PHASE 2 FINAL TECHICAL REPORT

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INVESTIGATION OF RARE EARTH ELEMENT EXTRACTION FROM NORTH DAKOTA COAL-RELATED FEEDSTOCKS

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1 EXECUTIVE SUMMARY

The rare earth elements (REE), among numerous other elements, have been designated as a critical mineral by the US Department of Interior[1], and comprise the lanthanide series minus promethium, and include yttrium and scandium. These elements, due to their unique properties, are essential and often non-substitutable in a variety of consumer goods, energy systems, and defense applications. With the global production and value chain largely controlled by a single source, the US has begun moving to generate domestic supplies of the critical resource. Mineral deposits have been exploited for their REE content in the US in the past; however, these deposits are dominated by low-value REE (such as La and Ce), and may be plagued with high naturally occurring radioactive material (NORM) content. It is imperative a sustainable, environmentally-friendly, domestic supply of the critical REE is developed. Coal and coal byproducts have been identified as a promising alternative to the mineral resources, particularly due to the existing mine infrastructure in place and with more favorable economic distributions of the REE. This report details a Phase 1 and 2 evaluation of the technical and economic feasibility of REE extraction and recovery from North Dakota lignite coal.

There were four major goals of this project: i) identify promising lignite or lignite-related feedstocks with total rare earth element content above 300 parts per million (ppm), ii) evaluate at the lab and bench-scale the extractability of the REE from the material, iii) determine the processing required to generate REE concentrates in excess of 2 wt%, iv) evaluate the economic feasibility of the process and develop a pathway for commercialization. In the Phase 1 study, work was primarily focused upon resource evaluation and lab-scale extractability of the REE, with a preliminary techno-economic assessment (TEA) conducted, whereas in the Phase 2 work, the extraction process was conducted at the bench scale, a method for cost-effective generation of higher purity mixed REE concentrates (up to 65%) was developed, and a refined TEA on the bench-scale data for a 1,000 kg coal processing test was conducted.

In total, between the efforts, a combined total of over 400 samples were gathered and analyzed, including a number of coals from active and inactive mining areas, clay partings, roof and floor rocks, as well as ash and coal processing samples. A number of samples were found to contain over 300 ppm on a whole sample basis, including two particular samples of pre-combustion lignite, the density-separated lightest fractions of the Harmon seam, and the entirety of the H-Bed seam. Within the coal-based samples, the REE were most prevalently found within organic complexes, as compared with potential mineral matter. Extraction of the high REE content of the coals, as compared with that of the mineral matter in the high-ash roof and floor rock (expected as monazite equivalents as sources of REE), was found to be significantly easier with dilute acids, and marked a significant reduction in potential costs associated with the resource. Identification of fingerprinting elements for indication of the REE's was not analyzed in this scope of this project but is being pursued within other funded work. The two coal samples with potential for > 300 ppm were gathered in large quantities (~6,000-7,000 lbs each) from outcrops for potential bench testing, with the H-bed utilized for the 1,000 kg production testing usage. Overall, leaching efficiency for the REE from pre-combustion lignite was typically in the range from 80-95% recovery from ore for the full extraction of the organically-bound materials.

The process developed within the scope of this project targets the extraction of the REE from pre-combustion lignite, as compared with previous research into fly ash and other byproduct extraction. This was based upon the high HREE content found in many lignite samples as compared with the mineral resources found outside of the organically-bound lignite sources, as well as the ease of extraction as compared with the mineral-based REE sources. The testing conducted in the Phase 2 project involved potential use of a sequential extraction method for impurity control, but was adjusted to a one-step leaching process for economic benefit. The leaching process is able to extract the REE and a number of deleterious elements for upgraded coal use *at minimal additional cost*, allowing a significantly improved lignite product as a byproduct from the process. Following the leaching process, a hydrometallurgical process was designed to generate REE concentrates of various purity, including a primary concentrate of averaged greater than 50% purity REO's, containing more than 70% of the total REE mass, and a secondary concentrate of ~ 7% purity REO containing essentially all of the Sc mass. Overall REE recoveries from coal into salable products of 30-50% were achieved at the bench-scale semi-continuous testing, with dewatering efficiency from the lignite found to be the largest contributor for the lack of recovery.

The upgraded lignite product contains reduced overall ash (35% → 18%), but more interestingly highly reduced organic-bound ash (6% → <0.5%), which is the target for non-fuel, added-value use. In terms of the lignite use as a thermal coal for steam production, the significantly reduced ash, and particularly the substantial shift in base/acid ratio (in some cases reducing below 1 from above 2) and the removal of the volatile and fouling Na content, is expected to be a significant value proposition from discussion with electric utilities. This reduction in fouling constituents could lead to significantly reduced outages, improved efficiency (and therefore reduced overall emissions), and a longer asset lifetime, particularly with variable load profiles.

The process developed, including the leaching, impurity removal, and REE recovery, utilizes industrially-proven equipment, and requires no novel reagent usage. The process also utilizes ambient temperature and moderate pH for mineral processing technologies, and has multiple solid products to minimize potential waste streams. offering a low-cost and environmentally friendly solution. The upgraded lignite material may be easily integrated into additional added-value coal opportunities, including activated carbon production, combined heat and power, humic acid production, and as an upgraded fuel for coal-fired utility/industrial use. Humic acid, an organic constituent of low rank coals (leonardite, lignite, and subbituminous coals) is valuable as an organic fertilizer, utilized in the pharmaceuticals industry, and a potential precursor for synthetic graphite and graphene materials. The techno-economic assessment conducted under this work evaluated two configurations of combined facilities: i) an activated carbon/combined heat and power facility, and ii) a combined humic acid production facility. In each base case, both were shown to have profitable economics utilizing the results of the bench-scale testing conducted in Phase 2, even at the small scale (less than 25 tons/hr) expected of small commercial demonstration facilities.

Naturally Occurring Radioactive Materials (NORM – more specifically U and Th), ubiquitous with REE mining projects, was identified as a minor challenge with the lignite-based extraction and concentration process, largely remaining within the source material (<15% extraction), and with combined final concentrations in REE concentrates below 0.25% on an oxide basis. Further testing to identify improved ways of controlling extraction of the NORM, and therefore reducing downstream management costs, will be researched in further work.

2 INTRODUCTION

The University of North Dakota has partnered with Microbeam Technologies Inc., Barr Engineering, and Pacific Northwest National Laboratory to determine the technical and economic feasibility of concentrating rare earth elements from North Dakota lignite coal and lignite coal-related feedstocks. This report encompasses the work over the Phase 1 and Phase 2 projects, with the Phase 1 final report found in Appendix A.

The overall goal of the Phase 2 project was to demonstrate at the bench-scale, a high performance, economically viable, and environmentally benign technology to recover rare earth elements from local lignite coal or lignite-related feed stocks. In order to meet this goal, the project team identified the following specific objectives at the project onset:

- Based on the design of the bench-scale system developed in Phase 1, construct a bench-scale system with a REE-rich feedstock throughput of about 10 kg/hr to produce a mixed REE stream of >2% by weight on a dry, elemental basis as a mixed oxide solid cake
- Obtain large samples (~2000 kg) of coal and associated sediments containing >300 ppm total REE dry whole sample basis for testing
- Conduct parametric testing of the bench-scale system to determine optimum conditions required to concentrate REE to >2%
- Conduct continuous testing of the bench-scale system at optimized conditions/configuration to produce a representative REE concentrate that is suitable for evaluation for further processing
- Provide splits of samples of the final product produced from the Phase 2 testing to NETL for independent analysis and verification of the quantity of REE present
- Update the technical and economic analysis of the REE recovery process conducted in Phase 1 with the results of testing obtained in Phase 2
- Identify opportunities for commercialization at existing mines/plants locally and/or build the commercially feasible case for opening a new mine in an area with most favorable REE content
- Work with industry supporters to develop a technology development and commercialization strategy

2.1 Scope of Work

The scope of work was broken down into nine tasks which are summarized below, with results, discussion and conclusions presented in detail in later sections of this report.

- *Task 1 – Project management and planning*: This task included work elements required to maintain and revise the Project Management Plan and to manage and report on activities in the accordance with the plan, as well as to ensure coordination and planning of the project with DOE/NETL and other project participants and sponsors. This included quarterly reporting, annual presentations, and project kick-off and close-out presentations/reporting.

- *Task 2 – Provide split samples:* This task involved the submission of the highest achieved REE purity concentrate for independent 3rd party analysis to NETL.

- *Task 3 – Bench-scale system procurement and construction:* Based on the design developed in Phase 1, this task included procurement of equipment, installation and construction, and shakedown tests on the installed system. This design was developed to be a system of 4 batch tanks, in which parametric testing could be expedited.

- *Task 4 – Sampling, characterization and large sample collection*: This task included testing to determine the optimal REE-enriched lignite feedstock for large-scale sampling, collection of large quantities of sample from several locations, and physical beneficiation processing of the large sample. Characterization methods were aimed at understanding the bulk chemistry of the samples as well as the forms and modes of occurrence of the REEs and other important elements. This task also included laboratory-scale extraction/concentration testing of selected feedstocks to concentrate REEs to a target of 2% by weight.

- *Task 5 – Parametric testing – batch tests:* This task included parametric testing to determine the optimal conditions for both leaching and processing of the leachate to recovery REE. Testing to determine the kinetics of leaching was also completed. This was conducted at the laboratory and bench-scale, and is documented in more detail in the Phase 2 Testing Report (Appendix B).

- *Task 6 – Bench-scale system modification for continuous tests:* In this task, the bench-scale system installed in Task 3 was modified to allow for semi-continuous operation for Task 7 testing. This included addition of flow control systems, sensors for pressure measurement of filtration, and multiple pressure-based filtration mechanisms.

- *Task 7 – Continuous testing – production tests:* This task involved using the optimized conditions established in Task 5 to process 1000 kg of coal for recovery of REE. REE concentrates, as well as all other solids and liquids generated during the process, were sampled for their composition and for mass balance purposes. The data generated from this testing was utilized to establish the base-case for the techno-economic assessment in Task 8.

