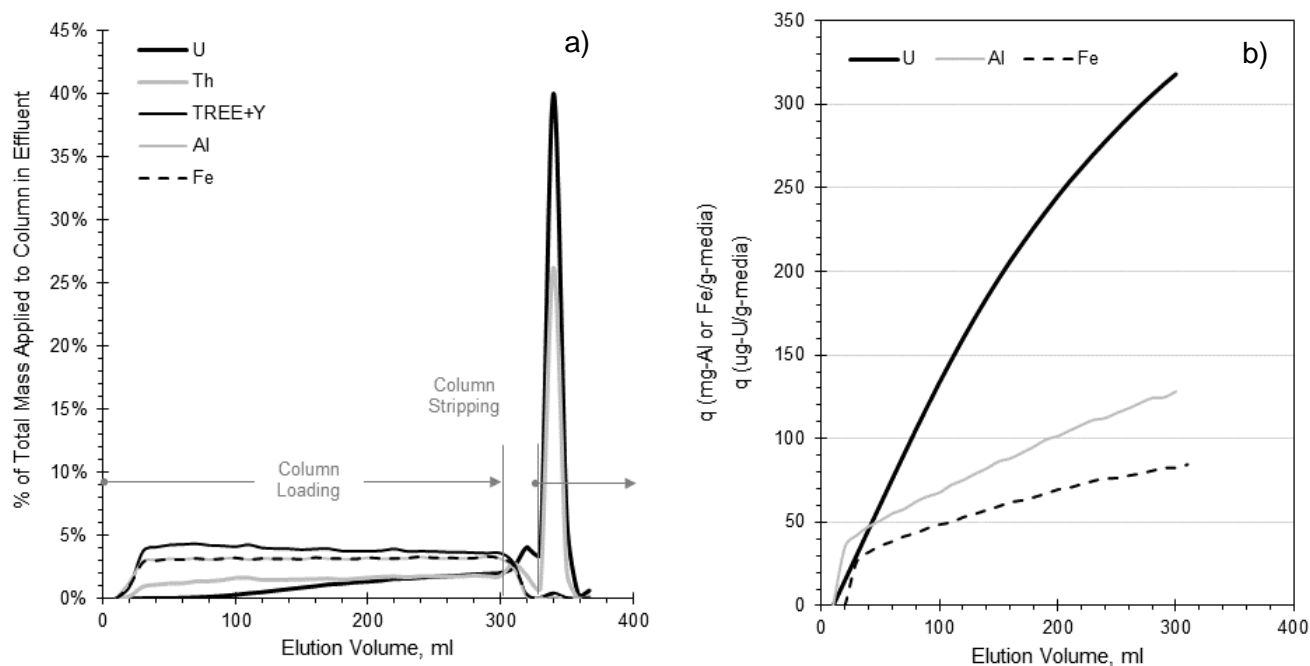


Figure E.5

a) Percentage of the total mass of each measured constituent (TREE+Y, Al, Fe, U, and Th) contacted with the carbon column during Test 2.2 (1 cm x 3.5 cm, 1.01 g-carbon, 0.96 ml/min) that was measured in the column effluent during different stages of column operation, and b) the relationship between adsorbed amount of each constituent onto adsorptive media during loading phase of column operation.

Results summarized in Figure E.5 show a rapid increase in Al and Fe concentration measured in the column effluent during loading with a slow increase in U and Th effluent concentration until loading is halted. The figure also illustrates the sharp increase in measured concentrations of U and Th when the fluid front of the acid strip

solution exits the column. The amounts of each constituent adsorbed onto the column media compared to the total mass contacted to the column and the amount of adsorbed removed during acid stripping are presented in Figure E.6.

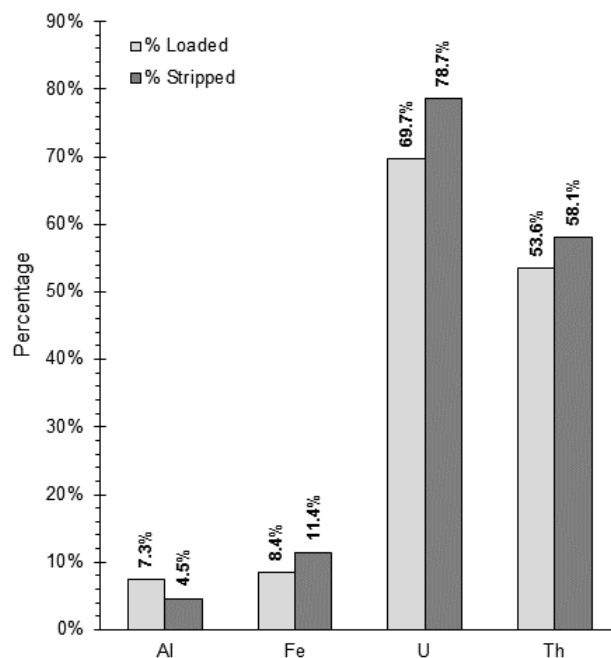


Figure E.6
Percentage of the total mass of each measured constituent adsorbed onto the media column and the amount of the loaded mass that was removed during acid stripping.

Approximately 70% of the U and 54% of the Th contacted with the column was adsorbed by the column media. Aluminum and iron had a lower loading, approximately from 7% to 8%. Measured TREE+Y concentration indicated that no TREE+Y loaded onto the sorption media. Based upon mass balances, only 4.5% of the loaded Al and 11% of the loaded Fe were removed during acid stripping. The cause for this low removal is not fully known. However, roughly 79% of the loaded uranium and 58% of the loaded thorium were removed from the column during acid stripping.

E.2.4 REE Extraction – REE Extraction Columns

A critical factor in the proposed system and an essential performance metric of the entire project was the separation and subsequent concentration of REEs within the process to a level in which a product can be produced with >2%RE. To meet his challenge, the recipient employed an approach where the liquor stream from the acid digestion system was first pH adjusted/filtered then contacted through an adsorption bed to remove U/Th (see Section E.2.3). The U/Th free solution was then pH adjusted again to approximately pH 4 to maximize REE sorption onto a different adsorption bed where REEs were subsequently sequestered and concentrated in a solution stream that was then pH adjusted to precipitate the recovered REEs as a product.

As stated in previous sections, two separate 200-g fly-ash batches were processed through the entire process in sequential order to mimic a larger, on-site batch process. The first batch was labeled Test 1.1 while the second batch was labeled Test 2.1. Digestion of these two batches resulted in similar treated liquor characteristics. Test 1.1 and Test 2.1 experimental adsorption columns used the same dimensions, used the same type and quantity of adsorptive material, but differed in applied flow rate. Test 1.1 column utilized and high flow rate of 6.9 ml/min while Test 2.1 used a low flow rate of approximately 0.9 ml/min. Column operational parameters are summarized in Table E.6.

Table E.6 REE Sorption Columns – Operational Parameters

	Test 1.1	Test 2.1
diameter (cm)	1.5	1.5
length (cm)	20	20
media (g)	17.5	17.5
media height (cm)	20	20
flow rate (ml/min)	6.9	0.9
velocity ^A (cm/min)	3.9	0.51
EBCT (min.)	5.1	39.3

A – Based upon column diameter and flow rate

Both tests were conducted in a “load-strip” mode in which a mobile phase was introduced into the column followed by a specific volume of REE containing solution (loading), then a small volume of mobile phase followed by a small volume of concentrated acid (strip - 3M HCl), and finally a small amount of mobile phase. Influent solution characteristics for each test are summarized in Table E.7.

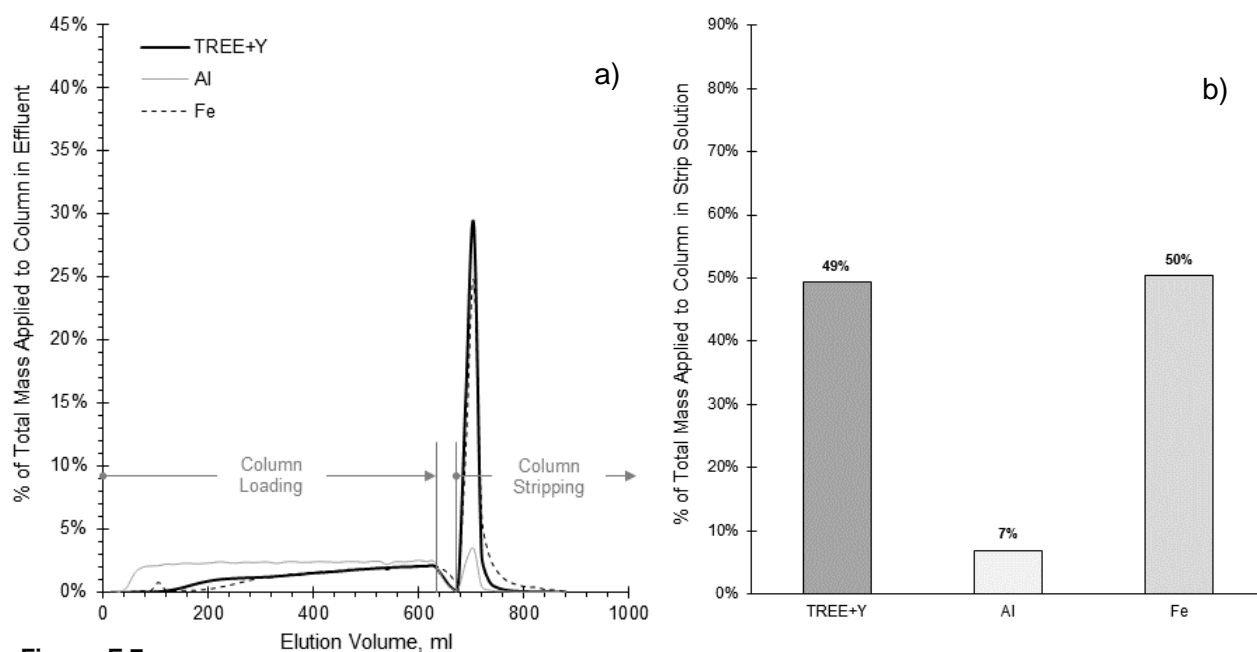
Table E.7 REE Sorption Columns – Influent Liquor Characteristics

Influent Concentration (mg/L)	Test 1.1 ^A	Test 2.1 ^B
Al	3,093	4,025
Fe	675	2,626
TREE+Y	19.4	22.1

A- Pretreatment: 30wt%, 3M base; Digestion: 20wt%, 2.67M acid

B- Pretreatment: 30wt%, 3M base; Digestion: 30wt% solids, 3M acid

Table E.7 shows there was 30% increase in aluminum concentration, a 300% increase in Fe, and a 14% increase in TREE+Y concentrations between Test 1 and Test 2. Although the REE concentration and extraction efficiency increased with a stronger acid solution during digestion, the increase in Al and Fe made REE purification more challenging. Figure E.7 summarizes column loading and stripping results for Test 1.

**Figure E.7**

a) Percentage of the total mass of each measured constituent (TREE+Y, Al, or Fe) contacted with the carbon column during Test 1 (1.5 cm x 20cm, 17.5 g-carbon, 6.94 ml/min) that was measured in the column effluent during different stages of column operation, and b) the percentage of the total mass of each constituent contacted with the column present in the “strip” solution, i.e. overall recovery through REE sequestration unit process.

Results summarized in Figure E.7-a) clearly show a rapid increase in Al concentration measured in the column effluent during loading with a slow increase in Fe and TREE+Y effluent concentration until loading is halted. The figure also illustrates the sharp increase in measured concentrations when the fluid front of the acid solution exits the column. The amount of each constituent adsorbed onto the column media compared to the total mass contacted to the column is presented in Figure E.7-b). Approximately 50% of the TREE+Y and Fe contacted with the column was adsorbed by the column media. Aluminum had a lower loading, approximately 7%. This low TREE+Y sequestration was most likely due to the high fluid flow rate through the adsorption column.

Based upon mass balances, 78% of the loaded Al, 95% of the loaded Fe, and 100% of the loaded TREE+Y was removed from the adsorption media during acid stripping. This was important since TREE+Y recovery efficiency was critical and also the fact that the amount of remaining metals on the adsorptive media may have decreased overall adsorptive capacity between successive loading-stripping operations. Previous experiments showed that TREE+Y capacity and stripping efficiencies were not affected by sequential load-strip operations.

Figure E.8 summarizes column loading and stripping results for Test 2.

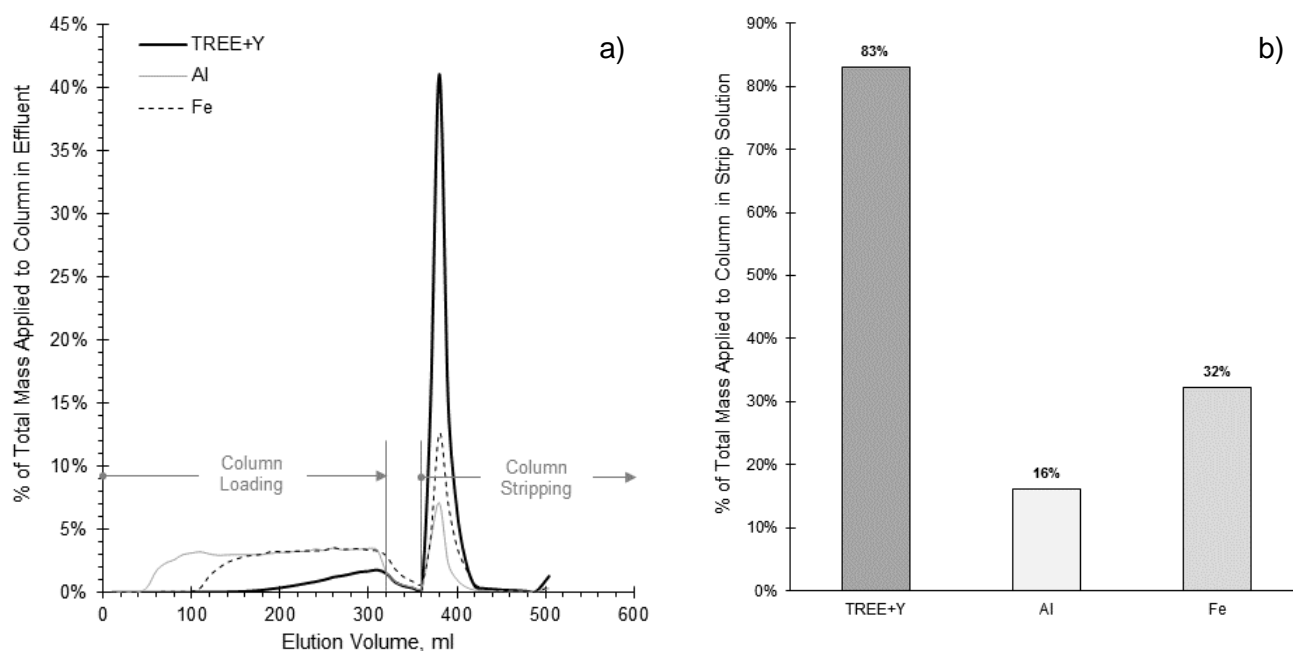


Figure E.8

a) Percentage of the total mass of each measured constituent (TREE+Y, Al, or Fe) contacted with the carbon column during Test 2 (1.5 cm x 20cm, 17.5 g-carbon, 0.91 ml/min) that was measured in the column effluent during different stages of column operation, and b) the percentage of the total mass of each constituent contacted with the column present in the "strip" solution, i.e. overall recovery through REE sequestration unit process.