- *<u>Task 8 – Updated technical and economic analysis and commercialization plan</u>*: Based on the results of Task 7, a technical and economic feasibility assessment (TEA) was completed by Barr Engineering that developed the design and determined the economic merits of a commercial-scale REE concentration facility. Two facilities were envisioned, including co-production with activated carbon or humic acid, at capacities of 5 and 20 tons of coal feedstock throughput per hour, respectively. Combined production from these facilities is planned at 100-150 tons MREO at a 90% purity per year.
- *<u>Task 9 – Final report</u>*: This document is the deliverable for this task.

This report contains detailed results for Tasks 3, 4, 5, 6, and 7. Additional detail may be found on Tasks 5 and 7 in the Phase 2 Testing Report (attached as Appendix B). A separate report for Task 8 is also attached (Appendix C). In this report, Chapter 3 contains a summary of the work conducted in the Phase 1 project, while Chapters 4 and 5 contain summaries of the progress of each Phase 2 task, and the summaries of the Phase 2 Testing Report and TEA, respectively.

3 PHASE 1 FINAL REPORT SUMMARY

This chapter contains a summary of the Phase 1 Final Report. Additional details can be found in the complete Phase 1 Final Report in Appendix A.

There were four major goals of the Phase 1 study: i) identify lignite or lignite-related feedstocks with total rare earth element content above 300 parts per million, a threshold dictated by DOE as the minimum for economic viability, ii) determine the geochemistry of the feedstocks and understand the forms and modes of occurrence of the rare earth elements, information necessary to inform the development of extraction and concentration methods, iii) identify processing methods to concentrate the rare earth elements from the feedstocks to a target of two weight percent, a value that would be sufficient to leverage existing separation and refining methods developed for the traditional mineral ore industry, and iv) develop a process that is economically viable and environmentally benign. To achieve these overall goals, the research scope was broken into three main efforts: i) sampling and characterization of potential feedstocks, ii) laboratory-scale development and testing of rare earth element extraction and concentration methods, and iii) process design and technical and economic feasibility evaluation. This was conducted over a 18-month effort, led by the University of North Dakota, with collaboration from Barr Engineering and Pacific Northwest National Laboratory.

In total, nearly 200 unique samples were collected from active lignite mines and outcrops of coal in North Dakota. Samples were collected of lignite coal and coal byproducts from North American Coal Corporation's Falkirk Mine, the Great River Energy Coal Creek Station power plant (including its coal beneficiation system based on the DryFining^{TM} technology), the Coyote Creek Mine, the Milton R. Young Station, the Antelope Valley Station, and the Freedom Mine. In addition to the samples collected from active mines and power stations, samples were also obtained from the Harmon-Hansen coal zone from outcrops, as this area is not currently being mined. Figure 3-1 shows an overall map of the coal producing regions in North Dakota, with the major coal zones including the Hagel, Beulah-Zap, and Harmon-Hanson.

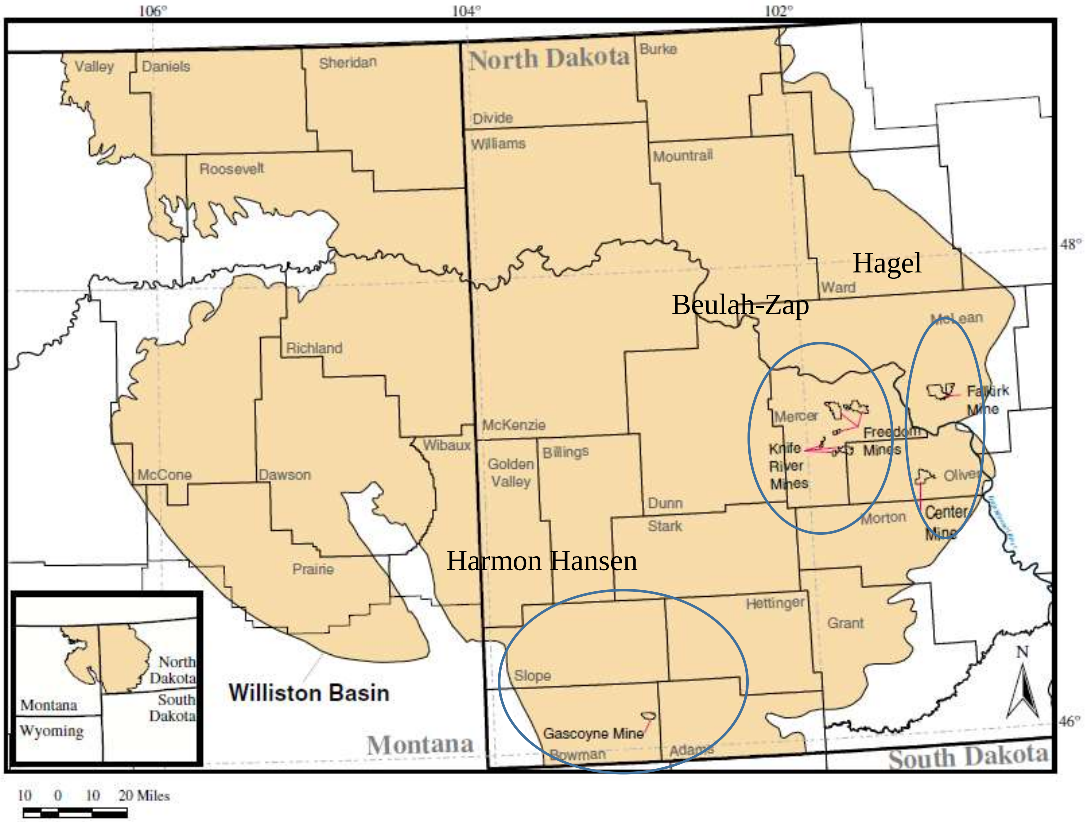


Figure 3-1. *Map of the Williston Basin and coal zones in North Dakota* [1]

From the samples collected, several locations were identified that exceeded the 300 ppm total rare earth elements target (Figure 3-2). The results showed that on a whole sample basis, the rare earths are typically most concentrated in the clay-rich sediments associated with the coal seams, but on an ash basis in certain locations within certain coal seams the content is significantly higher, an unexpected finding given prior research. At Falkirk Mine near Underwood, North Dakota three coal seams were found to have elevated levels of rare earths, ranging from about 300 to 600 ppm on an ash basis. Additionally, exceptionally high rare earths content was found in samples collected from several outcropping of the Harmon-Hansen coal zone in western/southwestern North Dakota that contained as high as 2300 ppm on an ash basis (26% ash content, dry basis) and over 600 ppm on a dry whole coal basis. The results dictated that extraction and concentration methods be developed for these rare earth element-rich coals, instead of the mineral-rich sediments. This effort also found that at a commercial-scale, due to non-uniformity of the rare earths content stratigraphically in the coal seams, selective mining practices will be needed to target specific locations within the seams. These include areas near the top and bottom of seams, as well as near clay partings, and may be less than one foot in depth. The bulk mining and blending practices as Falkirk Mine result in a relatively low total rare earths content in the feed coal through dilution with lower-REE coal seams entering the Coal Creek Power Station adjacent to the mine.

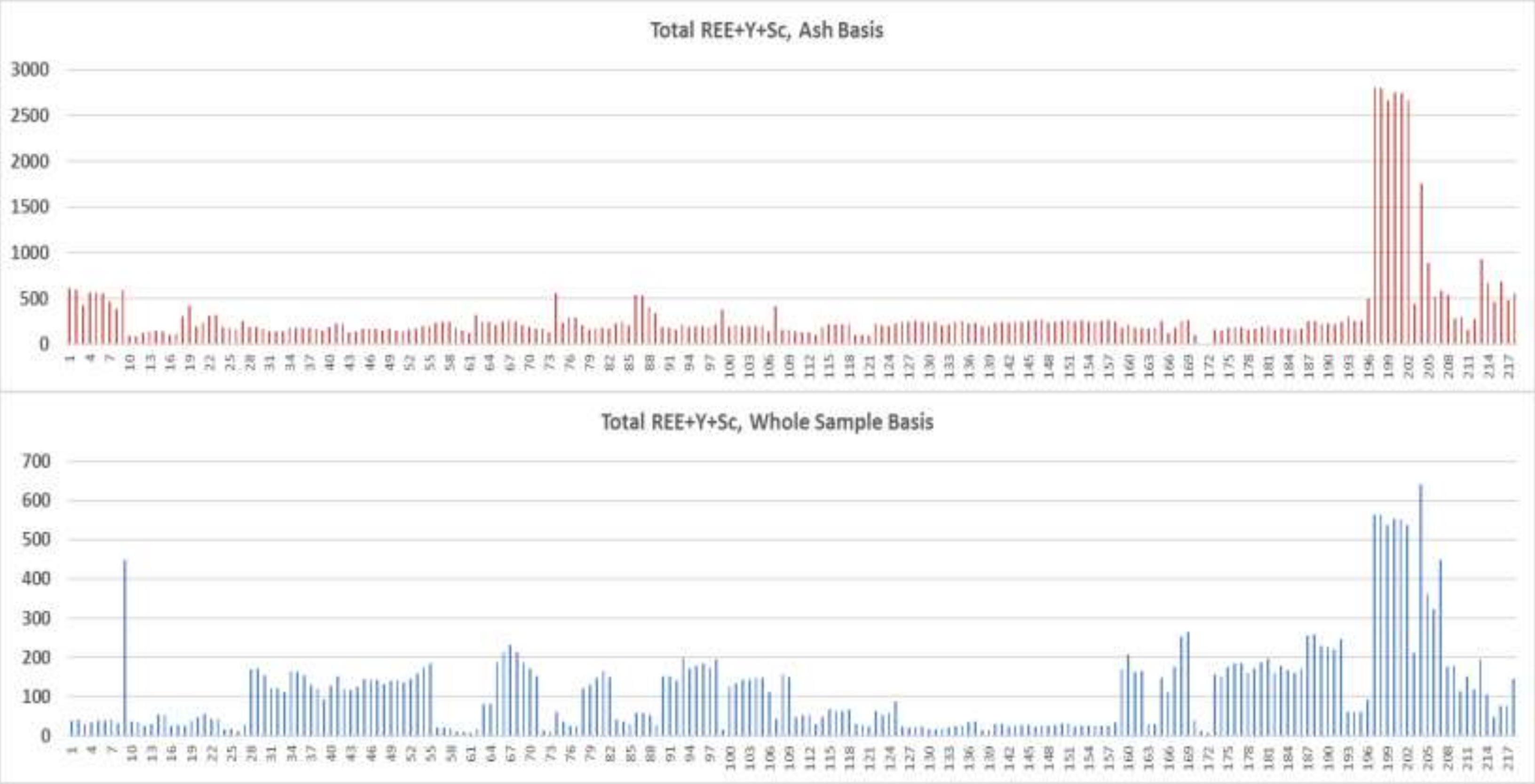


Figure 3-2. *Results of ICP-MS for total REE content (includes duplicates)*

Characterization of the coal samples to evaluate modes of occurrence of REE in lignite, was completed through utilization of a method which involved a series of sequential solvent extractions which targeted specific trace element associations in low-rank coals based on their solubility in water, ammonium acetate, and hydrochloric acid. The results, presented in Figure 3-3, identified that the predominant modes of rare earths occurrence in the lignite coals are associations with the organic matter, primarily as coordination complexes and a lesser amount as ion-exchangeable cations on oxygen functional groups. Overall it appears that about 80-95% of rare earths content in North Dakota lignite is organically associated, and not present in mineral forms, which due to the weak organic bonding, presented a unique opportunity for extraction.

In addition, a float-sink density analysis was employed on a sample of lignite to examine REE association in relation to particle density. Results showed a significant enrichment of REE in the light specific gravity material compared to the high specific gravity (SG) fractions, further confirming that the REE are associated with the organic matter in lignite (results similar to Figure 4-7). As a comparison, quartz, gypsum, and other rock/minerals have specific gravities of 2.0 and higher, substantially different than the 1.3-1.5 SG of the lignite.

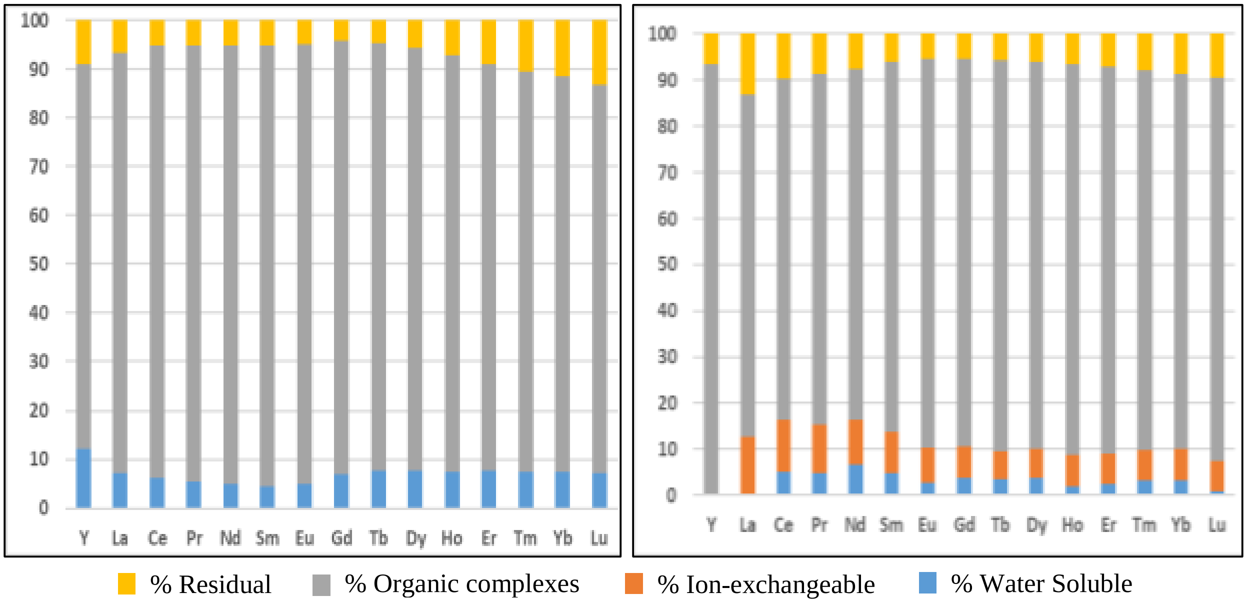


Figure 3-3. *Modes of occurrence of REE in a sample from the Harmon-Hanson coal zone (left) and the Hagel B seam (right) based on sequential extraction testing completed by UND.*

The process developed for extraction of rare earths was applied to the raw lignite coals instead of fly ash or other byproducts, investigated extensively in the literature. Rather, the process used a leaching process to selectively strip the organically associated rare earths from the lignite with very high liquid recovery from ore efficiency of about 70-90% at equilibrium contact times. Although the extraction kinetics are quite fast given commercial leaching operations, there is some tradeoff between extraction efficiency and contact time. However, at shorter contact time there is improved rare earths selectivity that results in a more concentrated product due to limiting extraction of unwanted impurities. There is also a significant difference in the extraction kinetics for the more valuable heavier molecular weight rare earths, which are much faster than the light rare earths. As shown in Figure 3-4, extraction of the heavy REE was significantly higher than the light REE for all contact times.

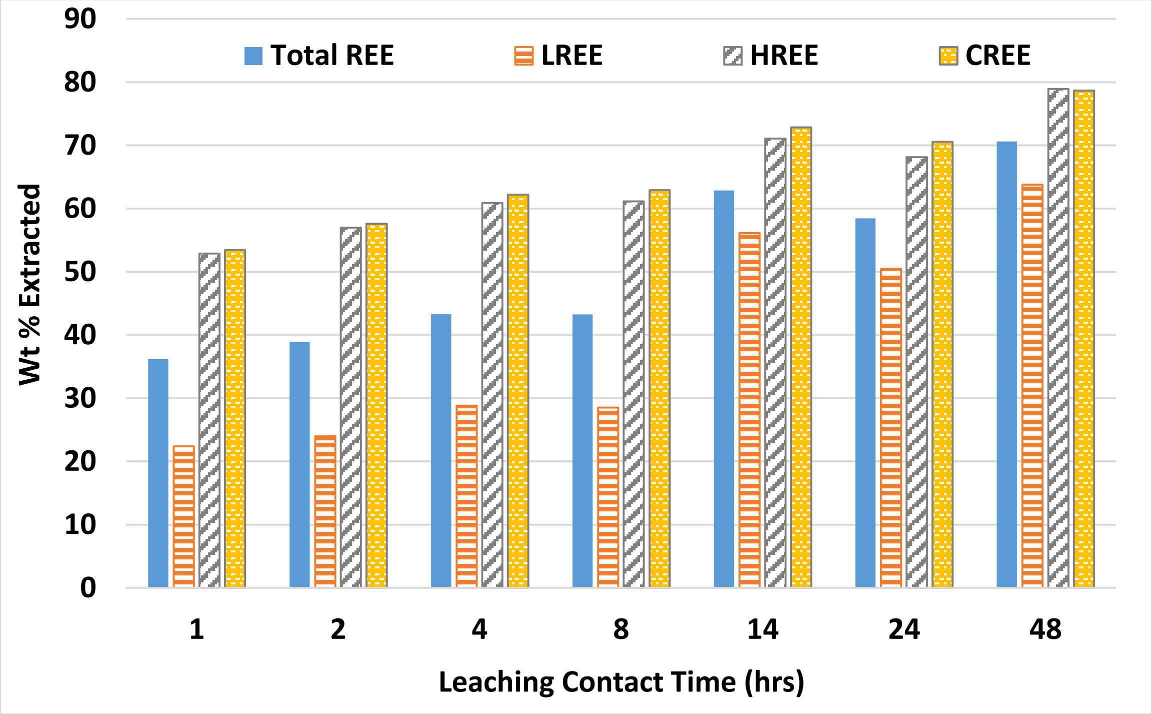


Figure 3-4. *Leaching kinetics for groupings of REE for Hagel B coal with Type B solvent.*

The testing showed that in a one-step process consisting of leaching for two hours with a selected solvent, a rare earth concentrate of about 1.4 weight percent rare earths could be achieved with about 70% total rare earths recovery, while also producing a residual coal byproduct that has superior qualities to the feed coal, such as reduced ash content. In a modified leaching approach, a 2.0wt% REE concentrate could be achieved in a single processing step, but with only about 36% total REE extraction. At 90% REE recovery, the solvent produced a 0.8wt% REE concentration. Higher REE concentrations could be achieved by a number of hydrometallurgical approaches to selectively precipitate impurities from the leachate.

The process developed in this project is simple, highly effective, low cost and novel. The process is environmentally benign and was demonstrated to be economically viable at the current market conditions. The process can be advantageously integrated with any number of coal utilization processes to augment economics, lower costs and maximize efficiency and synergies. The techno-economic analysis evaluated a configuration of rare earths extraction combined with activated carbon production co-located at a combined heat and power facility, and was shown to have highly attractive economics even at small scales representing a first-of-a-kind demonstration system. The work completed in Phase 1 was used as the basis for all testing completed in Phase 2.

4 SAMPLING, CHARACTERIZATION AND LARGE SAMPLE COLLECTION

This chapter contains details of the sampling and characterization efforts aimed at identifying locations of North Dakota lignite that are enriched in REEs, and selection of a location for collection of a large quantity of sample for testing.