Results summarized in Figure E.8-a) show a similar trend as Figure E.7-a) with a rapid increase in Al concentration measured in the column effluent during loading with a slow increase in Fe and TREE+Y effluent concentration until loading is halted. However, Fe loading occurred more rapidly in Test 2 compared to Test 1. This was likely due to the higher influent Fe concentration and the slow column flow rate (i.e. longer contact time through the column). Figure E.8 validates the response from Test 1 in that a sharp increase in measured concentrations occurs when the fluid front of the acid solution exits the column. The amount of each constituent adsorbed onto the column media compared to the total mass contacted to the column is presented in Figure E.8-b). Approximately 83% of the TREE+Y, 32% of the Fe, and 16% of the aluminum contacted with the column was adsorbed by the column media. This TREE+Y sequestration is higher than Test 1 showing that increased column contact time increased TREE+Y adsorption.

A comparison of the amount of Al, Fe, and TREE+Y removed in the column (mg-constituent per g-adsorptive media) was completed. Results are summarized in Figure E.9.

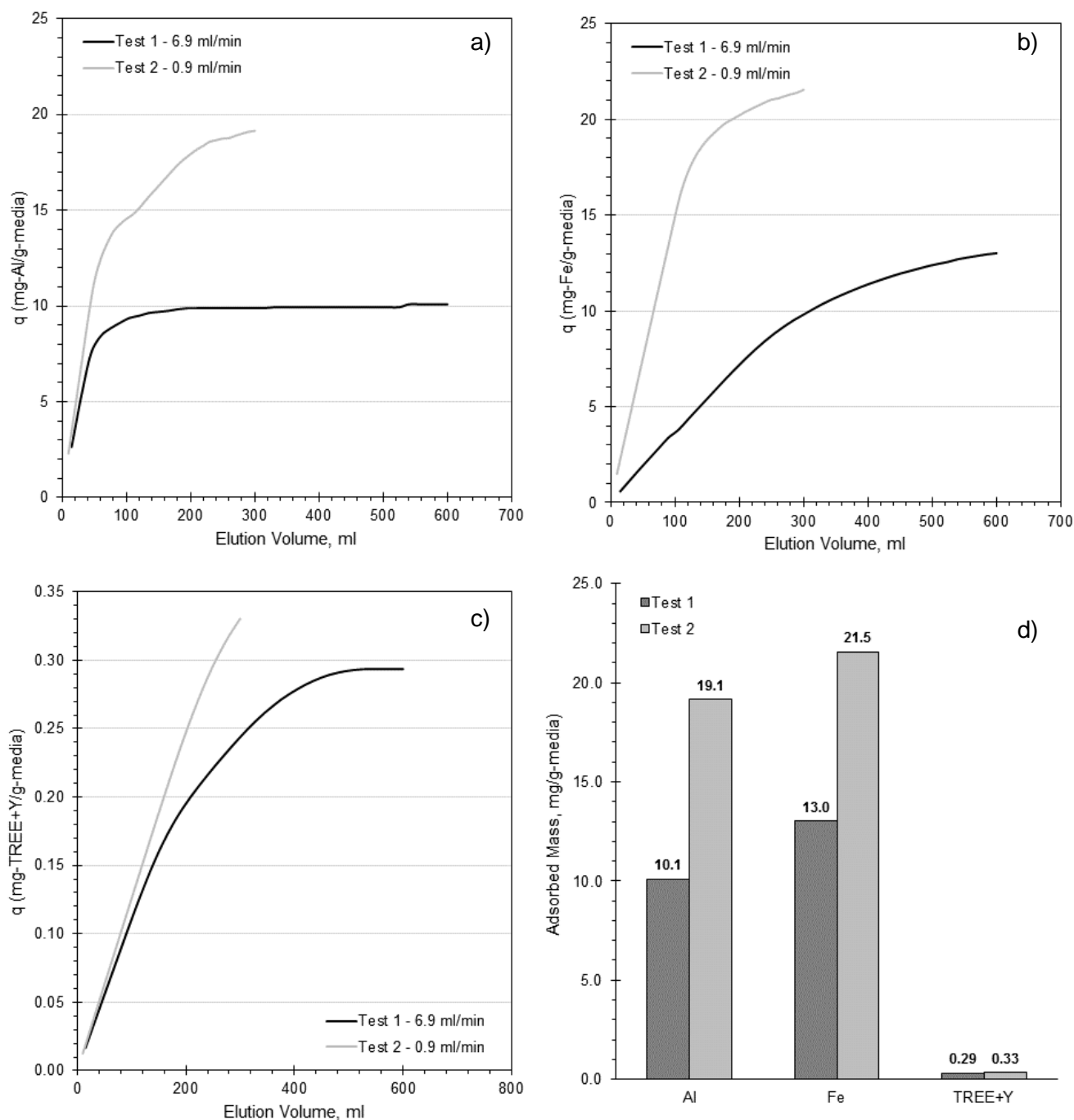


Figure E.9

Relationship between adsorbed amount of Al, Fe, and TREE+Y onto adsorptive media for both Test 1 and Test 2 at two different column flowrates; a) Al, b) Fe, and c) TREE+Y during loading phase of column operation. Plot d) of the total adsorbed amount of each constituent at the end of the column loading phase before stripping with 3M acid.

Figures E.9 a) to c) illustrate plots of the cumulative mass of each constituent adsorbed versus the elution volume from the adsorption columns at both flow rates tested; 6.9 and 0.9 ml/min. In general, the amount of each constituent adsorbed on to the media was higher for Test 2 which had a slower flow rate. This indicated that sorption was kinetically controlled with additional time leading to greater adsorptive removal. Test 1 results

in graphs a) through c) also suggest adsorptive equilibrium was reached (or almost reached). Although the curves for Test 2 are starting to reach asymptotic equilibrium sorption values, the curves indicate additional sorption was still occurring. Therefore, equilibrium was not reached. However, even with this limitation, final adsorption values are summarized in graph d). Since equilibrium was essentially reached in Test 1, the values shown give a general adsorptive capacity of 10 mg-Al/g-media, 13 mg-Fe/g-media, and 0.3 mg-TREE+Y/g-media. It was clear that the adsorptive capacities for Test 2 are higher (2X) that for Test 1.

The analysis between Test 1.1 and Test 2.1 results exposed a difficult dilemma from a column operational point of view such that a faster flow rate (lower contact time) decreases the mass of Al and Fe adsorbed compared to TREE+Y than for a slower column, thereby effecting the concentration of TREE+Y in the final REE product. This idea is best illustrated by examining Table E.8 and Table E.9.

Table E.8 REE Sorption Columns – Effluent Solution Characteristics

Effluent Concentration (mg/L)	Test 1.1	Test 2.1
Al	592	1,035
Fe	919	1,784
TREE+Y	24.8	43.2
TREE+Y concentration factor ^A	1.28	1.95
Change in Al Concentration	-81%	-74%
Change in Fe concentration	+36%	-32%

A – Ratio of effluent concentration to influent concentration

Table E.8 summarizes the effluent characteristics for Test 1.1 and Test 2.1. Column loading, and stripping increased the concentration of TREE+Y by 30% and 60% for Test 1.1 and Test 2.1 respectively. Aluminum concentration decreased by roughly 75 to 80% for both test solutions. Iron concentration increased by 36% in Test 1.1 and decreased in Test 2.1 by 32%. This increase witnessed during Test 1.1 may be explained by examining Figure E.7-b) and Figure E.8-b) which show a much higher percentage iron mass being adsorbed onto the adsorptive media in Test 1.1 than that witnessed in Test 2.1.

Table E.9 REE Column Performance

	TREE+Y Adsorption Efficiency ^A	% TREE+Y in Fractional Solution ^B	wt% TREE+Y in Final precipitate ^C
Test 1.1	44%	2.02%	1.6%
Test 2.1	91%	1.36%	1.4%

A- Mass of TREE+Y adsorbed onto column compared to mass applied to column

B- Mass TREE+Y compared to mass of all measured metals (61) in column effluent strip solution

C- Ash basis (not hydroxide)

Data in Table E.9 indicates the counteracting, competing factors between adsorption efficiency and the wt% of REEs in the final precipitate product. As the adsorption efficiency of the column increases so does the mass of other unwanted metals such as aluminum and iron to such an extent the REE concentration in the final product decreases. Based upon the result shown in Figure E.8-d) where the amount of adsorbed Al and Fe was much greater at a slower column flow rate (Test 2.1), the mass (not the percentage) of TREE+Y adsorbed was only marginally higher. Thus, it appears that the sorption media selected adsorbs Fe and Al without significantly affecting the adsorptive capacity of TREE+Y. This would suggest that an optimal solution feed into the adsorptive columns should produce low Al and Fe concentrations. This should improve TREE+Y adsorption efficiency greater than that witnessed in Test 1.1 and also decrease the amount of unwanted metals in the final product precipitate thereby increasing the wt% of TREE+Y in the final product.

E.2.5 REE Product Production

To determine the REE concentration in the precipitated product from the proposed treatment system, a controlled test was initiated to carefully maintain accurate mass balances between TREE+Y in the adsorption column effluent and the mass of TREE+Y in the final precipitate. The test consisted of using hydroxide precipitation on REE concentrate solutions, drying of solids, subsequent re-dissolution of the precipitated metals, and elemental analysis of the metals solution. Figure E.10 illustrates the treatment sequence.

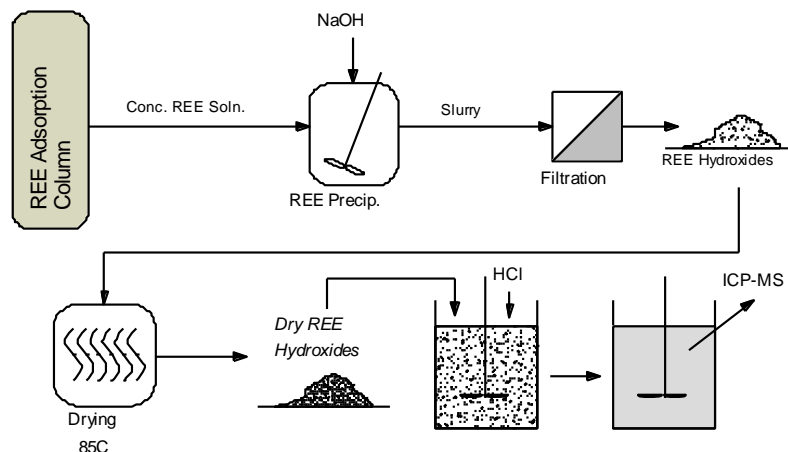


Figure E.10

Experimental sequence to determine REE wt% in final product.

Utilizing the sequence outlined in Figure E.10, REE effluent concentrate solutions from REE adsorption columns were pH adjusted with NaOH to precipitate the metal species in solution followed by filtration to produce REE hydroxide solids that were dried at 85°C. These hydroxide solids were re-dissolved in hydrochloric acid and assayed with ICP-MS to determine the concentration of each metals species. Results from these experiments are summarized in Table E.10.

Table E.10 REE Hydroxide Precipitation Summary

	Test 1.1	Test 2.1
vol. of concentrate (ml)	183	137
TREE+Y in concentrate (mg/L)	24.8	43.2
required 10M NaOH (ml)	47	31
vol. after pH adj. to 11.9	230	174
ml NaOH:ml concentrate	0.26	0.23
final soln. pH	10.99	11.90
mass of metals in influent concentrate soln. (mg)	299	401
precip. hydroxide mass (mg)	586	806
hydroxide subsample acid digested (mg)	101.6	101
TREE+Y hydroxide in solid subsample (mg)	0.750	1.02
total TREE+Y in hydroxide precipitate ^A (mg)	4.3	8.1
wt% TREE+Y hydroxide in final product	0.74	1.01
wt% TREE+Y on ash basis ^B	1.6	1.4

A – Calculated from total hydroxide mass and small sample mass ratio

B – Based upon 61 metal assay of solution

The most significant result from Table E.10 was the calculated wt% of TREE+Y in the final product of 0.74% and 1.01% for Test 1.1 and Test 2.1 respectively. These values are lower than that achieved during Q4 and Q5

activities. The most likely reasons for this lower wt% was the lower REE extraction efficiency witnessed during acid digestion (due to too high of solids concentration during base pretreatment) and the inability to effectively separate iron from REEs during column adsorption.

Another critical result from Table E.10 is the mass of TREE+Y hydroxide produced in relation to the amount of fly-ash processed, i.e. the process production efficiency. Based upon a 100-g fly ash sample, approximately 0.0484wt% of the ash is TREE+Y. This translates into a TREE+Y mass of 48.4 mg in the fly sample before processing. Based upon this influent TREE+Y mass input into the system and the measured TREE+Y in the final product, % system recoveries were calculated and summarized in Figure E.11.

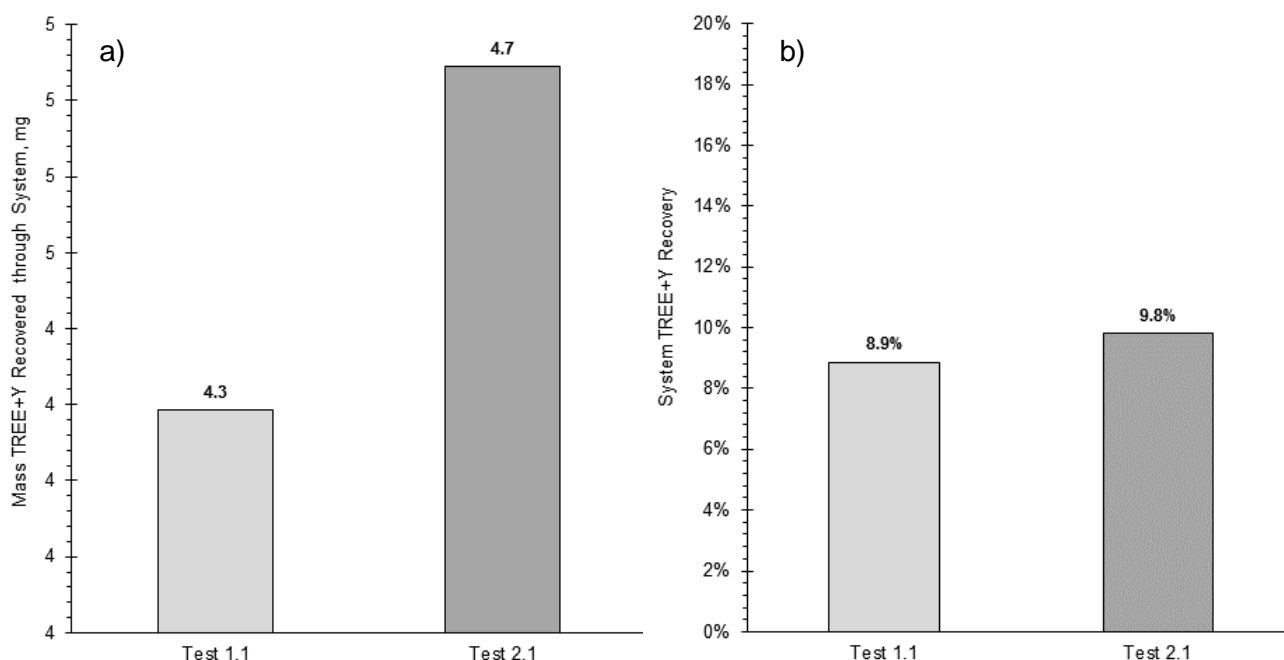


Figure E.11

Mass of TREE+Y recovered in the final product – graph a) and graph b) the recovery percentage of TREE+Y through the entire process compared from mass of TREE+Y in fly ash material to the mas of TREE+Y in the final product.

The results illustrated in Figure E.11 indicate approximately 9 to 10% of the TREE+Y that was introduced into the process (i.e. untreated fly-ash) was recovered in the precipitated product. This recovery percentage is approximately one-fourth of that achieved previously. Based upon this result, a detailed mass balance through the entire process was completed to determine at which point or points in the process the majority of TREE was lost from the process. Data from each stage of the process was used to complete the system mass balance.

Figures E.12 and E.13 summarize the mass balances from two large-scale tests (designated as Test 1 and Test 2).

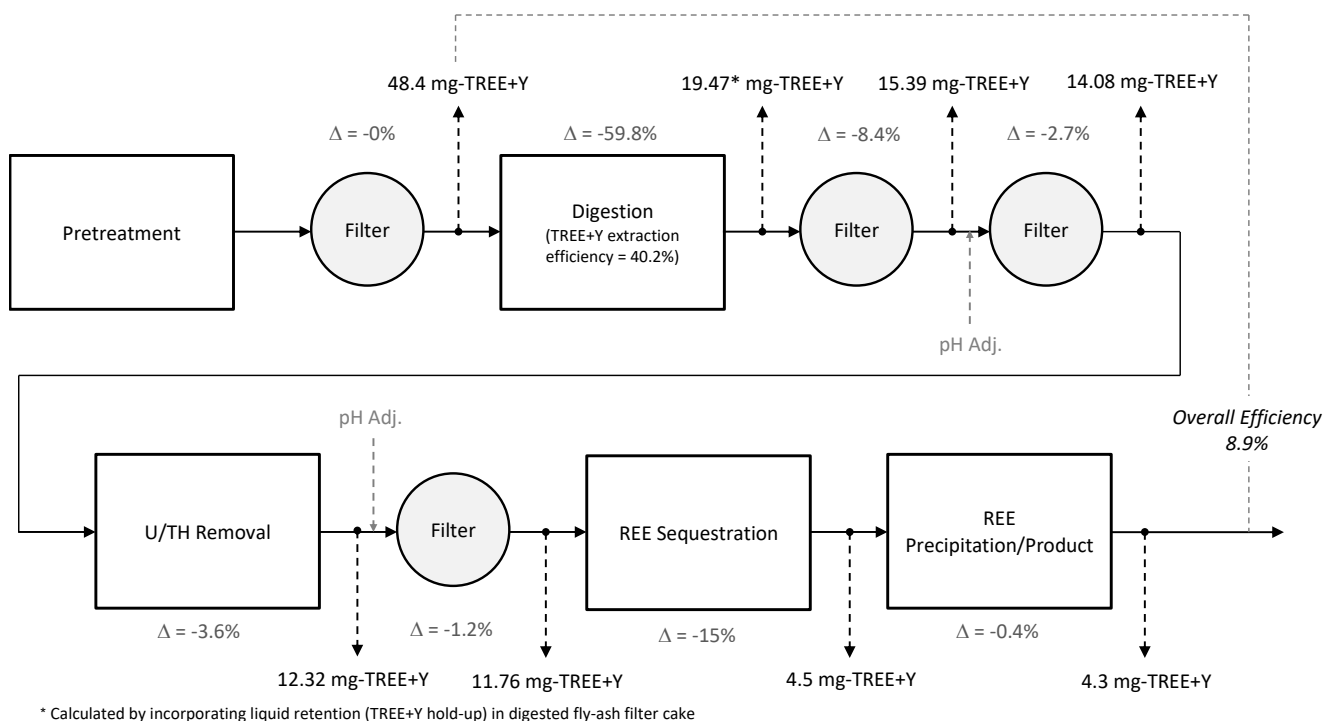


Figure E.12

Mass balance of TREE+Y through the proposed process for Test 1.1 ($\Delta\%$ values correspond to the mass loss through each unit process in relation to the initial TREE+Y mass put into the process, i.e. 48.4 mg TREE+Y).

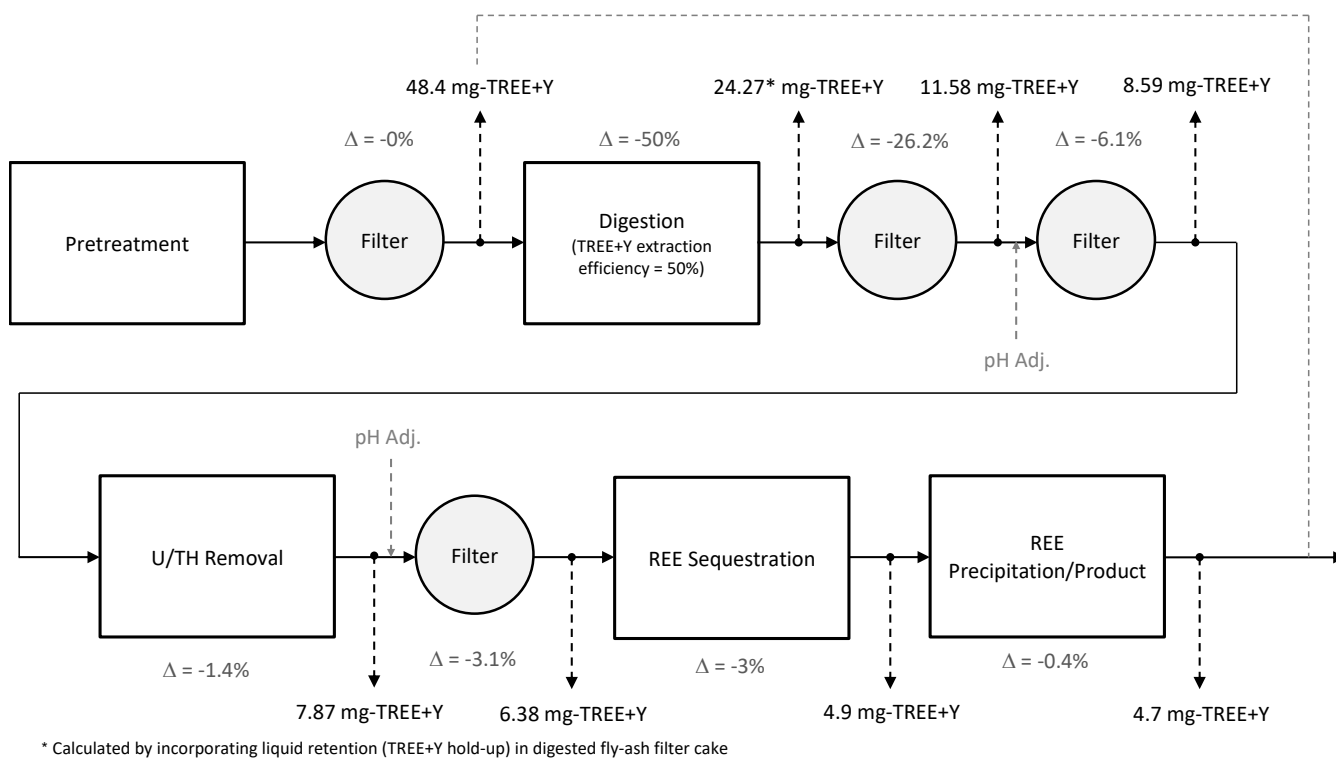


Figure E.13

Mass balance of TREE+Y through the proposed process for Test 2.1 ($\Delta\%$ values correspond to the mass loss through each unit process in relation to the initial TREE+Y mass put into the process, i.e. 48.4 mg TREE+Y).

The mass balance analysis in Figure E.12 for Test 1 shows that the two unit processes that resulted in the largest losses of TREE+Y were from acid digestion and REE separation which accounted for approximately 60% and 15% respectively. The loss during digestion was due to the pretreatment step that used a 30wt% solids loading compared to a 10wt% solids loading that typically results in a 70+% extraction efficiency. The loss of TREE+Y through the adsorption column was due to a high flow rate through the column which did not allow enough time for full TREE+Y adsorption on the media. If it is assumed that the efficiency through the digestion process is 70%, loss through adsorption is approximately 5%, and all other losses are equal to values presented in Figure E.12, then the overall efficiency through the process would be roughly 49%.

The mass balance analysis in Figure E.13 for Test 2 shows that the two unit processes that resulted in the largest losses of TREE+Y were from acid digestion and filtration of the digested fly-ash solids, accounting for approximately 50% and 26% loss of TREE+Y respectively. As stated previously, the loss of TREE+Y during digestion was likely due to the pretreatment step that used a 30wt% solids loading compared to a 10wt% solids loading that typically results in a 70+% extraction efficiency. The loss of TREE+Y through filtration of the digest liquor was due to poor liquid extraction from the solids. This poor extraction was caused by too thick of a filter cake during pressure filtration which did not release the digest liquor within the filter cake. If it is assumed that the efficiency through the digestion process is 70%, the loss through filtration is approximately 10%, and all other losses are equal to values presented in Figure E.13, then the overall efficiency through the process would be roughly 46%.

E.3 Techno-economic Analysis of Process

The proposed process design was the culmination of laboratory efforts that included the optimization of process parameters through multiple iterative evaluations and investigations into process yields and economic impacts to develop the most promising techno-economic solution. A detailed financial analysis model (Excel spreadsheet) was established to determine the usage of consumables, estimate waste and residual stream quantities, and understand the size of equipment necessary to treat a given amount of fly-ash. The financial model allowed for different sizes of fly ash process batches to be analyzed for overall efficiency and cost. The model was initially used to evaluate a preliminary pilot process model that could treat 1,000-kg of fly-ash input/day. Additional iterations of the model allowed us to project a commercial-scale process based upon 250,000-kg of fly-ash input/day rate. Figure E.14 summarizes capital cost estimates based upon the financial analysis model.

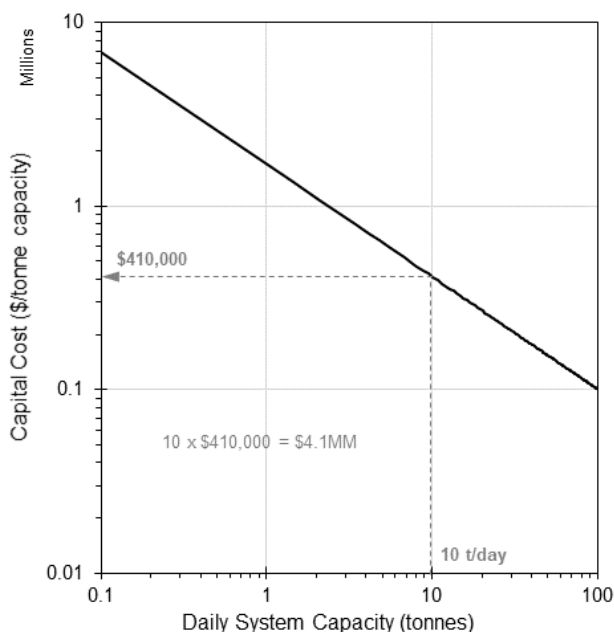


Figure E.14

Capital costing model results for process system sizes between 100-kg/d to 100,000 kg/d

Results in Figure E.14 show a standard power-law relationship between capital costs and system size, i.e. smaller systems cost more per tonne of fly ash processed than large system sizes. The figure allows for a general estimation of capital costs based upon system size. For example, if a 10 tonne/batch system size is targeted, the corresponding capital expenditure estimate is approximately \$4.1MM (10 x \$410,00). If a simple amortization of capital at 4.5% interest for 10 years is used, the estimated capital cost for a 10 tonne/ day system is \$88/tonne of fly ash.

It was determined during the development of the commercial model that, at the current market pricing for REEs, the major revenue generating product from the process was the zeolite material produced from repurposing of the caustic pretreatment liquor (see Section D.7). This zeolite product (Type Na-P1) can be used in a significant number of applications making it an attractive value-added product. Na-P1 zeolite products currently have a selling price that ranges between \$0.24 and \$1/kg based upon use as an agricultural amendment material. A point that makes zeolite production more attractive is that two of the main components used in production, aluminum and silica, are extracted along with the REEs from the fly-ash and are subsequently separated during processing. Therefore, the majority of the base materials required to make the zeolite product are readily available from the process. Since these streams would have been disposed of as waste residuals, repurposing the streams also decreases waste generated from the process.

The economic model used a zeolite production rate of approximately 1.4 kg-zeolite produced per 1 kg fly ash treated. Using a selling price of zeolites at \$355/tonne, the estimated zeolite revenue per tonne of fly ash processed was \$495 to \$500. This additional revenue was included in the operating cost analysis. Operating costs were separated into four main areas; 1) fixed costs, 2) consumables, 3) waste disposal, and 4) fuel/feedstock costs and based 260 operational days per year. Figure E.15 summarizes estimated operating costs with and without zeolite production for process batch sizes between 100 kg up to 100 tonnes.