Sampling focused on active mines in North Dakota as well as several outcrops of coal in Slope County in southwestern North Dakota. The mines sampled were Freedom Mine and Falkirk Mine, which are both operated by project partner North American Coal (NAcoal) who provided several drill cores representing multiple locations within the mines and several coal seams along the strata of the cores. Both the Harmon bed outcrop and the H Bed outcrop had been sampled by the North Dakota Geological Survey (NDGS) on separately-funded efforts and were known to contain very high REE concentrations. The following sections describe the sampling efforts at each location and provide the REE abundance for each of the samples analyzed.

4.1 Characterization of Existing Lignite Mine Samples

In total six intact drill cores (3” diameter), three each from Freedom and Falkirk mines, were provided by NAcoal to UND. A photograph of one of the drill cores is provided in Figure 4-1.

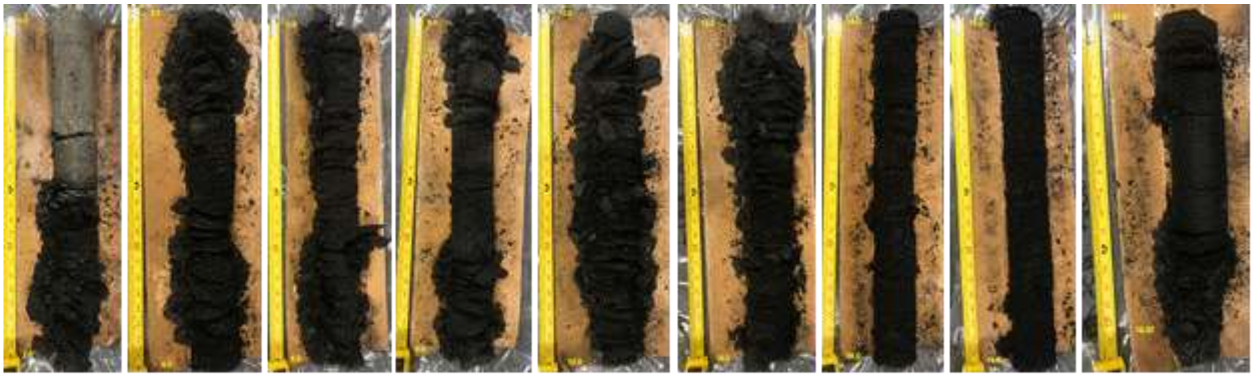


Figure 4-1. *Photographs of one of the drill cores from Freedom Mine in North Dakota. The core is oriented stratigraphically top to bottom and each subsequent photo left to right represents the next ~2ft of the core. The left most photo shows the margin of the roof clay and the coal. The right most figure shows the bottom of the drill string which represents the bottom margin of the coal, just above the floor clay.*

Each of the cores was visually inspected and split into stratigraphic intervals by lithology. Each split was separately crushed, milled and dried for analysis by ICP-MS to determine REE abundance. The results of the analysis for each of the drill cores is presented in Table 4-1 for Freedom Mine and for Falkirk Mine.

Table 4-1**.** *Sample description and REE abundance for Freedom Mine drill cores. Samples highlighted in yellow were selected for additional analysis.*

REE-1 Core

Seam	Sample ID	Interval (inches)	Ash Yield (dry wt%)	Total REE (coal), ppm	Total REE (ash), ppm	HREE/LREE	Sample Description
Beulah	2REE17032	0-3	41.6	34.6	83.0	1.32	coal below roof clay
	2REE17035	3-12	14.1	30.2	214.5	1.05	coal
	2REE17039	12-48	15.3	20.7	135.6	0.40	coal
	2REE17047	48-120	14.2	20.1	141.5	0.46	coal
	2REE17054	120-192	8.4	14.6	173.3	0.65	coal
	2REE17055	192-209	11.1	34.9	314.4	2.14	coal above floor clay

REE-2 Core

Seam	Sample ID	Interval (inches)	Ash Yield (dry wt%)	Total REE (coal), ppm	Total REE (ash), ppm	HREE/LREE	Sample Description
Beulah	2REE17058	22.5-26	34.6	31.1	90.0	1.38	coal below roof clay
	2REE17061	26-48	84.4	140.2	166.2	0.94	clay/coal
	2REE17065	48-84	79.6	117.7	147.9	0.44	clay/coal
	2REE17071	84-150	13.3	15.8	118.4	0.44	coal
	2REE17075	153-160	11.9	16.5	138.3	0.21	coal below 3" clay parting
	2REE17077	176-180	11.0	8.8	80.2	0.51	coal
	2REE17085	180-258	13.2	23.9	180.4	0.69	coal
	2REE17087	259.5-262.5	45.5	32.3	70.9	0.66	coal below 1.5" clay parting
	2REE17088	262.5-270	15.4	50.2	326.4	1.83	coal above floor clay

Schoolhouse Core

Seam	Sample ID	Interval (inches)	Ash Yield (dry wt%)	Total REE (coal), ppm	Total REE (ash), ppm	HREE/LREE	Sample Description
Schoolhouse	2REE17090	0-4	93.5	84.0	89.8	0.28	roof clay
	2REE17091	4-18	16.5	15.9	95.9	0.96	coal below roof clay
	2REE17092	18-24	7.5	15.0	199.5	0.82	coal
	2REE17093	24-36	40.1	73.9	184.5	0.37	clay/coal
	2REE17094	36-42	93.8	152.7	162.8	0.23	clay parting
	2REE17095	42-48	27.8	60.3	217.1	0.87	coal below clay parting
	2REE17096	48-52	66.0	139.5	211.4	0.33	clay/coal
	2REE17097	52-64	32.1	106.8	332.1	0.55	coal above floor
	2REE17098	64-72	91.4	179.3	196.3	0.36	floor clay

Table 4-2. *Sample description and REE abundance for Falkirk Mine drill cores. Samples highlighted in yellow were selected for additional analysis.*

203C Drill Core

Seam	Sample ID	Interval (inches)	Ash Yield (dry wt%)	Total REE (coal), ppm	Total REE (ash), ppm	HREE/LREE	Sample Description
Hagel A	2REE17100	12-18	20.03	56.6	282.6	1.42	coal below roof clay
	2REE17101	18-24	6.38	22.5	351.9	2.12	coal
	2REE17104	24-78	7.78	14.2	182.0	0.51	coal
	2REE17105	78-100	7.49	21.5	287.4	1.59	coal
	2REE17106	100-102	45.82	110.4	241.0	0.52	coal above floor clay

192C Drill Core

Seam	Sample ID	Interval (inches)	Ash Yield (dry wt%)	Total REE (coal), ppm	Total REE (ash), ppm	HREE/LREE	Sample Description
Coal Lake Coulee	2REE17109	5-12	20.98	63.1	300.5	1.25	coal below roof clay
	2REE17110	12-30	14.57	43.1	295.8	0.91	coal
	2REE17111	30-42	13.56	51.5	380.0	1.16	coal
	2REE17112	42-48	15.2	71.4	469.9	1.76	coal above floor clay
Tavis	2REE17114	0-12	10.87	33.9	312.0	1.17	coal below roof
	2REE17115	12-31	12.34	20.5	166.1	0.74	coal
	2REE17119	31-115	7.63	9.9	130.0	0.38	coal
	2REE17120	115-131	8.69	22.4	258.0	0.51	coal
	2REE17121	131-136	9.28	28.5	307.5	1.25	coal above floor

194C Drill Core

Seam	Sample ID	Interval (inches)	Ash Yield (dry wt%)	Total REE (coal), ppm	Total REE (ash), ppm	HREE/LREE	Sample Description
Hagel A	2REE17123	6-12	22.43	68.5	305.6	1.32	coal below roof clay
	2REE17124	12-26	8.27	27.5	332.2	1.52	coal
	2REE17127	26-65	8.08	10.7	132.5	0.51	coal
	2REE17129	66-75	15.81	27.1	171.3	0.43	below 1" clay parting
	2REE17132	75-99	8.25	20.4	247.2	0.49	coal
	2REE17133	99-114	8.54	26.5	310.0	1.41	coal
	2REE17134	114-123	39.71	73.1	184.1	0.78	coal above floor clay
Hagel B	2REE17136	10-13	44.18	133.5	302.1	0.60	coal below roof clay
	2REE17137	13-18	10.49	33.3	317.3	1.43	coal
	2REE17138	18-28	16.22	42.4	261.4	1.13	coal
	2REE17139	28-37	10.88	43.0	395.5	1.74	coal above floor clay

The results show relatively modest REE concentrations on a whole coal basis, but several samples with ash basis REE concentration exceeding 300 ppm. As with previous investigations, the most promising samples tended to be located near the margins of the coal seams, near the roof and floor clays. At Freedom Mine the best samples were located at the bottom margin of the Beulah seam (highlighted in yellow in Table 4-1). At Falkirk Mine the best samples were located at the bottom margin of the Coal Lake Coulee seam and the Hagel B seam (highlighted in yellow in Table). In terms of uniformly high REE concentration, the Coal Lake Coulee seam appears most promising. Based on the REE abundance results, four samples – those highlighted in yellow in Table 4-1 and – were selected for additional characterization/testing.

4.2 Harmon Outcrop

The NDGS has sampled numerous lignite outcrops in west and southwest North Dakota, primarily in the Harmon, Hanson and H beds that are found in the Harmon-Hanson coal zone[2] [3]. The goal of the NDGS work is to characterize the coal-based REE resources in portions of the State without active mines to provide justification for the potential opening of a new mine. They have performed the largest amount of sampling on one particular outcrop in northern slope county where both the Harmon and Hanson lignite beds are exposed. The top of the Harmon bed was identified to have REE concentrations ranging from about 250 to 550 ppm on a dry coal basis at various locations along the length of the outcrop. Combined with the relative ease of accessibility for large-scale sampling, this location was initially selected by the UND team as the target for feedstock sourcing for the bench-scale test program in Tasks 5-7.

The NDGS work on the Harmon bed in this location had mostly focused on the upper margin of the bed. To examine the REE distribution along the full strata, NDGS provided UND with a channel sample that was split into multiple stratigraphic intervals. A photograph of the sampling location as well as a schematic representing the Harmon bed strata and the sample intervals is provided in Figure 4.2.

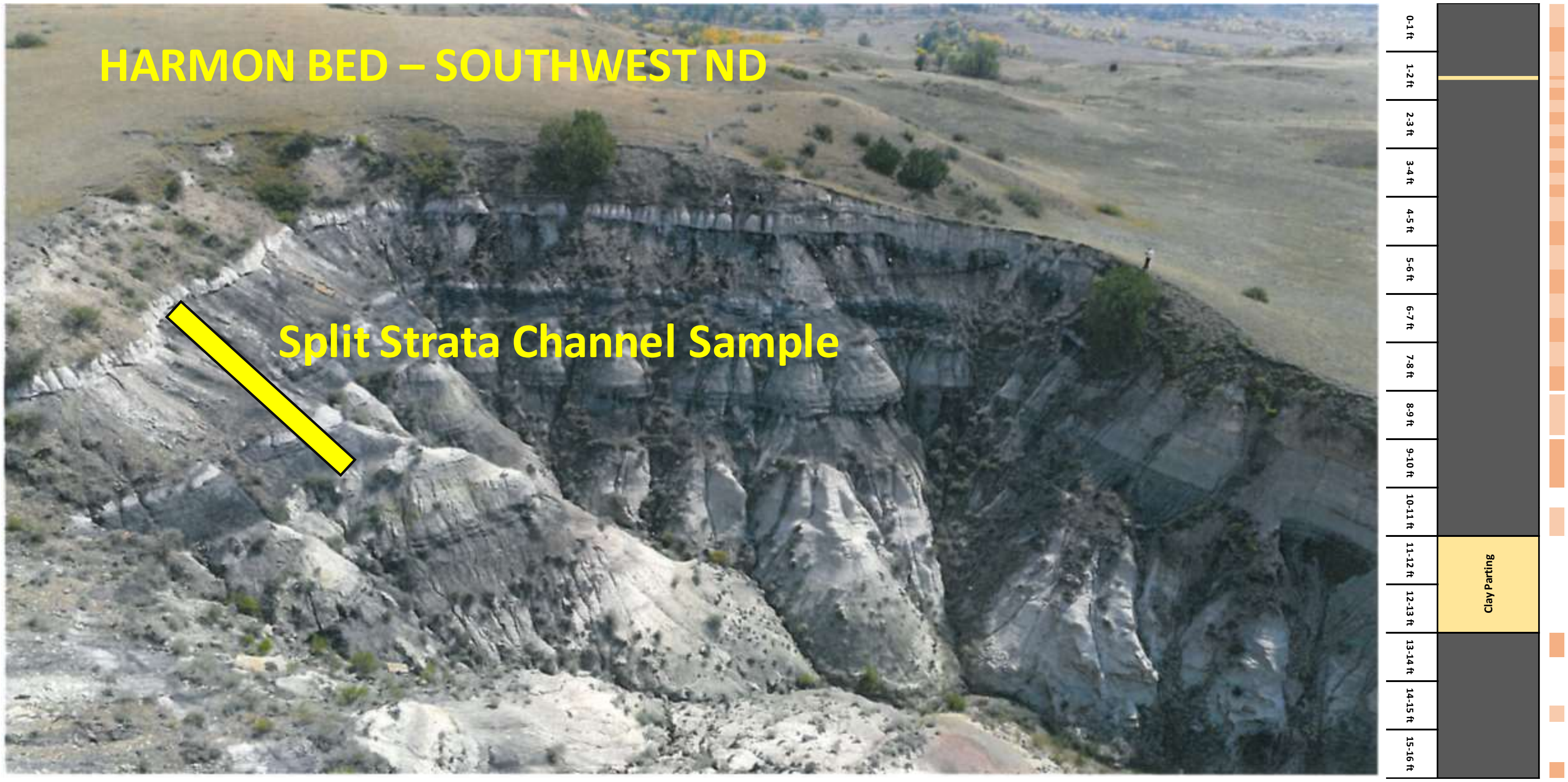
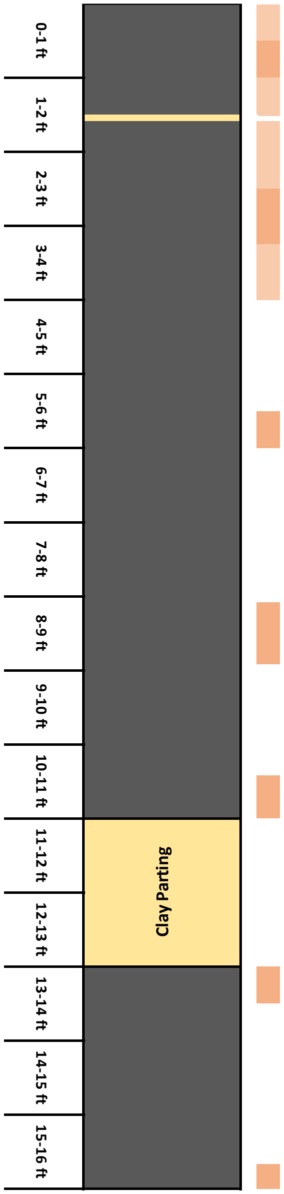


Figure 4-2. *Photograph of the sampling location for the Harmon bed in Slope County, ND. The yellow box indicates the location of the channel sample collected by NDGS along the depth of the Harmon bed. The Hanson bed (not sampled in this effort) is also exposed at this location and can be seen as the darker section beneath the Harmon bed. The Harmon bed at this location is about 16 feet thick, and the samples were split into the intervals depicted by shades of pink in the schematic to the right of the photograph.*

Select samples or composites of samples from those identified in Figure 4-2 were submitted for ICP-MS analysis to determine REE abundance. The results are provided in Table 4-3, which also includes a schematic identifying the stratigraphic intervals covered by the analyses. Based on these results, which showed very high REE concentration in the top six inches (sample ID 17001), another larger sample (~130 lb) from this same location was acquired and subjected to more detailed characterization as described in later in this section of the report. The coal directly below the thick clay parting (sample ID 17029), although having lower REE concentration on a coal basis, was a very low ash yield lignite (~6wt% ash) and had an exceptionally high REE concentration on an ash basis. This sample was also selected for some additional testing.

Table 4-3. *REE abundance and descriptions for samples taken from an outcrop of the Harmon bed in Slope County, ND. Sample intervals in pink.*

ID	Description	Interval (inches)	REE Conc. (Coal), ppm	REE Conc. (ash), ppm
17001	coal below roof clay	0-6	262.5	933
17002	coal	6-12	89.0	495
17003	coal above 1" parting	12-18	65.4	467
17009	coal below 1" parting	21-30	39.5	116
17013	coal	30-39	67.0	273
17017	coal	39-48	39.2	240
17021	coal	66-72	71.3	281
17026	coal	97-107	27.9	204
17028	coal above 2' parting	125-132	67.2	446
17029	coal below 2' parting	156-162	105.1	1773
17031	coal above floor clay	188-192	29.0	247



4.3 Initial REE Leaching Performance Evaluation

Based on the sampling and REE abundance measurements described previously in this section, six of the samples were selected for laboratory-scale REE leaching experiments using the methods developed in Phase 1 of the project. A simplified block flow diagram of the major unit operations in the process is presented in Figure 4-3. The overall reaction mechanisms for the leaching processes are provided in Figure 4-4.

The samples tested included two samples each from the Falkirk Mine, Freedom Mine and the Harmon bed outcrop. For these tests, the raw coals (crushed to about -4 mesh) were contacted with a dilute mineral acid in a dry coal to liquids ratio of 60g to 125mL. The results are presented in Figure 4-5 (a-f). Note that these are very non-optimized process conditions and leaching results would likely improve with optimization. In each of the cases it is likely that the acid was fully consumed or the pH of the leaching solution was increased to a point where the REE leaching was no longer possible. The differences in leaching between the samples can likely be explained (at least in part) by the differences in acid consuming species (Na and Ca minerals, other organic bound elements) besides the REE in each of the samples. Therefore, significant improvements are expected with implementation of a pH based leaching step, thus providing more active hydrogen ions for the REE leaching.

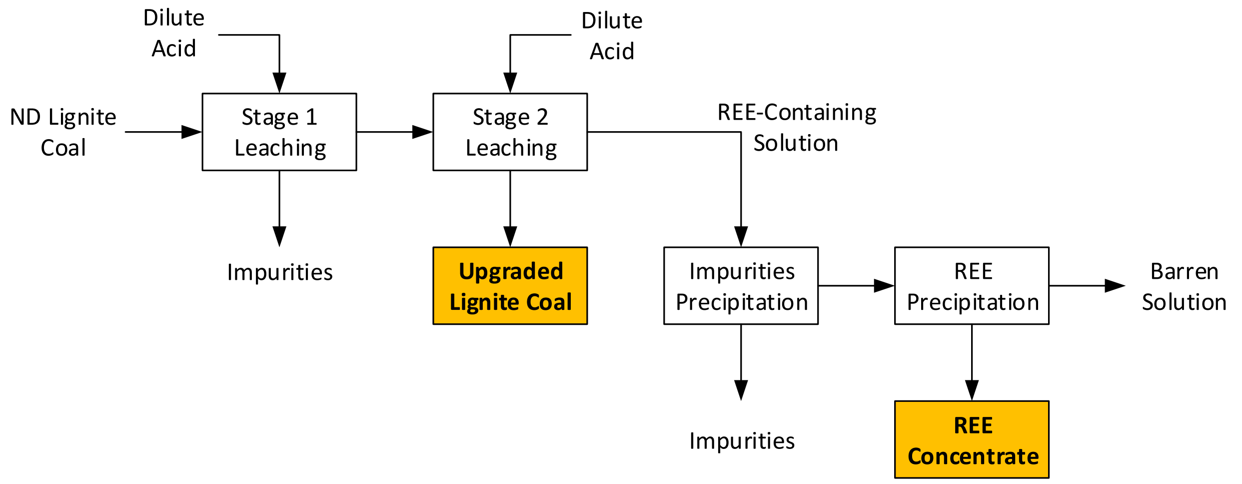


Figure 4-3**.** *Planned simplified flow diagram for the UND REE concentration process at the beginning of Phase 2. Stage 1 and Stage 2 leaching processes expected to follow the reaction mechanisms described in Figure 4-4. Typical impurities include Fe, Ti, and V removed in the precipitation step noted above.*