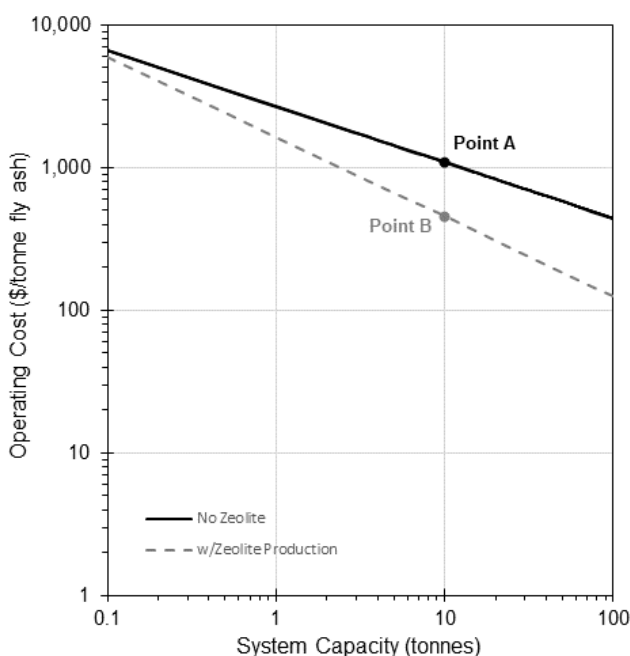


Figure E.15

Operating costs for process system sizes between 100-kg/batch to 100,000 kg/batch

Point A in Figure E.15 illustrates the estimated operating cost of \$1,090/tonne fly ash processed for a 10 tonne capacity system without the production of zeolite Na-P1. If zeolite revenue is subtracted from the total operating cost, operating costs drop dramatically at larger system sizes. Point B in Figure E.15 illustrates the estimated net operating cost of approximately \$450/tonne of fly ash processed at a 10 tonne capacity. The production of

zeolites drops the net operating cost by 59%. Although operating cost savings due to zeolite production is significant, the capital + operating cost for a 10 tonne system is still more expensive than the total dollar value of REEs present in the fly ash material. Specifically, the estimated cost to treat 1-tonne of fly ash with a 10 tonne per batch system is approximately \$540 while the estimated value of REEs in the fly ash is \$18-\$20/tonne. This is an excessive difference showing that the proposed process is not economically feasible strictly on the basis of REE revenue compared to extraction costs.

Operational costs per tonne of fly ash processed are estimated to be approximately 5X the capital cost. Capital expenses (CAPEX) can be funded by various financing scenarios. However, operational costs can significantly vary depending on supplier and vendor costs. In an effort to determine the operational area to focus cost reduction efforts, a cost breakdown between operational cost based upon general categories is provided in Figure E.16.

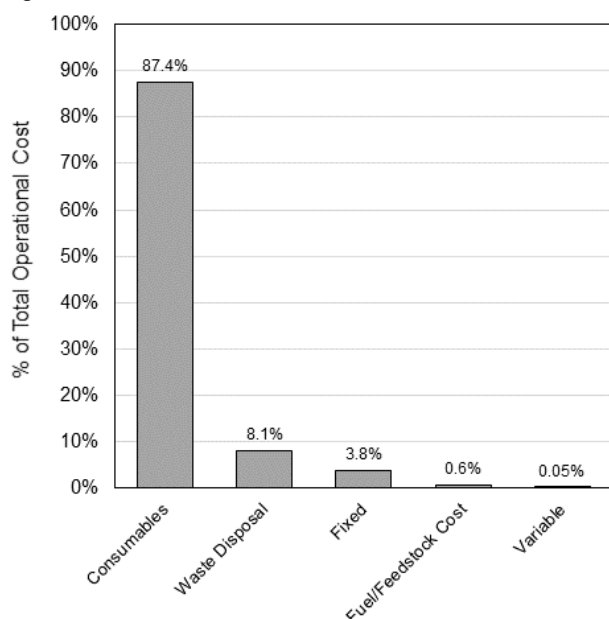


Figure E.16
Operating cost breakdown for a 100 t/batch system

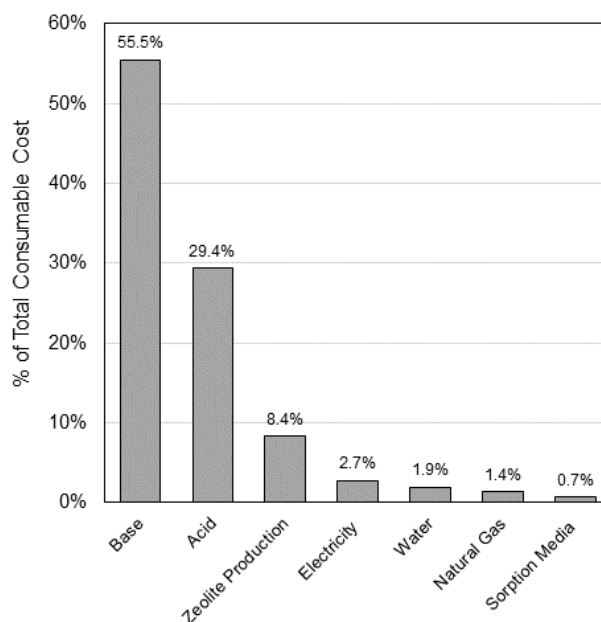


Figure E.17
Consumable cost breakdown for a 100 t/batch system

It is clear from Figure E.16 that the largest operational cost category is consumables, accounting for over 87% of total operating expenditures. Waste disposal costs including sewerage and solids waste disposal accounts for roughly 8% of operating costs. Fixed cost including labor is only 3.5 to 4% of operating costs. Further analysis of consumable costs is presented in Figure E.17. Not surprisingly, NaOH and HCl costs account for the vast majority of consumable cost, approximately 85%.

Obviously reducing chemical costs could dramatically decrease overall operating costs. For example, if chemical costs could be decreased by 50%, then the overall operating costs would decrease by roughly \$460/tonne of fly ash processed for a 10t/day system size. As stated previously, if zeolite production and subsequent revenues offset operational costs, then the estimated operating cost is estimated at \$450/tonne of fly ash produced. Therefore, decreasing chemical costs by 50% would result in a net zero operating cost with zeolite production. Obviously there are many factors that could change this conclusion, but it is interesting exercise to show that system costs could at the very least, begin to approach reasonable values.

Although the current proposed system does not produce a sufficient quantity of REEs to offset operational and capital costs, additional factors including US strategic concerns, commercial demands, and defense department requirements must be factored. The strategic need for a rapid, alternative, local source has been repeatedly stressed by US supply chain planners.

F.1 Project Extension Details

F.1.1 Motivation

Project activities within the original project schedule provided the framework for the development of a treatment method to extract REEs from coal fly ash. Performance of the developed process met all but two of the six original performance benchmarks, namely:

- | | |
|---|--|
| • Reasonableness of Economic Justification | Actual: Production Cost >> Product Revenue |
| • > 50% Removal of U-Th from Source Fly Ash | Actual: 30% - U, 25% - Th |

Research into developing new processing approaches to decrease chemical consumption while simultaneously increasing REE extraction efficiency were a project focus since the approval of the GO/NO GO decision. During the last 2 months of the original project timeline, significant technical developments and improvements were made to increase REE extraction efficiency and reduce overall chemical usage. Results showed that REE extraction efficiency could be increased by a factor of 2X with a subsequent reduction in acid usage by employing a new acid digestion method. These results prompted additional research into this revised acid digestion method.

Although U-Th removal criterion was not met, the fact that the fly ash only leached 30% of the uranium and 25% of the thorium even after extensive pretreatment and aggressive acid digestion shows that removal of high percentages of radionuclides from fly ash is difficult. Experiments conducted near the end of the original project timeline suggested that U-Th removal percentages could be increased above 50% by employing a dual digestion strategy. Therefore, the removal of U-Th was a focus area during the project extension.

F.1.2 Goals and Objectives

The following were the major goals during the project extension:

- Investigate impact of new processing method on final REE product REE
- Determine best method to remove >50wt% of U and Th from fly ash

The overall theme of these goals was to refine a new digestion method that decreased chemical usage and to assess performance impact on subsequent down-stream processes. Also a dual-digestion scheme was investigated to meet the >50wt% removal of U-and Th from fly ash. Specific objectives of the project extension included:

- Evaluate and optimize new digestion method by REE extraction efficiency and decrease in ancillary metals as success metrics
- Finalize U/TH extraction procedure to remove >50% U/TH from fly ash material
- Enhance the efficiency of REE separation by column adsorption and stripping
- Improve the overall REE product (>2wt%)
- Leverage previous results from project and recent research developments to “finish” the study with the best developed technology

F.1.3 Tasks

Project extension tasks were separated into three main segments; 1) optimize new digestion method, 2) finalize U/Th extraction procedure, and 3) if necessary, update economic feasibility analysis. Specific tasks included:

- Determine best digestion composition to minimize Al/Fe leaching and maximize REE extraction
- Re-use acid digestion liquor to further decrease chemical costs
- Test low molarity – longer time extraction procedure on fly-ash that has been digested to remove >50% U/Th from the original fly ash.
- Determine best residuals management of U/Th solutions, i.e. column adsorption or liquid disposal.
- Use new chemical usage and reuse data to update economic costing model

F.2 Project Extension Details

Project goals at the end of Q6 and through the Q7 project extension focused on:

- increasing the removal efficiency of REEs by optimizing pretreatment and digestion process conditions
- investigate dual-digestion method to increase removal of uranium (U) and thorium (Th)

Activities during this quarter of the project focused on:

- defining operational parameters utilizing chloride salt addition to maximize REE extraction while simultaneously decreasing extraction of unwanted constituents (namely aluminum and iron).
- Determining the possibility of a dual-digestion sequence to first remove REEs from fly-ash materials followed by a second digestion to remove uranium/thorium to required low-level concentration in post-treated fly-ash.

Based upon these project goals and activities during this reporting period, results and observations are separated into two sections; 1) REE extraction optimization with chloride addition, and 2) dual digestion U/Th removal.

F.2.1 REE Extraction Optimization – Chloride Addition

Over the course of the project it was observed that the extraction efficiency of REEs would decrease when the processing batch size increased and that the cost of processing was high (see Section D.2.6). It was postulated that the decreased REE extraction in larger batch sizes and high solids loading was due to the formation of silicic acid type polymers. Therefore, decreasing the required acid strength was deemed a potential solution to increase digestion efficiency by investigating the use of chloride catalyzed reactions and at the same time, decrease overall processing costs (i.e. chemical consumption and residuals management).

An additional issue revealed during main project activities was that when the extraction process maximized REE recovery, the process also increased the extraction of aluminum and iron (the two metals with the highest concentration in the process liquor) therein impacting REE purification and final product mass percentages. Based upon these facts, it was deemed necessary to investigate digestion methodologies that could increase REE extraction efficiency while simultaneously decreasing aluminum and iron extraction percentages was an intriguing research approach.

To meet this research challenge, a series of digestion tests were performed using various concentrations of sodium chloride (NaCl) along with hydrochloric acid. The fly-ash was pretreated with the standardized project method of 3M NaOH for 4 hours at 80°C with a 10wt% solids loading. A baseline digestion was performed using 2M HCl with no sodium chloride addition followed by experiments with the addition of NaCl to maintain a chloride ion concentration of 2.67M (the optimal HCl concentration from earlier experiments). Based on results from these experiments, a final test was performed to determine if a high acid concentration (2M HCl) at a high NaCl concentration (1.335 M) would maximize REE extraction while minimizing Al, Fe, U, and Th extraction. Figure F.1 outlines the test matrix.

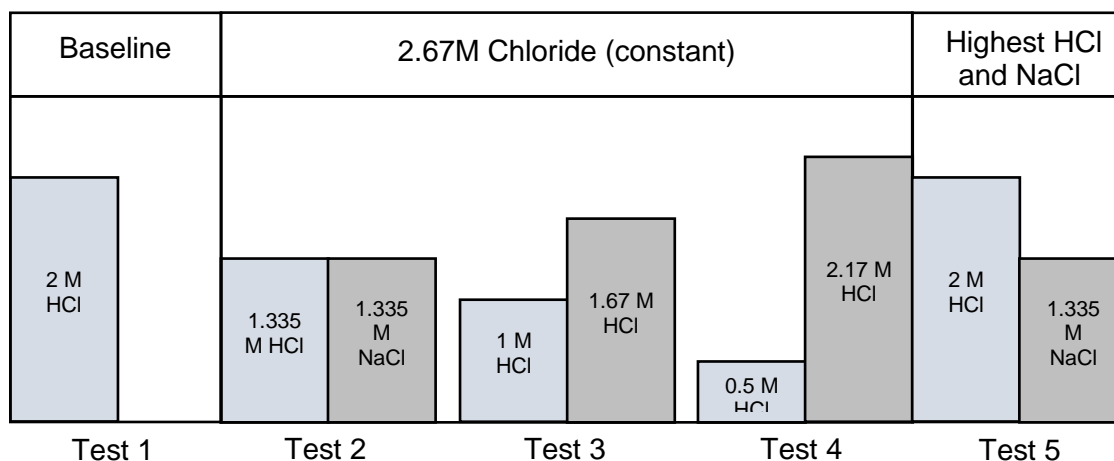


Figure F.1

Summary of test matrix investigating the impact of NaCl concentration in REE extraction efficiency.

A baseline digestion was performed using a 2M HCl solution at 80C for 4 hours to extract REEs from pretreated (3M NaOH, 10wt% solids, 90°C, 4 hrs.) fly ash. Figure F.2 summarizes the extraction efficiencies for TREE+Y, Al, Fe, U, and Th from the pretreated fly-ash material. Results show that a high TREE+Y extraction efficiency of greater-than 80% was achieved along with relatively high extraction efficiencies of Al, U, and Th. Although this graph is useful, it provides a potentially misleading conclusion since the percentage values are based off of the individual concentrations of each component. For example, iron has a concentration within the parent fly-ash of approximately 150 mg/g-fly ash while TREE+Y accounts for 0.48 mg/g-fly ash. Therefore, the mass of iron per gram of fly-ash is 300X greater than the mass of TREE+Y per gram of fly-ash. At a 41% extraction efficiency for iron and 82% for TREE+Y, approximately 63-mg of iron and 0.4-mg of TREE+Y are leached out of 1-g of fly ash. Even with one-half the extraction efficiency for iron compared to TREE+Y, the mass of iron extracted compared to TREE+Y is 150-times greater. For aluminum, the ratio is even higher at 190x. This example underscores the necessity to minimize extraction efficiencies of both iron and aluminum during digestion.

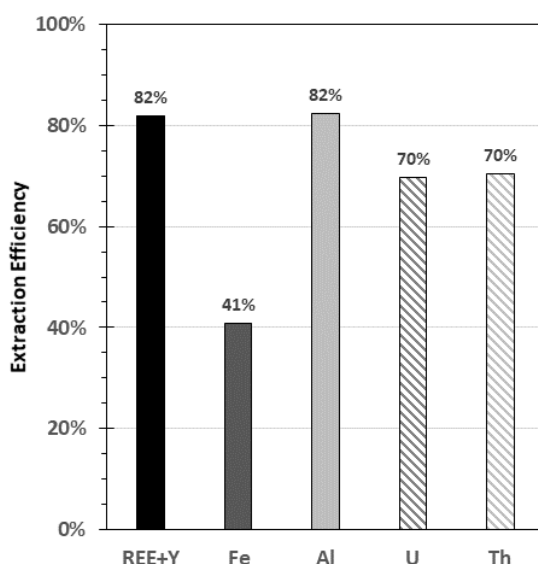


Figure F.2

Extraction efficiency of REE+Y, Al, FE, U, and Th using a 2M HCl.