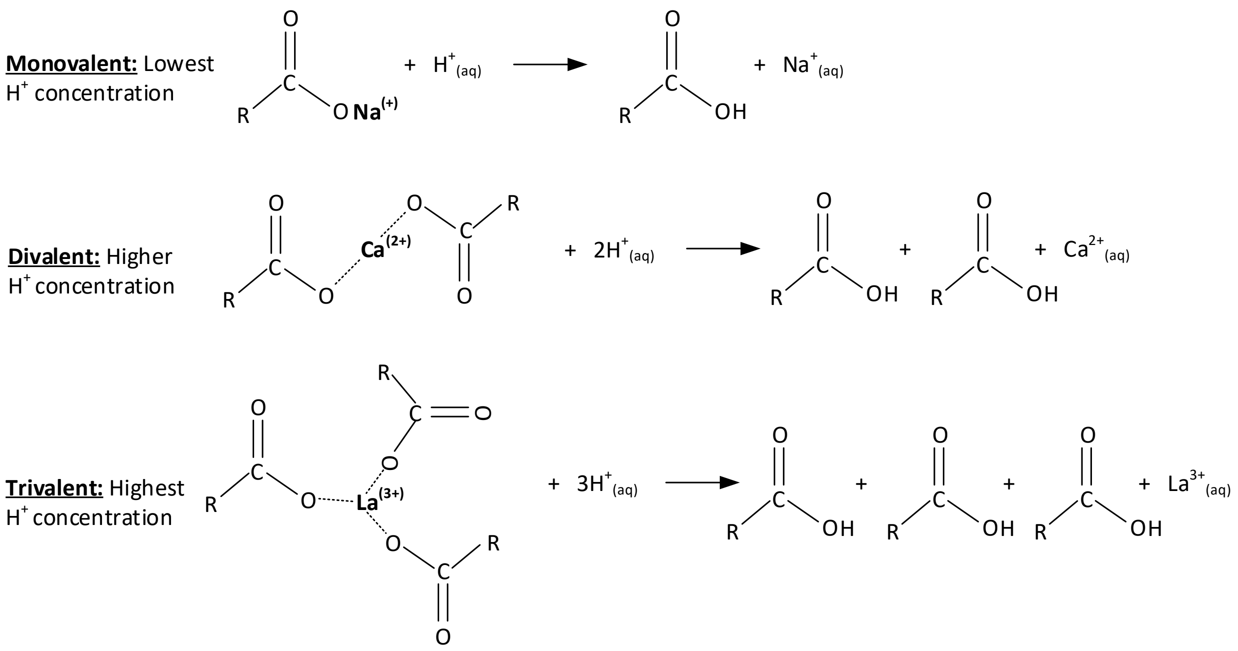


Figure 4-4. *Apparent reaction mechanisms describing the leaching processes shown in Figure 4-3. Several inorganic species in lignite are organically associated in the form of carboxylic acid salts (monovalent cations) or complexes of carboxyl functional groups (multivalent cations). Stage 1 leaching would involve the addition of a dilute acid with minimal concentration as to prevent trivalent liberation.*

Based on these results, the project team decided to move forward with the Hagel B coal from Falkirk Mine (Figure 4-5f – sample ID 17139) as one of the materials for large sample collection. The leaching data, combined with the large amount of analysis that has been done on Hagel B coal in Phase 1 and Phase 2, provided confidence that the Hagel B would be a good material to use as a control or comparative material to the REE-rich coal for evaluation in the TEA later in the project.

While the leaching results for the top six inches of the Harmon bed (Figure 4-5a – sample ID 17001) were relatively modest under these conditions, the project team decided to continue on with more detailed evaluation of this material.

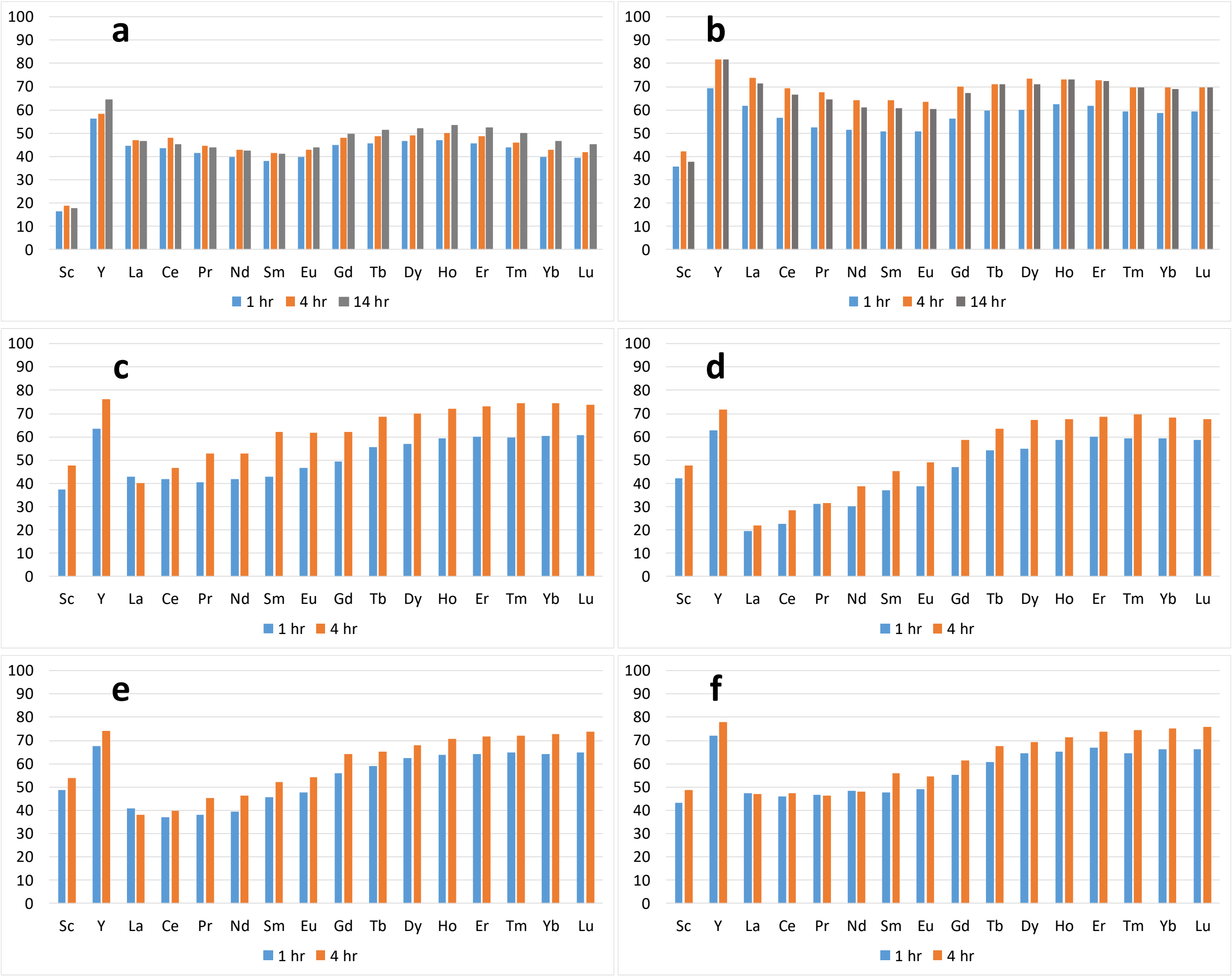


Figure 4-5. *REE leaching performance for select lignite coals (wt% leached from raw coal). a – sample ID 17001 (Harmon bed), b – sample ID 17029 (Harmon bed), c – sample ID 17055 (Freedom Mine), d – sample ID 17088 (Freedom Mine), e – sample ID 17112 (Falkirk Mine), f – sample ID 17139 (Falkirk Mine).*

4.4 Detailed Characterization of Harmon Lignite

The Harmon lignite evaluated previously (sample ID 17001, Table 4-3) was a relatively high ash yield sample (28wt%), as are many of the metalliferous coals that have been located and characterized in efforts by UND and NDGS. Based on float-sink density separation data that was obtained in Phase 1 for a different metalliferous lignite with high ash yield, the hypothesis was that the REE would be enriched in the coal-rich fractions of the sample (low density fractions) and depleted in the mineral-rich fractions. In addition, based on the reaction mechanisms proposed in Figure 4-4, the project team anticipated that the leaching efficiency of the REE would be inversely correlated to the density fraction of the coal (best leaching in light density coal fractions). Therefore, to maximize the potential REE concentration and the ease of recoverability, float-sink density separations were performed on a larger sample of the top margin of the Harmon bed. The NDGS provided the UND team an approximately 130 lb sample very close to where sample ID 17001 was sourced. With that material the following examinations were performed:

- REE abundance in whole sample
- Sieving into 4x20, 20x40 and 40x60 size fractions (from one bulk sample crushed to -4 mesh) and subjecting approximately 7 kg of each size range for multi-specific gravity float-sink separations
- Ash yield and composition as a function of specific gravity (SG) fraction
- REE abundance as a function of SG fraction
- Mineralogy as a function of SG fraction
- REE leaching as a function of SG fraction
- Bulk ash forming species leaching as a function of SG fraction
- Mineralogy changes as a function of SG fraction after leaching

The bulleted points below provide definitions for the measurements/performance metrics that are discussed in the subsequent sections of this report:

- <u>Cumulative mass yield of coal or total REE</u> – defined as the mass fraction of coal or REE contained in a designated range of specific gravity. For example, cumulative coal mass yield of 80wt% at a specific gravity cut point of 1.7 means that 80wt% of the whole coal sample was contained in the specific gravity range of <1.7.
- <u>Ash yield</u> – defined as the mass fraction of inorganic (non-combustible) material contained in a given sample of whole coal. For example, an ash yield of 30wt% indicates that when combusted, 30wt% of the starting coal mass will be retained as an ash residue. The ash yield is provided both on a cumulative basis as described above (i.e. <1.5, <1.7…etc) or on a single point basis as described below (i.e. 1.7 to 1.8).
- <u>Measurement within each specific gravity fraction</u> – on several occasions measurements within a defined specific gravity fraction are provided. These are not on a cumulative basis as described in the first bullet above, but rather within a single point SG range (i.e. 1.7 to 1.8).
- <u>FL (float)</u> – when provided on the x-axis of subsequent figures for non-cumulative data, this designates that the data point was taken on material that lies in a SG range of less than the x-axis

number, but greater than the previous x-axis number. For example, the data point contained above the 1.7 FL x-axis point, refers to a measurement on the material with SG between 1.6 and 1.7.

- SK (sink) – when provided on the x-axis of subsequent figures for non-cumulative data, this designates that the data point was taken on material that has a specific gravity range of > 2.2.

4.4.1 Float-Sink Mass Balance and REE Abundance

The coal mass yield on a cumulative basis at each specific gravity fraction for each of the three size ranges tested is shown in Figure 4-6a. In general, the data shows that the majority of the sample mass is recovered through a SG cut point of about 1.7, depending on the size fraction. This is more evident for the 4x20 fraction than the smaller sizes. There is a jump in the mass between the 2.2 float (< 2.2 SG) and the 2.2 sink (>2.2 SG). This is apparently due to a significant mass of very high density material that is well liberated from the coal particles. A visual inspection of the in-situ coal from these sites shows bands or veins of clays or other inorganic materials dispersed within the organic coal materials. This leads to relatively coarse liberation particle size as is demonstrated by this data. The ability to generate acceptable mass recovery with these particle sizes means that standard coal washing methods that are commonly employed for higher rank coals are applicable to this lignite.

Figure 4-6b shows the ash yield within each SG fraction (non-cumulative). As expected the ash yield increases with SG. The relatively high ash yield of the lightest SG fractions, however, are a little surprising. Even at <1.3 SG, which should be very nearly pure organic materials, the ash yield was 13-17wt%. This could indicate that there is a large amount of very finely disseminated mineral matter and/or a large amount of organically associated inorganic elements.

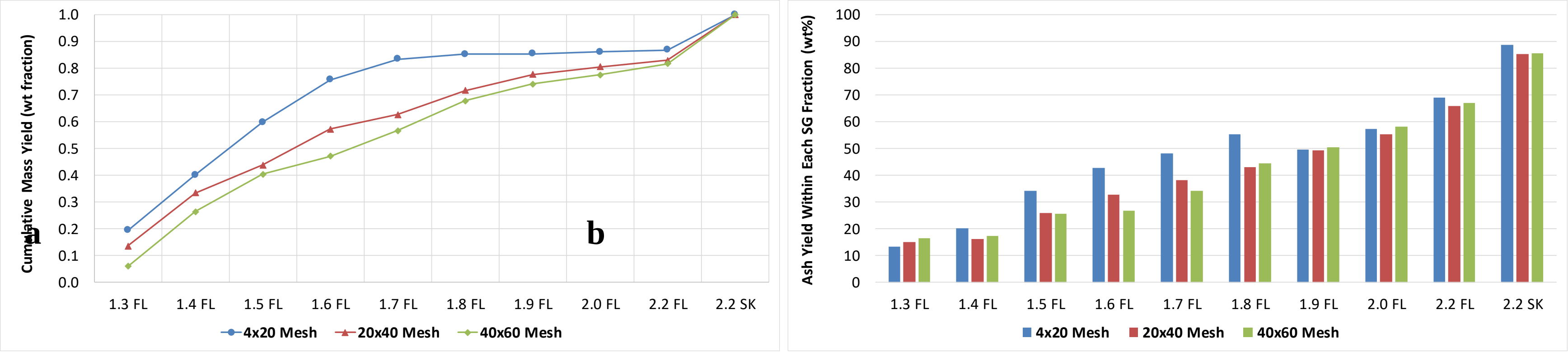


Figure 4-6. ***a*** *- Cumulative coal mass yield through each specific gravity for three particle size ranges. FL – float (< SG number); SK (sink > SG number). This sample has a fairly coarse liberation particle size, indicating standard coal washing techniques are applicable.* ***b*** *– ash yield within each specific gravity fraction. Even the lightest SG has a relatively high ash yield, indicating presence of very finely disseminated mineral matter or a large amount of organically associated inorganic elements.*

Figure 4-7 (a-c) shows the REE concentration within each SG fraction on a coal basis (a) and an ash basis (b), as well as on a cumulative basis through each SG cut point (c – on a coal basis). Quite clearly, there is significant enrichment of the REE in the organic-rich light SG fractions. This is consistent with previous float-sink data of a metalliferous lignite from Phase 1. On a cumulative basis (Figure 4-7c), the programmatic target of 300 ppm REE concentration (dry coal basis) is achieved with a SG cut point of about 1.7. This is accompanied by a cumulative REE yield of about 80wt% and a cumulative coal mass yield of about 70wt% (Figure 4-6a) and a cumulative ash yield of about 26wt% (Figure 4-8).

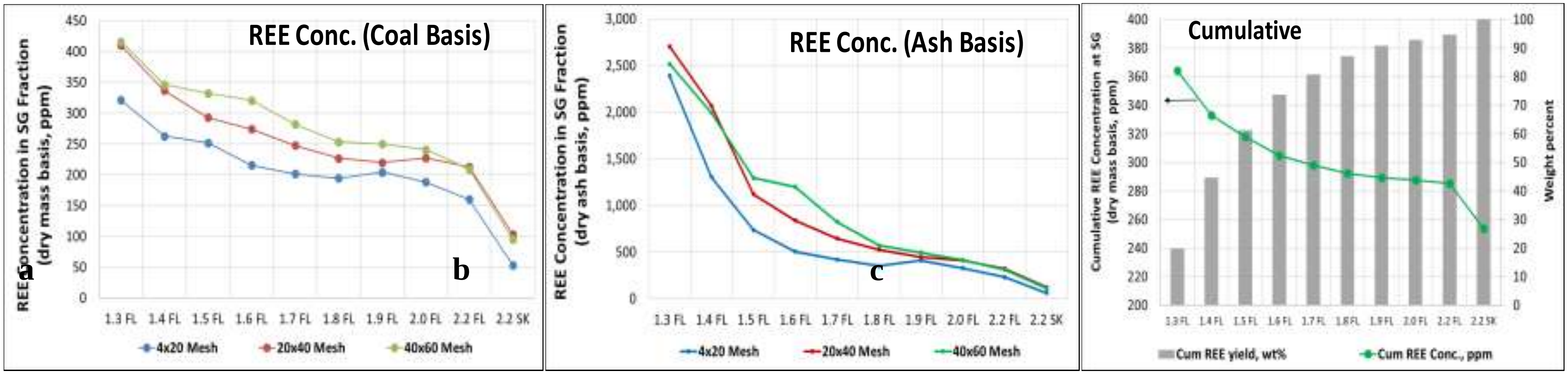


Figure 4-7. *REE concentration in each specific gravity fraction on a coal basis (**a**) and ash basis (**b**). REE concentration on a cumulative basis through each specific gravity cut point and cumulative REE yield through each specific gravity cut point (**c**). The REE are significantly enriched into the organic-rich light specific gravity fractions (a, b). 300 ppm REE concentration (coal basis) is achieved with a specific gravity cut point of about 1.7 and REE mass yield of about 80% from the whole coal sample (c).*

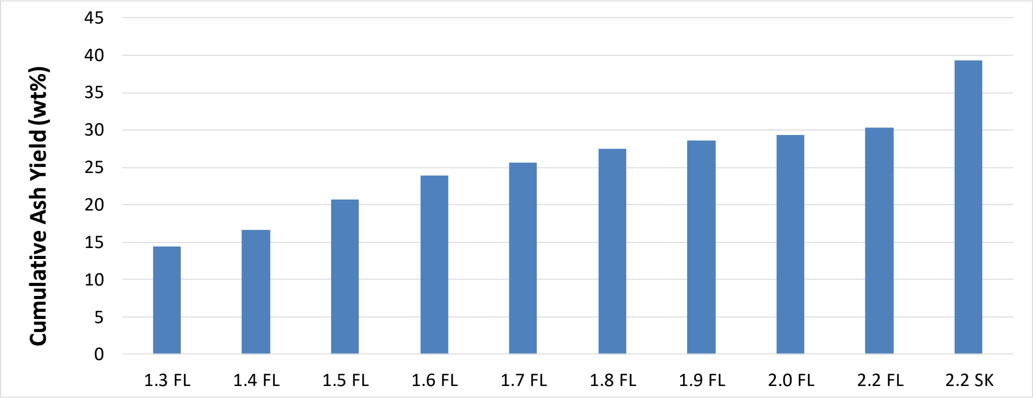


Figure 4-8. *Cumulative ash yield through each SG cut point. At the programmatic target of 300 ppm REE concentration with a <1.7 SG cut point, the ash yield of the lignite is about 26wt%.*

4.4.2 Inorganic Composition and Mineralogy Before and After REE Leaching

To provide representative materials for leaching studies, composite samples were prepared from each of the separated SG fractions in the three size ranges examined. Thus, the leaching studies were completed on 4x60 mesh composite samples in each of the SG fractions. All of the leaching was completed using a dilute mineral acid with a contact time of 1 hour and a dry coal to liquids ratio of 60 g to 125 mL. To investigate the impact of leaching on the inorganic composition of the lignite, the ash composition and mineralogy were both examined. Overall composition of the material was measured via ASTM D6349, with specific mineralogy was determined via computer controlled scanning electron microscopy (CCSEM) with energy dispersive X-ray spectroscopy (EDS). Mineralogical typing software available through project partner Microbeam Technologies Inc. was utilized to identify the concentrations of each mineral type within the samples.