A second stage of testing investigated the impact of various concentrations of NaCl on the extraction efficiencies of TREE+Y, Al, Fe, U, and Th. A constant chloride concentration, a combination of HCl and NaCl,

was maintained at 2.67M for all experiments. Sodium chloride/hydrochloric acid molar combinations of 1.335 to 1.335, 1.67 to 1, and 0.5 to 2.17 were investigated. The quantities of TREE+Y, Al, Fe, U, and Th extracted were determined and compared. Figure F.3 summarizes the results.

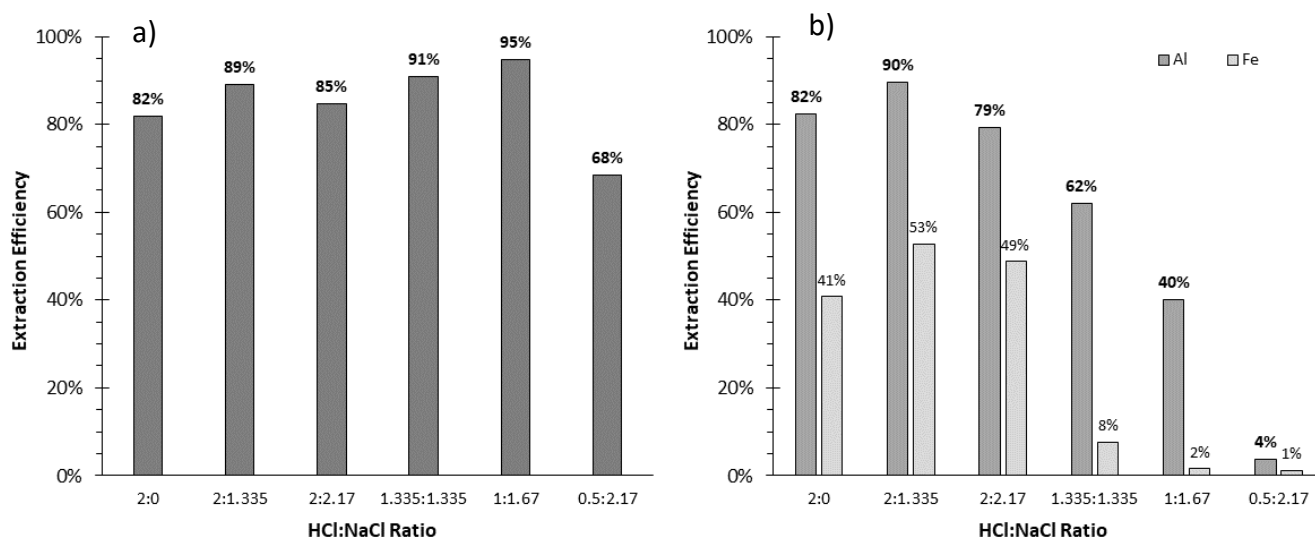


Figure F.3

Impact of NaCl addition on the extraction efficiencies of a) TREE+Y and b) Fe and Al.

It is evident from Figure F.3-a that, in general, the TREE+Y extraction efficiency remains relatively consistent between approximately 85% to 95% with various NaCl additions. The best overall extraction efficiency of 95% was achieved with a HCl concentration of 1M with a 1.67M concentration of NaCl. When the HCl concentration is decreased to 0.5M, the TREE+Y extraction efficiency decreases significantly. Figure F.3-b shows that the percentage of aluminum and iron extracted decreases as the NaCl to HCl ratio increases. This decrease is dramatic for both aluminum and iron, 90% to 4% for aluminum and 53% to 1% for iron. A comparison was made between HCl addition at a constant NaCl concentration of 1.335M and a comparison was investigated at a constant HCl acid concentration of 2M with varied NaCl concentrations. Results of this efforts are summarized in Figure F.4-a and F.4-b respectively.

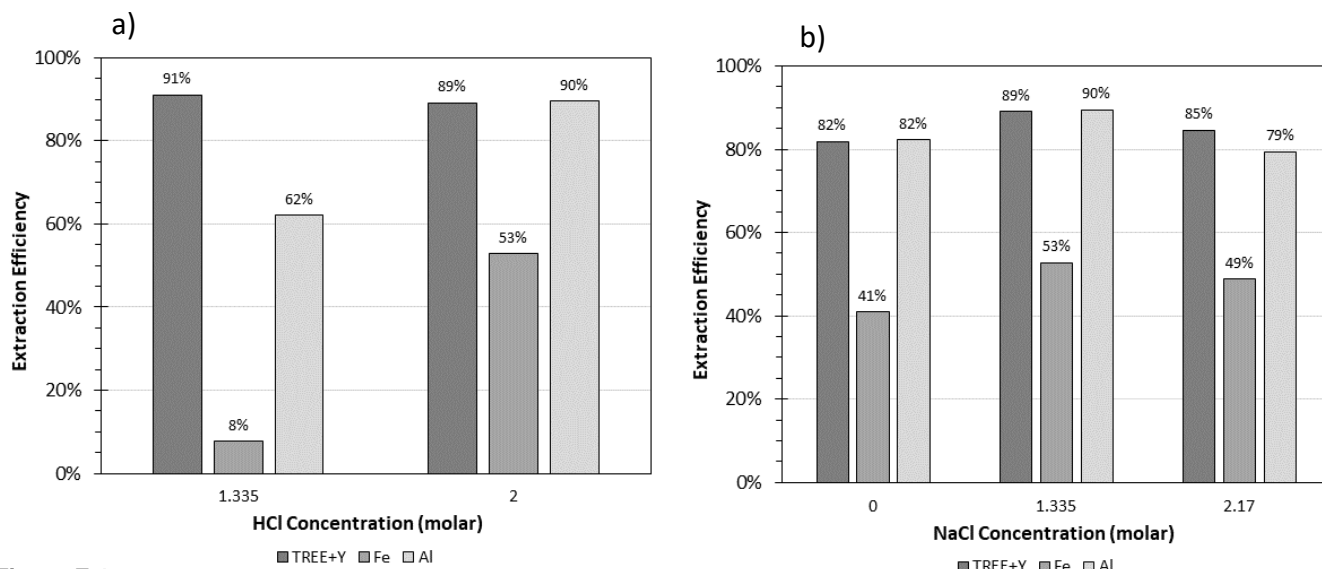


Figure F.4

Comparison of the impact of a) different HCl concentrations (1.335M and 2M) at a constant NaCl concentration of 1.335M and b) the impact of varied NaCl concentration at a constant HCl concentration of 2M.

Results at a constant NaCl concentration of 1.335M with HCl concentrations at 2M and 1.335M show that there is minimal difference in TREE+Y extraction efficiencies at these two conditions. However, for Fe and Al the extraction efficiencies increased from 8% to 53% for iron and increased from 62% to 90% for aluminum as the HCl concentration was increased from 1.335M to 2M. Interestingly, when the HCl concentration was maintained at 2M with and without NaCl addition to achieve NaCl concentrations of 1.355M and 2.17M, there was no significant change in TREE+Y extraction efficiency. Although a slight increase from 82% to 89% in the extraction efficiency of TREE+Y occurred when 1.335M of NaCl was added into the digestion solution, without statistical analysis, this increase may reflect variability in the data. Fe and Al extraction efficiencies also slightly increased when 1.335M NaCl was added into the digestion liquor suggesting that the small uptick in extraction efficiencies may be tangible. Comparison to the extraction efficiencies when 2.17M of NaCl was used in the digestion solution reveals little to no impact.

Based on the observations in Figure F.4, there is little to no impact of adding NaCl into the digestion mixture when a HCl concentration of 2M is used. Only when the concentration of HCl is decreased with the addition of NaCl does the extraction efficiencies for Fe and Al decrease significantly. Although there are multiple hypotheses of why this may occur, the most important finding is that the amount of Fe and Al in solution can be significantly reduced while maintaining high TREE+Y extraction efficiencies. This is a very important result since it leads to a major decrease in operating costs as well as making the entire process more efficient since a smaller amount of unwanted constituents (Fe and Al) need to be processed. Since these experiments were completed in small-batches, not enough TREE+Y mass was produced to precipitate a final product. In an effort to qualify the impact of lowered Fe and Al concentrations in the digestion solution, a comparison was completed looking at the ratios of Al and Fe to TREE+Y to get an idea of the mass reduction of unwanted materials in the finished product. Figure F.5 summarizes the mass ratios of Fe and Al to TREE+Y between a 2M HCl digestion (typical) and a digestion using 1M HCl and 1.67M NaCl.

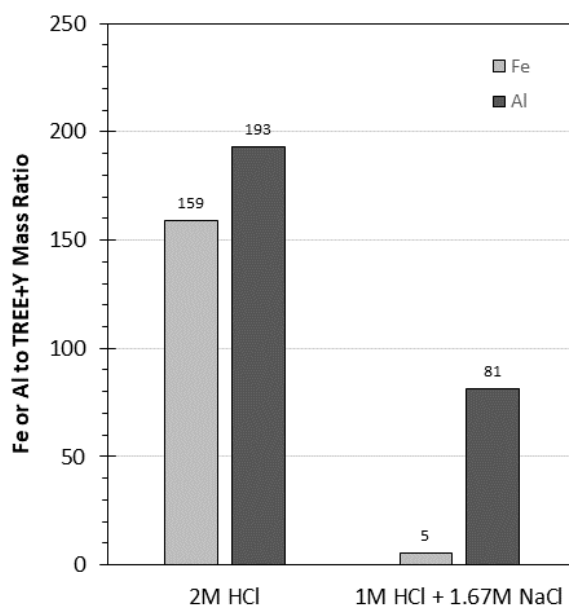


Figure F.5
Mass ratio of Fe and Al to TREE+Y extracted from 1-g of fly-ash

Tables E.8 and E.9 in Section E provide typical Fe and Al concentrations in the influent to the REE precipitation process. Using these values and the reduction in Al and Fe in the precipitation solution as shown in Figure F.5, an estimated TREE+Y mass percentage of roughly 5wt% (ash basis) is calculated. This is an increase from the 1 to 1.4wt% value typically observed when the standard 2M acid digestion is utilized. Therefore, the use of chloride addition appears to increase TREE+Y in the final product by over 3% (absolute increase). This is a significant

increase when also accounting for the decrease in acid usage of approximately 50%. Since HCl and NaOH chemicals account for roughly 70% of total operating costs (see Section E.3), reducing chemical usage by 50% will translate into an operating cost reduction of 30 to 35%. This translates into an estimated operating cost reduction of \$400/tonne fly ash produced. This cost reduction is discussed within Section E.3. However, even with this cost reduction, the overall cost of per tonne of fly ash processed is greater than the revenues from the process (REEs and zeolites).

F.2.2 Dual Digestion U-Th Removal

A main metric used to evaluate the treatment was the removal percentage for both U and Th from the original fly-ash material which needed to be greater-than 50%. Experiments completed during the original project timeline were able to achieve a 30% removal of uranium and a 25% removal of thorium from the original fly-ash material. This was surprising since the fly-ash material was subjected to vigorous pretreatment and digestion chemistry with a 3M solution of NaOH at 90°C for 4 hours followed by 2.67M HCl digestion at 80°C for 4 hours. The data suggested that a more vigorous solution chemistry extracted “more” U and Th. However, as the treatment process time, concentration, and temperature are increased, so does the extraction of other unwanted chemical constituents that decrease the quality of the final REE product, namely iron and aluminum.

Given this counterbalancing effect between increasing U and Th removal while simultaneously minimizing unwanted chemical constituents in the TREE+Y digestion liquor, a modification to the process developed during main project activities was investigated. This modification consisted of using a dual digestion sequence; first step was to use standard NaOH pretreatment and acid digestion to remove the bulk of REEs, followed by the second step of additional acid digestion treatment on the residual fly-ash material. This first-stage of this testing scheme produces a process liquor that is high in TREE+Y with relatively low Fe, Al, U, and Th concentrations. The second-stage treatment is designed to remove additional U and Th from the fly ash in an effort to extract virtually all of U and Th present in the fly-ash.

A series of tests were completed to determine the optimal 1st stage digestion operational parameters. The main thrust of the tests in 1st stage processing was to maximize TREE+Y removal while extracting the lowest amount of Al, Fe, U, and Th from the starting fly-ash material. Figure F.6 summarizes the extraction efficiencies for U and Th for all 1st stage digestion tests.

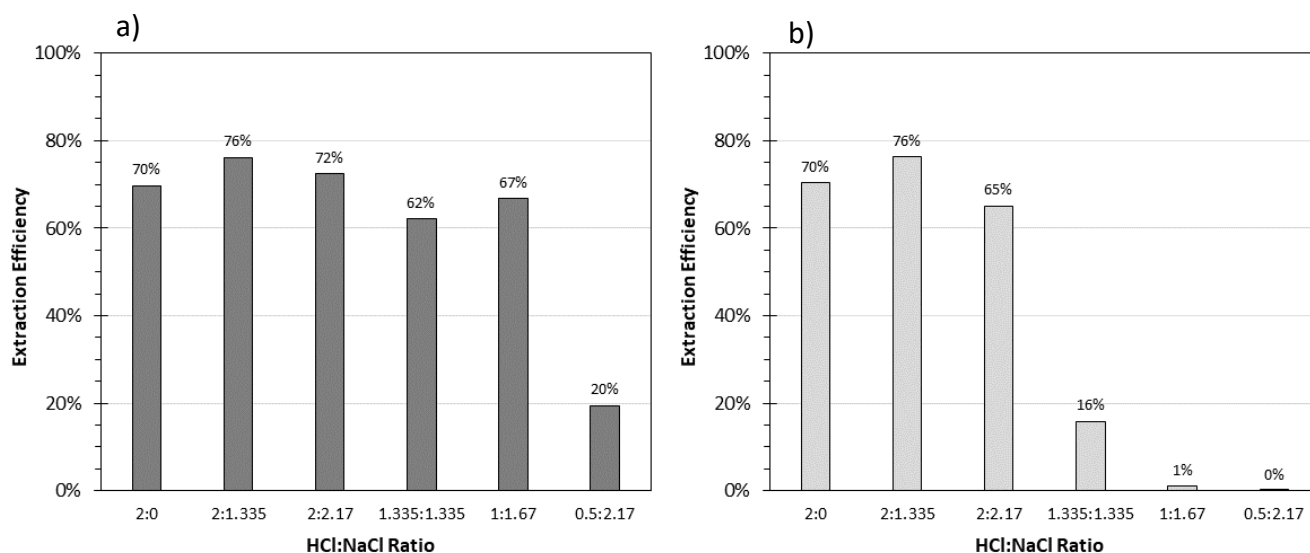


Figure F.6

Extraction efficiencies in relationship to 1st stage digestion chemistries for a) uranium and b) thorium.

Results in Figure F.6 show the impact of HCl acid strength on U extraction efficiency with a sharp decrease in extraction at HCl concentrations less-than 1M and the significant impact of both HCl and NaCl concentration on Th extraction with a minimal amount of Th extracted from the fly ash when the NaCl concentration was greater-than the HCl concentration (1:1.67 and 0.5:2.17 ratios). Comparing Figure F.6 to Figure F.3, it appears that utilizing a HCl:NaCl ratio of 1:1.67 maximizes TREE+Y extraction efficiency at upwards of 90% while drastically limiting Fe and Th extractions and minimizing Al and U extraction. This was chosen as the target HCl to NaCl ratio for all 1st stage tests. Three 2nd stage digestions were completed using this same 1.335M HCl and 1.335M NaCl solution chemistry followed by 2M HCl digestion.

Figure F.7 summarizes the average mass of fly-ash used before 1st stage digestion (Initial), after 1st stage digestion, and after 2nd stage digestion. The graph shows that approximately a 21% loss of fly-ash mass was observed after the 1st stage digestion with an additional 30% during the 2nd. The total fly-ash mass loss through the dual digestion process was roughly 45%. This is a significant mass loss, showing that almost half of the solid fly ash mass has been solubilized into an aqueous solution. In an effort to put this result in into further context, the amount of U and Th extracted during each digestion stage is summarized in Figure F.8.

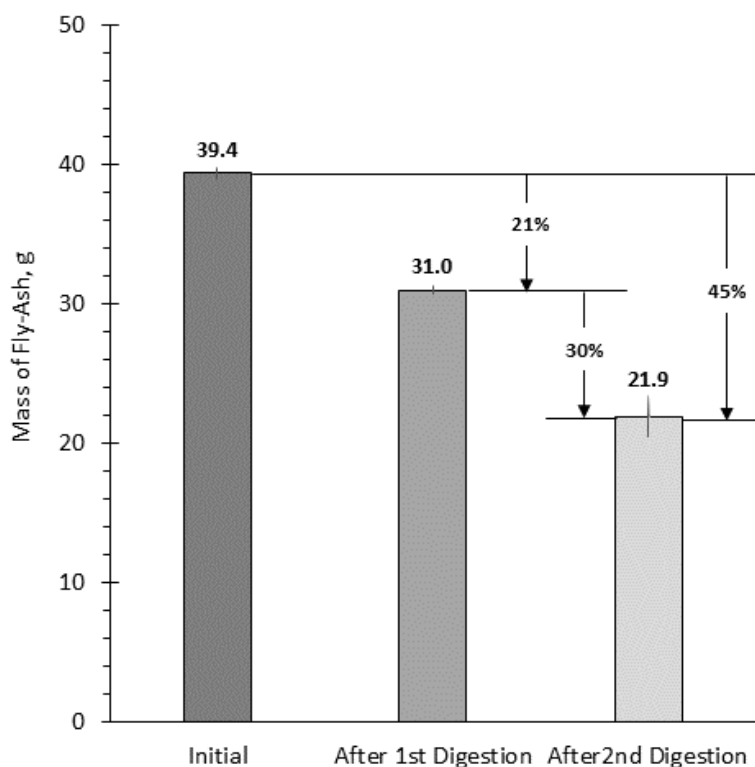


Figure 7

The loss of fly-ash mass between subsequent acid digestions

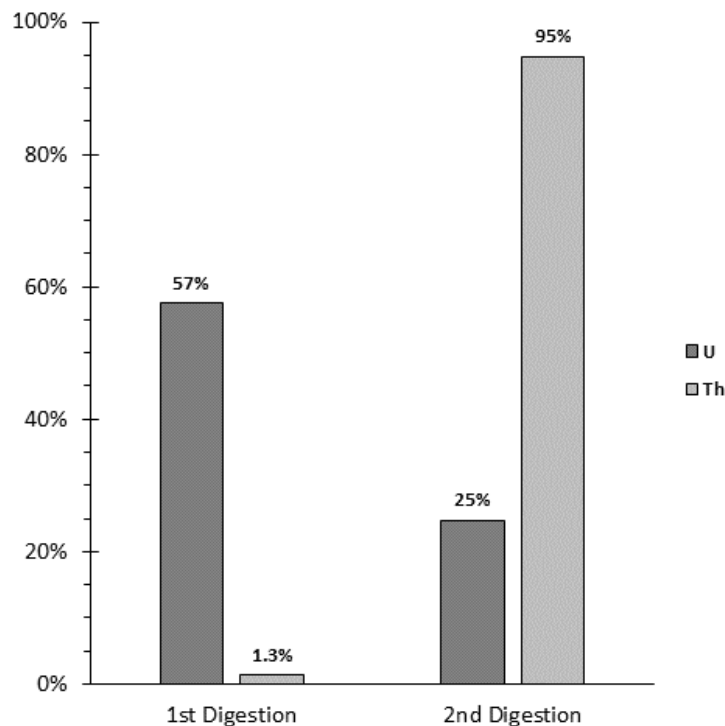


Figure 8

The impact of each digestion stage on the amount (based upon fusion analysis) of uranium (U) and thorium (Th) extracted from the selected fly-ash material.

Figure F.8 shows that Th is not readily extracted during 1st stage digestion using 1.335M HCl and 1.335M NaCl while uranium witnessed a 57% removal. This pretreatment/digestion followed by the second acid digestion with a 2M HCl solution extracted an additional 25% of the uranium and over 95% of the thorium. Therefore, the total uranium extracted during the dual digestion (from three-independent tests) was 82% and for thorium roughly 96% was extracted. It is clear from Figure F.8 that additional digestion is required to meet the target of 50% removal for uranium and thorium from the original fly-ash material.

Based upon this analysis, it is concerning that even when 50% of the original fly-ash material is converted during digestion, only 82% of the uranium present in the fly-ash is extracted. Although the majority of uranium and thorium were removed from the fly-ash by utilizing the dual digestion method, the amount of chemicals and processing efforts to reach this performance may be significant. This brings to light the possibility that target of 50% removal of both U and Th from the original fly-ash material may not be economically possible. Rather than have an absolute percentage target, a concentration-based metric may be a better choice to use in future evaluations.

APPENDIX A: Representative Sampling

Background

A representative sample for any source material obviously depends on the physical and chemical properties of the material (target population). At best, a representative sample should show no bias while at the same time being as precise as possible. Based upon the sampling requirements for this study, the error in sampling (i.e. sampling error) is the most critical factor. For fly ash materials, total sampling error is a combination of both compositional heterogeneity and distributional heterogeneity. Compositional heterogeneity is related to the fundamental sampling error (FSE) while distributional heterogeneity is related to the grouping and segregation error (GSE). The overall approach to obtaining a representative sample is to sample the containers (5-gal buckets) at different spatial locations with a sample thief, at a specified sample mass to produce an ideal composite sample.

Fundamental Sampling Error (FSE)

FSE is a statistical measure of the compositional heterogeneity. Compositional heterogeneity is the difference between individual fly ash particles and can be significant while distribution heterogeneity can be problematic with materials with broad particle size distributions since smaller and larger particles can segregate during transport and handling. The FSE for particle applications has been empirically formulated that relates the relative variance of the sampling error (percent relative standard deviation) to critical particle mass, particle heterogeneity, diameter, shape, density and mass of the sample. A lower FSE represents a highly representative sample. The FSE of a target population when a small sample size is used can be estimated by:

$$\sigma_{FSE}^2 = \frac{K d_{max}^3}{M_{Sample}} \quad \text{Eq. A1}$$

where:	M_{Sample}	sample mass for a specified relative standard deviation (RSD), [g]
	σ_{FSE}^2	fundamental sampling error, percent relative standard deviation (%RSD)
	K	empirical constant that accounts for particle shape, size range, mineralogical composition, and particle liberation, [cm ³ /g]
	d_{max}	maximum particle diameter, size of screen opening retaining 5% by weight of material, [cm]

Further refinement of Eq. A1 show that the fundamental sampling error is proportional to the following empirical equation:

$$\sigma_{FSE}^2 \propto f_{shape} \cdot g_{cf} \cdot C_{max} \cdot I \cdot d_{max}^3 \left(\frac{1}{M_{Sample}} - \frac{1}{M_{Lot}} \right) \quad \text{Eq. A2}$$

The equation can be rearranged to estimate required sample mass:

$$M_{Sample} \approx \frac{1}{\left(\frac{\sigma_{FSE}^2}{f_{shape} \cdot g_{cf} \cdot C_{max} \cdot I \cdot d_{max}^3} + \frac{1}{M_{lot}} \right)} \quad \text{Eq. A3}$$

where:	M_{Sample}	sample mass for a specified relative standard deviation (RSD), [g]
	σ_{FSE}^2	fundamental sampling error, percent relative standard deviation (%RSD)
	f_{shape}	shape factor of analyte particles, approximated by the following for spherical particles with a nominal particle diameter(d); = volume/d ³ = (4/3)π/8 ≈ 0.5

g_{cf}	granulometric factor, approximated by the 5 th percentile size (typical max. diam.) divided by the 95 th percentile size (typical max. diam.) $\approx d_{5\%}/d_{95\%}$. For typical fly-ash material $d_{5\%} = 7 \mu m$ and $d_{95\%} = 85$, $\therefore d_{5\%}/d_{95\%} = 0.0824$.
C_{max}	compositional maximum heterogeneity, calculated as the analyte particles and everything else. Typically estimated by using analyte density (λ_a), matrix density (λ_m), average material density (λ_{ave}), and analyte concentration $= \frac{(1-a_L)^2 \lambda_a \lambda_m}{a_L \lambda_{ave}}$ <p>In fly ash samples the analyte concentration, i.e. the amount of REE in fly ash, is very low so the compositional maximum heterogeneity can be approximated by: $\approx \lambda_a/a_L$</p> <p>Assuming a close-packed density of $\lambda_a = 1.59$ and an analyte concentration of 0.01%, $a_L = 0.0001$, then $C_{max} = 15,900$</p>
I	liberation factor, empirical factor, proportion of critical content particles separated from non-analyte containing particles. A value of $I = 1$ represents high heterogeneity while $I = 0.05$ represents a very homogeneous matrix. Since REE is liberated from fly ash particles (i.e. matrix particles), a value of $I = 1$ is used
d_{max}	maximum particle diameter, size of screen opening retaining 5% by weight of material, [cm] $= 0.08 \text{ cm}$
M_{Lot}	mass of lot being sampled, [g]

Grouping and Segregation Error (GSE) – Obtained Fly-Ash Samples

Segregation error accounts for the difference between particles spatially or temporally. Since the fly ash sample lots from each source are the only samples used during this study, only spatial differences between particles will contribute to overall sampling error. Segregation is influenced by particle size, size distribution, particle shape, density, moisture content, etc. The basic strategy used to limit GSE for the lot samples in this study was the use a sampling thief at different special positions (both radially and depth in a 5-gallon bucket) to obtain a representative (ideal) composite sample.

Error Estimates and Required Sample Size

The empirical equation given in Eq. A3 can be simplified using the estimated values above to:

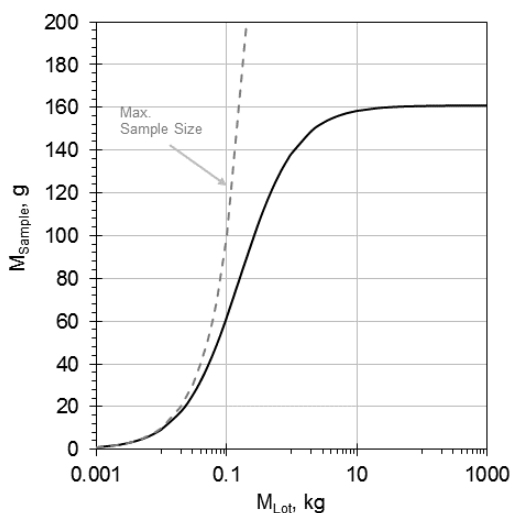
$$M_{Sample} \approx \frac{1}{\left(\frac{\sigma_{FSE}^2}{f_{shape} \cdot g_{cf} \cdot C_{max} \cdot I \cdot d_{max}^3} + \frac{1}{M_{lot}} \right)} \quad \text{Eq. A4}$$

$$= \frac{1}{\left(\frac{\sigma_{FSE}^2}{0.2834} + \frac{1}{M_{lot}} \right)}$$

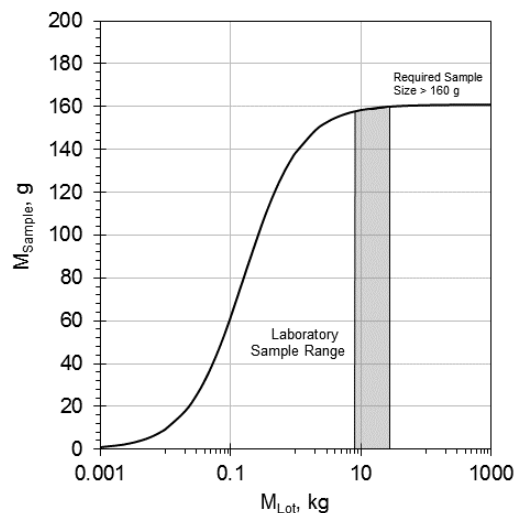
Based upon Eq. A4, it can be seen that when M_{Lot} becomes very large the required sample mass to obtain a representative sample from a uniform heterogeneous fly-ash mixture is inversely dependent on the targeted fundamental standard error:

$$M_{Sample} \approx \frac{0.2834}{\sigma_{FSE}^2} \quad \text{Eq. A5}$$

Using this equation, the minimum required sample volume for obtaining a representative onsite sample at each source is illustrated in the following diagrams.



Required minimum sample mass versus mass of fly-ash lot to achieve a 0.05% standard error in sampling.

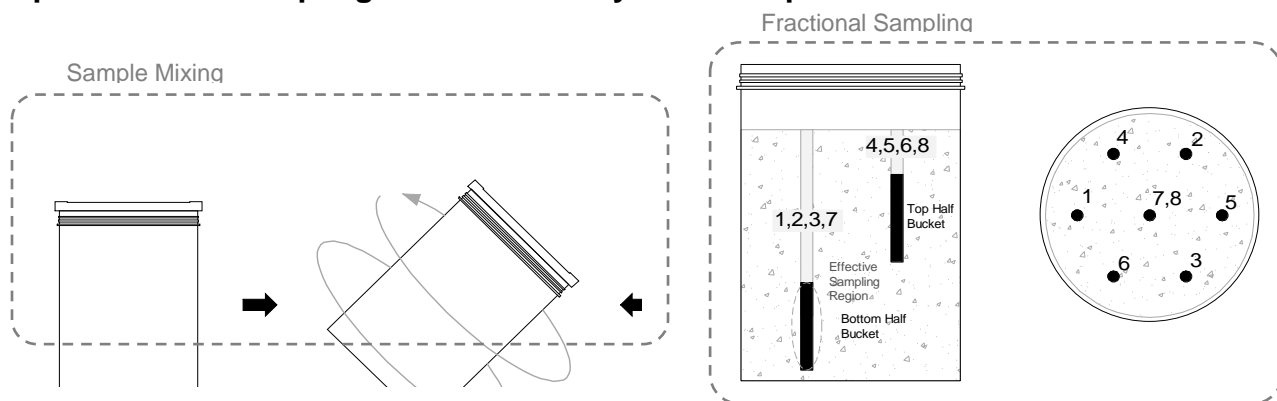


Required sample (composite) size from fly-ash source samples delivered to Tusaar's laboratory.

These figures show that for sample lots greater-than 10-kg (the case for power generating facilities), the required sample mass remains constant at approximately 113-g. This assumes (very critical) that the distributional heterogeneity throughout the entire lot sample is constant. Although there will be variability in the distributional as well as the compositional heterogeneity on a short-term basis, this variability should be relatively low if the same type of coal is combusted to produce the fly-ash. Compositional variability in the coal used has a larger impact on fly ash composition and day-to-day, month-to-month sample heterogeneity. Given the complexity of fly-ash generation at each power facility (i.e. different coal blends, production rates, etc.), the composite samples obtained at each site are generally representative of the fly-ash produced.

The figures above illustrate the size range of onsite source samples that were sent to Tusaar's laboratory. Based upon these sample sizes, a sample size (composite) of at least 113-g is required to obtain a representative sample based upon a target standard error of 5%.

Representative Sampling from Laboratory Bulk Samples



Received sample mixing procedure to ensure sample homogeneity and sampling sequence and location of fraction samples within large sample container to obtain representative composite sample for subsequent chemical and physical characterization.

APPENDIX B: Process Design Calculations

Unit Process No. 1: Pretreatment - Design Assumptions

Input Parameters		
General		
Desired Plant Capacity	200	t/d
Reactor Process Trains	4	
Number of Batches per Day	1	
Fly-Ash Storage and Transfer		
Storage Capacity	5	day(s)
Max. Fly-Ash Storage Volume	488	m ³
Number of Storage Basins	2	
Fly-ash Influent Transfer Rate	0.15	m ³ /min
Apparent Bulk Density	2.05	kg/L
Specific Gravity	2.6	kg/L
Pretreatment Reactor(s)		
Reaction Time	4	hrs
Reactor Volume Buffer	10	%
Reactor Diam.	3.66	m
Solids Loading	30	wt.%
Base Concentration (liquid vol.)	2	Molar
% Wash Liquor Recycle (of total vol.)	0	%
Influent Tempertaure	20	°C
Reaction Temperature	80	°C
Time to Heat	2	hr(s)
Heat Transfer Efficiency	85	%
Slurry Effluent Transfer Rate	350	lpm
wt% loss from fly-ash solids	-0.5	%
Chemical Storage and Dosing No. 1		
Base Strength	19.1	Molarity
	50	%
Base Density	1.530	kg/L
Reclaimed Filtrate Base Strength	0.50	Molarity
Storage Capacity	5.0	days
Base Transfer Rate	75	lpm
Filtration System 1		
H ₂ O Wash Volume Ratio	0.575	
Moisture in Wet Solids ¹ (w t% of fly-ash)	15	%
Processing Time	4	hr(s)
Value-Added Product No. 1 Reactor(s)		
Required Reaction Time	48	hr(s)
Reactor Diam.	3.66	m
Starting Temperature	25	°C
Reaction Temperature	95	°C
Time to Heat	4	hr(s)
Heat Transfer Efficiency	40	%
Reactor Volume Buffer	10	%
# of Process Effluents per Reactor	1	
Ratio of Al Conc. Vol. to Filtrate Vol.	0.125	
Value-Added Product Produced	0.24	kg/L
Value-Added Product Price	0.8	\$/kg
Electrical Consumption	0.005	kW/kg
Operational Input Assumptions		
Electrical Price	0.12	\$/kWh
Peak Charge	no	
Natural Gas Cost ^A	0.01	\$/cf
NaOH Cost ^B	355	\$/m ³
Fly Ash Cost ^C	5	\$/m ³
General Energy Usage ^D	1,250	kWh/d
H ₂ O Cost ^F	4.65	\$/1,000 gal

A - Inducstrial natural gas price in Kentucky, USA 2016 , \$10/1,000cf

A- NaOH 50w t% Alibaba, 275 gal. (3250 lbs), \$500/tonne @50% discount = \$250/tonne

C- Including transportation and off-loading costs

D- Usage for pumps, controls, mixers, slurry conveyance, etc.

E- CleaverBrooks Model CB Ohio Special, 9,415cfh at max. demand, 940cfh during temp. maint.

F- Tier 2 non-residential, 6" inlet @ \$125/month, \$4.65/1,000 gal

612

Calculated Parameters		
General		
Pretreated Fly-Ash per Batch	50,000	kg
H ₂ O/Wash/NaOH per Batch	116,667	kg
Max. Processing Time	9.64	hrs
Fly-Ash Storage and Transfer		
Influent Transfer Time	2.71	hrs
Average Fly-Ash Treatment Rate	8.33	kg/hr
Pretreatment Reactor (per process train)		
Total Reactor Volume	34.9	m ³
Required Reactor Volume	31.77	m ³
	8,393	gal
Number of Process Trains	4	
Reactor Height	3.02	m
Wash Water Reuse	0.0	m ³
H ₂ O Make-Up	22.8	m ³
Fly-Ash Volume	4.8	m ³
Composite Slurry Density	1.31	kg/L
Heat Energy	34,505,882	kJ
Power Consumption	4792.5	kW
Boiler Size	489	BHP
Effluent Transfer Time	1.51	hrs
Chemical Storage and Dosing No. 1 (per process train)		
Base Required per Batch	4,163	liters
	6368.8	kg
Base Transfer Time	0.93	hr(s)
Base Storage Tank Size	83.3	m ³
Filtration System 1 (per process train)		
Required Tank Vol.	34.9	m ³
H ₂ O Wash Vol.	18.3	m ³
Total Filtration Vol.	50.0	m ³
Min. Processing Rate	208	lpm
Total Filtrate Volume	21.8	m ³
Total Solids	50,250	kg
Liquid in Solids	8,868	kg
Total Wet Solid Volume	28.19	m ³
Wet Solid Density	2.10	kg/L
Filtrate Density	1.07	kg/L
Value-Added Product Reactors No. 1 (for all process trains)		
Filtrate Vol.	87.4	m ³
Required Al Conc. Vol.	10.9	m ³
Available Al Conc. Vol. per day	31.8	m ³ /d
# of Batches per day	1	
Usable Reactor Vol.	98.3	m ³
Total Reactor Vol.	108.1	m ³
Reactor Height	10.29	m
Number of Reactors	3	
Heat Energy per Reactor	72,064,891	kJ
Value-Added Product Produced (per batch)	23588	kg
Power Consumption (for 4 reactors)	15,014	kW
Boiler Size	1531	BHP
Discharge Liquid Volume	93.56	m ³
Operational Cost Calculations		
Pretreatment (per process train)		
H ₂ O Cost	\$	50
Chemical Cost	\$	1,502
Electrical Cost	\$	58
Natural Gas Cost ^E		327
Total Cost	\$	1,937
Value-Added Product No. 1 (per process train)		
Chemical Cost		
Electrical Cost	\$	1,019
Natural Gas Cost		5,191
Total Cost	\$	6,210
Revenue	\$	18,195

Cost per day	\$	13,957
Revenue per day	\$	18,195

Unit Process No. 2: Digestion - Design Assumptions

Input Parameters		
General		
Desired Plant Capacity	200	t/d
Reactor Process Trains	4	
Number of Batches per Day	1	
Digestion Reactor(s)		
Reaction Time	4	hr(s)
Reactor Volume Buffer	20	%
Reactor Diam.	3.658	m
Solids Loading	18	wt%
Base Concentration (liquid vol.)	2.67	Molar
Total Influent Slurry Volume (per batch)	28.2	m ³
Influent Tempertaure	20	°C
Reaction Temperature	80	°C
Time to Heat	2	hr(s)
Heat Transfer Efficiency	85	%
Slurry Effluent Transfer Rate	350	lpm
wt% Loss from Fly-Ash Solids	20	%
Chemical Storage and Dosing No. 2		
Reaction Time	1	hr(s)
Acid Strength	11.7	Molarity
	36	%
Acid Density	1.180	kg/L
Acid Requirement	0.0767	kg-acid/kg
Storage Capacity	5	days
Acid Transfer Rate	75	lpm
Chemical Storage and Dosing No. 3		
Base Strength	19.1	Molarity
Base Density	1.530	kg/L
Storage Capacity	5	days
Base Transfer Rate	25	lpm
Final pH	2	
Required Base Dose	0.528	moles/l
Filtration System 2		
H ₂ O Wash Volume Ratio	2	m ³ /t-solid
Moisture in Wet Solids	64	wt%
Processing Time	4	hr(s)
Filtration System 3		
Solids Concentration	30	wt%
Solids Produced	36	kg/m ³
Processing Time	4	hr(s)
pH Adjustment Tank No. 1		
Required Reaction Time	2	hr(s)
Reactor Diam.	2.44	m
Reactor Volume Buffer	10	%
Solids Dryer ¹		
Dried Solids Concentration	75	wt%
Processing Capacity	1.014	m ³ /hr
Power Requirement	7.2	kW
Natural Gas Consumption	200	cfh
Number of Units	4	
Sludge Dryer ¹		
Dried Solids Concentration	75	wt%
Processing Capacity	1.014	m ³ /hr
Power Requirement	7.2	kW
Natural Gas Consumption	200	cfh
Number of Units	4	
Operational Input Assumptions		
Electrical Price	0.11	\$/kWh
Peak Charge	no	
Natural Gas Cost ^A	0.004	\$/cf
NaOH Cost ^B	355	\$/m ³
HCl Cost ^C	350	\$/m ³
General Energy Usage ^D	1,000	kWh/d
H ₂ O Cost ^E	4.65	\$/1,000 gal
Pozzolanic Fly-Ash Selling Price	15	t
Sludge Disposal Cost	0.1	\$/kg

A - Inducstrial natural gas price in Kentucky, USA 2016 , \$4/1,000cf

A- NaOH 50w t% Alibaba, 275 gal. (3250 lbs), \$500/tonne @50% discount = \$250/tonne

C - 36% HCL

D - Usage for pumps, controls, mixers, slurry conveyance, etc.

E - Tier 2 non-residential, 6" inlet @ \$125/month, \$4.65/1,000 gal

F - CleaverBrooks Model CB Ohio Special Boiler, 9,415cfh at max. demand, 940cfh during temp. maintenance

1 - M.W. Watermark Sludge Dryer Model DM-380G

Calculated Parameters		
General		
Pretreated Fly-Ash (per batch)	50,250	kg
H ₂ O/HCl (per batch)	228,917	kg
Max. Processing Time (per batch)	8.77	hrs
Digestion Reactor(s) (per process train)		
Total Reactor Volume	45.7	m ³
Required Reactor Volume	38.1	m ³
	10,064	gal
Number of Process Trains	4	
Reactor Height	4.35	m
H ₂ O in Influent Slurry	8.87	m ³
H ₂ O Requirement	5.60	m ³
Fly-Ash Volume	19.33	m ³
Composite Slurry Density	1.83	kg/L
Heat Energy	67,705,471	kJ
Power Consumption	9404	kW
Boiler Size	959	BHP
Effluent Transfer Time	1.81	hrs
Total Effluent Solids	40200	kg
Chemical Storage and Dosing No. 2 (per process train)		
Acid Required per Batch	4,302	liters
	5077	kg
Acid Transfer Time	0.96	hr(s)
Acid Storage Tank Size	86.0	m ³
Chemical Storage and Dosing No. 3 (per process train)		
Base Required per Batch	1,428	liters
	2185	kg
Base Transfer Time	0.95	hr(s)
Base Storage Tank Size	28.6	m ³
Filtration System 2 (per process train)		
Feed Tank Vol.	50.3	m ³
H ₂ O Wash Vol.	100.5	m ³
Total Filtration Vol.	138.6	m ³
Min. Processing Rate	215	lpm
Total Filtrate Volume	51.7	m ³
Total Solids	40,200	kg
Liquid in Solids	71,467	kg
Total Wet Solid Volume	86.93	m ³
Wet Solid Density	1.28	kg/L
Filtration System 3 (per process train)		
Feed Tank Vol.	152.5	m ³
Min. Processing Rate	577	lpm
Total Filtrate Volume	132.7	m ³
	4989	kg
Total Wet Solid Volume	5.93	m ³
pH Adjustment Tank No.1 (per process train)		
Filtrate Vol. per Batch	51.7	m ³
Required Tank Vol. per Batch	53.1	m ³
Total Tank Vol.	58.4	m ³
Tank Height	12.51	m
Solids Dryer (per process train)		
Solids Processed	86.93	m ³
Processing Time	21.4	hr(s)
	17,146	cf
Power Consumption	617.2	kWh
Dry Solids Produced	53,600	kg
Sludge Dryer (per process train)		
Solids Processed (inc. Wet Solid No. 4 & 6)	65.51	m ³
Processing Time	16.2	hr(s)
Natural Gas Consumption	12,921	cf
Power Consumption	465.2	kWh
Dry Solids Produced	6653	kg
Operational Cost Calculations		
Digestion (per process train)		
Chemical Cost	\$	2,013
Electrical Cost	\$	53
Natural Gas Cost	\$	-
H ₂ O Cost		130.3
Sludge Disposal Cost	\$	665
Total Cost	\$	2,066
Value-Added Product No. 2 (per process train)		
Revenue	\$	804
Chemical Cost	\$	-
Electrical Cost	\$	533
Natural Gas Cost ^F	\$	120
Total Cost	\$	653

Cost per day	\$	10,876
Revenue per day	\$	3,216

Unit Process No. 3: U/Th Removal

Input Parameters		
General		
Desired Plant Capacity	200 t/d	
Process Trains	4	
Number of Batches per Day	1	
Chromatography Column(s)		
Carbon Media Requirement ¹	0.25 kg/m ³ liquor	
Bulk Density Packed Carbon	385 kg/m ³	
Column Volume Buffer	5 %	
Num. of Columns per Process Train	1	
Number of Columns	4	
Column L/D Ratio	8	
Influent Liquor Volume (per batch)	132.7 m ³	
Make-up Mobile Phase Soln.	0.051 m ³ /m ³ -liquor	
Mobile Phase Recycle Vol.	0.464 m ³ /m ³ -liquor	
Days between Media Replacement	60 d	
min. EBCT	7.0 min.	
Target Column Throughput Velocity	2.41 m/hr	
Target Hydraulic Loading	40 lpm/m ²	
Al Concentrate - % of Influent Flow	6 %	
U Adsorption Column(s)		
Carbon Media Requirement ¹	0.25 kg/m ³ liquor	
Bulk Density Packed Carbon	385 kg/m ³	
Column Volume Buffer	5 %	
Number of Columns	4	
Column L/D Ratio	8	
Influent Liquor Volume (per batch)	124.7 m ³	
Days between Media Replacement	60 d	
min. EBCT	7.0 min.	
Target Column Throughput Velocity	5.1 m/hr	
Target Hydraulic Loading	115 lpm/m ²	
Chemical Storage and Dosing No. 4		
Base Strength	19.1 Molarity	
Base Density	1.530 kg/L	
Storage Capacity	5 days	
Base Transfer Rate	75 lpm	
Final pH	2	
Required Base Dose	0.570 moles/l	
Filtration System 4		
Solids Concentration	30 wt%	
Solids Produced	81.6 kg/m ³	
Processing Time	4 hr(s)	
pH Adjustment Tank No. 2		
Detention Time	2 hr(s)	
Reactor Diam.	2.44 m	
Reactor Volume Buffer	10 %	
Operational Input Assumptions		
Electrical Price	0.11 \$/kWh	
Peak Charge	no	
NaOH Cost ^A	355 \$/m ³	
General Energy Usage ^B	500 kWh/d	
Carbon Replacement Cost	4 \$/kg	
Sludge Disposal Cost	0.1 \$/kg	

A - NaOH 50wt% Alilbaba, 275 gal. (3250 lbs), \$500/tonne @50% discount = \$250/tonne

B - Usage for pumps, controls, mixers, slurry conveyance, etc.

1 - Based upon 0.04 wt% U capacity and splitting requied carbon into tw o columns

Calculated Parameters		
General		
Total Liquor Vol. Processed	530.7 m ³ /d	
Max. Processing Time	18.9 hrs	
Chromatography Column(s) (per process train)		
Required Carbon Media Mass	995.0 kg	
Carbon Media Volume	2.58 m ³	
	682.8 gal	
Recircr. Mobile Phase Vol.	61.56 m ³	
Added Mobile Phase Vol.	6.77 m ³	
Total Treated Vol.	200.99 m ³	
Required Column Vol.	211.04 m ³	
Column Height	4.66 m	
Column Diameter	0.500 m	
Flowrate	369.2 lpm	
Processing Time	6.0 hrs	
Actual Hydraulic Loading	1880 lpm/m ²	
Actual Throughput Velocity	112.8 m/hr	
Carbon Media Replacement Loss	16.6 kg/d	
Tot. Al Conc. Vol. (from all columns+batches)	31.84 m ³	
Tot. Effluent Vol. (from all columns+batches)	498.8 m ³	
U Adsorption Column(s) (per process train)		
Required Carbon Media Mass	995.0 kg	
Carbon Media Volume	2.58 m ³	
	682.8 gal	
Column Height	4.66 m	
Column Diameter	0.500 m	
Flowrate	369.2 lpm	
Processing Time	5.6 hrs	
Actual Hydraulic Loading	1880 lpm/m ²	
Actual Throughput Velocity	112.8 m/hr	
	16.6 kg/d	
Tot. Effluent Vol. (from all columns+batches)	498.8 m ³	
Chemical Storage and Dosing No. 4 (for all columns and batches)		
Base Required	14,887 liters	
	22,776 kg	
Base Transfer Time	3.31 hr(s)	
Base Storage Tank Size	14.9 m ³	
Filtration System 4 (for all columns and batches)		
Feed Vol.	513.7 m ³	
Min. Processing Rate	2140 lpm	
Total Filtrate Volume	454.7 m ³	
Total Solids	40,705 kg	
Total Wet Solid Volume	44.15 m ³	
pH Adjustment Tank No.2 (for all columns and batches)		
Filtrate Vol.	498.8 m ³	
Influent Flow Rate	88.6 m ³ /hr	
Total Required Tank Vol.	177.2 m ³	
Total Tank Vol.	194.9 m ³	
Tank Height	41.76 m	
Operational Cost Calculations		
U/Th Removal (total per day)		
Chemical Cost \$	5,285	
Electrical Cost \$	55	
Carbon Disposal Cost \$	2,123	
Total Cost \$	7,462	
Cost per day \$	7,462	
Revenue per day \$	-	

Unit Process No. 4: REE Separation

Input Parameters		
General		
Desired Plant Capacity	200	t/d
Process Trains	4	
Number of Batches per Day	1	
Extraction Column(s)		
Carbon Media Requirement	2.5	kg/m ³ liquor
Bulk Density Packed Carbon	385	kg/m ³
Media Requirement Multiplier	0.82	
Column Volume Buffer	5	%
Num. of Columns per Process Train	2	
Total Num. of Columns	8	
Column L/D Ratio	8	
Extraction Column(s) - Adsorption Phase		
Inf. Liquor Volume (per process train)	113.7	m ³
min. EBCT	7.0	min.
Target Column Throughput Velocity	0.31	m/hr
Target Hydraulic Loading	5.1	lpm/m ²
Extraction Column(s) - Stripping/Conditioning Phase		
Strip/Cond. 3M Acid Requirement	0.180	m ³ /m ³ -liquor
Strip/Cond. Mobile Phase Soln.	0.018	m ³ /m ³ -liquor
Strip/Cond. Mobile Phase Recycle Vol.	0.164	m ³ /m ³ -liquor
min. EBCT	7.0	min.
Target Column Throughput Velocity	5.1	m/hr
Target Hydraulic Loading	115	lpm/m ²
Chemical Storage and Dosing No. 5		
Acid Strength	11.7	Molarity
Acid Density	1.180	kg/L
Storage Capacity	5	days
Acid Transfer Rate	1	lpm
Final pH	4	
Required H ₂ O	2.046	m ³
Chemical Storage and Dosing No. 6		
Acid Strength	11.7	Molarity
Acid Density	1.180	kg/L
Storage Capacity	5	days
Acid Transfer Rate	1	lpm
Final Molarity	3	M
Operational Input Assumptions		
Electrical Price	0.11	\$/kWh
Peak Charge	no	
HCl Cost ^A	350	\$/m ³
General Energy Usage ^B	250	kWh/d
H ₂ O Cost ^C	4.65	\$/1,000 gal

A - 36% HCL
B - Usage for pumps, controls, mixers, slurry conveyance, etc.
C- Tier 2 non-residential, 6" inlet @ \$125/month, \$4.65/1,000 gal

Calculated Parameters		
General		
Total Liquor Vol. Processed	454.7	m ³ /d
Total Processing Time	24.00	hrs
Extraction Column(s) (per process train)		
Required Carbon Media Mass	115.9	kg
Carbon Media Volume	0.30	m ³
Column Height	2.08	m
Column Diameter	0.200	m
Extraction Column(s) (per process train) - Adsorption Phase		
Loading Inluent Vol.	113.7	m ³
Flowrate	43.0	lpm
Processing Time	22.0	hrs
Actual Hydraulic Loading	1369	lpm/m ²
Actual Throughput Velocity	82.1	m/hr
Extraction Column(s) (per process train) - Stripping/Conditioning Phase		
Recirc. Mobile Phase Vol.	18.64	m ³
Added Mobile Phase Vol.	2.05	m ³
Total Mobile Phase Vol.	134.36	m ³
Total Acid Strip Volume	20.46	m ³
Flowrate	43.0	lpm
Processing Time	2.0	hrs
Actual Hydraulic Loading	1369.1	lpm/m ²
Actual Throughput Velocity	82.1	m/hr
Chemical Storage and Dosing No. 5 (for all columns and batches)		
Acid Required	0.017488	liters
	0.0206	kg
Total Solution Vol.	2.046	m ³
Acid Transfer Time	0.00	hr(s)
Acid Storage Tank Size	0.1	m ³
Chemical Storage and Dosing No. 6 (for all columns and batches)		
Acid Required	20.99	m ³
	25	kg
H ₂ O Required	60.86	m ³
Acid Soln. Transfer Time	7.93	hr(s)
Acid Soln. Storage Tank Size	102.3	m ³
Operational Cost Calculations		
U/Th Removal (total per day)		
Chemical Cost	\$	7,345
Electrical Cost	\$	28
Total Cost	\$	7,372
Cost per day	\$	7,380
Revenue per day	\$	-

Unit Process No. 5: Discharge

Input Parameters		
General		
Desired Plant Capacity	200	t/d
Process Trains	4	
Number of Batches per Day	1	
Wastewater Precipitation Tank		
Detention Time	1	hr(s)
Reactor Diam.	6.10	m
Num. of Tanks	4	
Reactor Volume Buffer	10	%
Chemical Storage and Dosing No. 7		
Base Strength	19.1	Molarity
Base Density	1.530	kg/L
Storage Capacity	5	days
Base Transfer Rate	200	lpm
Final pH	6	
Required Base Dose	0.085	m ³ /m ³ -liquor
Required Reaction Time	1	hr(s)
Filtration System 5		
Solids Concentration	30	wt%
Solids Produced	45	kg/m ³
Processing Time	8	hr(s)
Precipitated Solids Density	1.15	kg/L
Chemical Storage and Dosing No. 8		
Acid Strength	12.0	Molarity
Acid Density	1.180	kg/L
Storage Capacity	5	days
Acid Transfer Rate	100	lpm
Final pH	6	
Required Acid Dose	0.030	L/m ³ -liquor
Final pH Adj. Tank Tank		
Reaction Time	2	hr(s)
Reactor Diam.	2.438	m
Reactor Volume Buffer	20	%
ial Input Assumptions		
Electrical Price	0.11	\$/kWh
Peak Charge	no	
NaOH Cost ^A	355	\$/m ³
General Energy Usage ^C	500	kWh/d
HCl Cost ^A	350	\$/m ³

A- NaOH 50w t% Alibaba, 275 gal. (3250 lbs), \$500/tonne @50% discount = \$250/tonne
B - Usage for pumps, controls, mixers, slurry conveyance, etc.
C - 36% HCL

Calculated Parameters		
General		
Value-Added Product No. 1 Waste Stream	93.6	m ³
Extraction Column Cond. Effluent	8.18	m ³
Treated Process Solution	454.7	m ³
Filter Sys. 6 Filtrate	95.90	m ³
Max. Processing Time	5.62	hrs
Wastewater Precipitation Tank (per tank)		
Filtrate Vol.	163.1	m ³
Total Required Tank Vol.	179.4	m ³
Tank Height	6.15	m
Chemical Storage and Dosing No. 7		
Base Required	55,448	liters
	84,835	kg
Base Transfer Time	4.62	hr(s)
Base Storage Tank Size	55.4	m ³
Total Treatment Time	5.6	hr(s)
Filtration System 5		
Feed Vol.	218.5	m ³
Min. Processing Rate	455	lpm
Total Filtrate Volume	203.1	m ³
Total Solids	9,834	kg
Total Wet Solid Volume	15.43	m ³
Final pH Adj. Tank		
Filtrate Vol.	203.1	m ³
Total Required Tank Vol.	213.3	m ³
Tank Height	195.00	m
Chemical Storage and Dosing No. 8		
Acid Required	203.1	liters
	239.7	kg
Acid Transfer Time	0.03	hr(s)
Acid Storage Tank Size	203.1	liters
Total Treatment Time	2.0	hr(s)
Operational Cost Calculations		
U/Th Removal (total per day)		
Chemical Cost	\$	19,755
Electrical Cost	\$	55
Total Cost	\$	19,810
Cost per day	\$	19,810
Revenue per day	\$	-

Unit Process No. 6: Production

Input Parameters		
General		
Desired Plant Capacity	200	t/d
Process Trains	4	
Number of Batches per Day	1	
REE Precipitation Tank		
Detention Time	2	hr(s)
Reactor Diam.	6.10	m
Reactor Volume Buffer	10	%
Chemical Storage and Dosing No. 9		
Base Strength	19.1	Molarity
Base Density	1.530	kg/L
Storage Capacity	5	days
Base Transfer Rate	100.0	lpm
Final pH	6	
Required Base Dose	0.200	m³/m³-liquor
Filtration System 6		
Solids Concentration	30	wt%
Solids Produced	18	kg/m³-liquor
Processing Time	2	hr(s)
Precipitated Solids Density	1.15	kg/L
% Metal Hydroxides in Wet Solids	15	%
Kiln		
Detention Time	6	hr(s)
Chamber Size	0.53	m³
Max. Temp.	600	C
Power	4,000	kW
% REEs in Final Solid	18	%
Ave. REE Selling Price ^D	19	\$/kg
Operational Input Assumptions		
Electrical Price	0.11	\$/kWh
Peak Charge	no	
NaOH Cost ^A	355	\$/m³
General Energy Usage ^B	1,500	kWh/d

A - NaOH 50w t% Alibaba, 275 gal. (3250 lbs), \$500/tonne @50% discount = \$250/tonne
B - Usage for pumps, controls, mixers, slurry conveyance, etc.
C - Carbolite Gero Ltd. Model HT6/28
D - Based upon \$15/tonne in original fly ash with 380g TREE, assuming all REE fractions are equally removed during the process

Calculated Parameters		
General		
Total Acid Strip Volume	81.84	m³
Max. Processing Time	2.73	hrs
REE Precipitation Tank		
Process Vol.	81.84	m³
Total Tank Vol.	90.0	m³
Tank Height	3.08	m
Chemical Storage and Dosing No. 9		
Base Required	16,369	liters
	25,044	kg
Base Transfer Time	2.73	hr(s)
Base Storage Tank Size	81.84	m³
Filtration System 6		
Feed Vol.	98.21	m³
Min. Processing Rate	818	lpm
Total Filtrate Volume	95.90	m³
Total Solids	1,473	kg
Total Metal Hydroxides	221.0	kg
Total Wet Solid Volume	2.31	m³
Kiln		
Detention Time	2	hr(s)
Reactor Diam.	2.44	m
Reactor Volume Buffer	10	%
REO Mass	39.8	kg
% REE Recovery Efficiency	41.4	%
Operational Cost Calculations		
U/Th Removal (total per day)		
Chemical Cost	\$	5,811
Electrical Cost ^C	\$	2,640
Total Cost	\$	8,451
Cost per day	\$	8,491
Revenue per day	\$	756