4.4.2.1 Inorganic composition and leaching behavior – Bulk ash forming species

The ash composition pre- and post-leach expressed as equivalent oxides is presented in Table 4-4, and as elemental on a sulfur-free coal basis in Table 4-5. The base to acid (B/A) ratio (Ca+Mg+Na+K+Fe)/ (Si+Al+Ti) and the aluminum to silicon ratio (both ratios on mass basis) are shown in Figure 4-9a for the pre-leach coal and Figure 4-9b for the post-leach coal. Figure 4-10 shows the leaching efficiency for the alkali and alkaline earth metals (AAEMs) as well as aluminum and iron. Figure 4-11 provides plots of the concentration of the AAEMs, Fe and Al (sulfur-free coal basis) on the y-axis versus ash yield of the sample on the x-axis before and after leaching. Discussion of these data are provided in the subsequent paragraphs.

As shown in Table 4-4 and Table 4-5 for the pre-leach coal, the dominant inorganic species in the Harmon sample are silicon, aluminum and iron. The light SG fractions also have a large amount of AAEMs and sulfur, suggesting primarily organic association for these components. Silicon is relatively depleted in the light SGs, while Al and Fe are relatively enriched. The intermediate SGs appear to be mainly silicates, while the heavy SGs appear to be a combination of silicates and clays. The 2.2 sink SG fraction has a large amount of Ca and S that is likely in the form of gypsum, indicating that the sample is oxidized. Oxidation of pyrite in the coal releases sulfuric acid, which may react with organically associated calcium and forms gypsum. Therefore, in a non-oxidized sample of this lignite, one would expect a significant increase in the organic Ca level in the light SGs.

Table 4-4. *Ash composition analysis (expressed as equivalent oxides, wt% of ash)*

Pre-Leach	SiO2	Al2O3	Fe2O3	TiO2	P2O5	CaO	MgO	Na2O	K2O	SO3	SrO	BaO	MnO2
1.3 FL	20.29	21.56	19.77	1.08	0.12	4.46	7.89	4.33	0.77	13.93	0.2	0.26	0.26
1.4 FL	36.7	20.5	13.61	1.15	0.11	3.62	6.28	3.37	0.78	9.83	0.16	0.19	0.22
1.5 FL	65.25	13.33	6.58	1.37	0.05	1.96	3.08	1.65	0.68	3.7	0.09	0.16	0.11
1.6 FL	75.72	9.87	3.71	1.35	0.04	1.42	2.06	1.14	0.42	2.25	0.07	0.19	0.08
1.7 FL	80.35	8.05	2.93	1.48	0.03	1.14	1.61	0.89	0.28	1.5	0.06	0.14	0.06
1.8 FL	84.99	7.18	2.23	1.37	0.03	0.92	1.24	0.7	0.27	1.13	0.04	0.09	0.05
1.9 FL	82.59	8.94	2.95	1.19	0.02	0.95	1.11	0.6	0.59	1.17	0.04	0.11	0.04
2.0 FL	74.5	13.23	4.7	0.87	0.02	1.11	1.28	0.57	1.6	1.55	0.04	0.13	0.03
2.2 FL	64.5	18.51	5.2	0.51	0.02	2.67	1.45	0.47	3.06	3.75	0.03	0.12	0.03
2.2 SK	33.38	10.98	3.5	0.23	0.01	19.92	0.66	0.18	1.81	28.34	0.07	0.45	0.02
Post-Leach	SiO2	Al2O3	Fe2O3	TiO2	P2O5	CaO	MgO	Na2O	K2O	SO3	SrO	BaO	MnO2
1.3 FL	34.72	16.23	31.36	1.72	0.2	4.01	0.81	0.36	0.9	5.27	0.2	0.45	0.04
1.4 FL	54.16	14.8	18.72	1.61	0.13	2.68	0.57	0.18	0.92	3.34	0.12	0.28	0.03
1.5 FL	77.91	9	7.29	1.62	0.05	0.95	0.3	0.1	0.69	1.05	0.05	0.2	0.01
1.6 FL	85.36	6.63	3.74	1.62	0.05	0.56	0.19	0.07	0.42	0.65	0.04	0.22	0.01
1.7 FL	87.79	5.39	2.83	1.55	0.03	0.44	0.14	0.06	0.28	0.51	0.03	0.16	0.01
1.8 FL	90.26	5.07	2.1	1.36	0.03	0.28	0.13	0.05	0.27	0.33	0.02	0.1	<0.01
1.9 FL	87.91	7.26	2.68	1.25	0.03	0.39	0.19	0.05	0.61	0.41	0.02	0.11	<0.01
2.0 FL	78.6	12.24	4.07	0.92	0.02	0.57	0.42	0.07	1.65	0.54	0.02	0.15	<0.01
2.2 FL	68.3	18.69	4.5	0.53	0.02	1.72	0.78	0.08	3.19	1.96	0.02	0.13	0.01
2.2 SK	34.63	11.2	3.15	0.26	0.01	19.3	0.45	0.06	1.87	27.28	0.07	0.57	<0.01

Table 4-5. *Elemental inorganic analysis on a sulfur-free coal basis (wt% of dry whole coal)*

Pre-Leach	Si	Al	Fe	Ti	P	Ca	Mg	Na	K	S	Sr	Ba	Mn
1.3 FL	2.66	3.20	3.87	0.18	0.01	0.89	1.33	0.90	0.18	0.00	0.05	0.07	0.06
1.4 FL	5.50	3.48	3.05	0.22	0.02	0.83	1.21	0.80	0.21	0.00	0.04	0.05	0.05
1.5 FL	15.89	3.68	2.40	0.43	0.01	0.73	0.97	0.64	0.30	0.00	0.04	0.07	0.04
1.6 FL	22.93	3.38	1.68	0.52	0.01	0.66	0.80	0.55	0.23	0.00	0.04	0.11	0.04
1.7 FL	28.44	3.23	1.55	0.67	0.01	0.62	0.73	0.50	0.18	0.00	0.04	0.09	0.04
1.8 FL	35.33	3.38	1.39	0.73	0.01	0.58	0.66	0.46	0.20	0.00	0.03	0.07	0.03
1.9 FL	39.51	4.84	2.11	0.73	0.01	0.69	0.68	0.45	0.50	0.00	0.03	0.10	0.03
2.0 FL	39.76	7.99	3.75	0.60	0.01	0.91	0.88	0.48	1.52	0.00	0.04	0.13	0.03
2.2 FL	39.23	12.75	4.73	0.40	0.01	2.48	1.14	0.45	3.32	0.00	0.03	0.14	0.03
2.2 SK	23.15	8.62	3.63	0.20	0.01	21.12	0.59	0.20	2.24	0.00	0.09	0.60	0.02
Post-Leach	Si	Al	Fe	Ti	P	Ca	Mg	Na	K	S	Sr	Ba	Mn
1.3 FL	3.03	1.61	4.10	0.19	0.02	0.54	0.09	0.05	0.14	0.00	0.03	0.08	0.01
1.4 FL	6.26	1.94	3.24	0.24	0.01	0.47	0.08	0.03	0.19	0.00	0.03	0.06	0.01
1.5 FL	17.40	2.28	2.43	0.46	0.01	0.32	0.09	0.04	0.27	0.00	0.02	0.09	0.00
1.6 FL	24.69	2.17	1.62	0.60	0.01	0.25	0.07	0.03	0.22	0.00	0.02	0.12	0.00
1.7 FL	30.31	2.11	1.46	0.69	0.01	0.23	0.06	0.03	0.17	0.00	0.02	0.11	0.01
1.8 FL	37.40	2.38	1.30	0.72	0.01	0.18	0.07	0.03	0.20	0.00	0.01	0.08	0.00
1.9 FL	42.11	3.94	1.92	0.77	0.01	0.29	0.12	0.04	0.52	0.00	0.02	0.10	0.00
2.0 FL	42.81	7.55	3.32	0.64	0.01	0.47	0.29	0.06	1.60	0.00	0.02	0.16	0.00
2.2 FL	42.57	13.19	4.20	0.42	0.01	1.64	0.63	0.08	3.54	0.00	0.02	0.16	0.01
2.2 SK	24.41	8.94	3.32	0.24	0.01	20.80	0.41	0.07	2.35	0.00	0.09	0.77	0.00

As shown in Figure 4-9a, the unleached coal shows a high Al/Si ratio in the light and heavy SGs, with lower ratio in the intermediate SGs. A similar trend is observed for the B/A ratio. The Al/Si ratio for kaolinite clay is 1; all other clay types are <1. Therefore, the Al/Si ratio of 1.2 in the 1.3 FL SG is indicative of a form of aluminum other than aluminosilicate clays. No alumina (Al_2O_3 minerals) was found in the samples, indicating an organic association in addition to clay sources. The very low Al/Si ratios for the intermediate

SGs is likely indicative of a high proportion of Si in the form of quartz or possibly amorphous silica. For the B/A, the high ratio in the light SG indicates a large amount of organically associated basic elements. The high B/A in the 2.2 SK is consistent with the high proportion of gypsum. For the post-leach coal (Figure 4-9b), the Al/Si ratio in the 1.3 FL is significantly lower than in the pre-leach, indicating that the Al has been leached from the coal. In general, the trends for the Al/Si and B/A are the same post-leach, but the magnitudes are lower, suggesting that aluminum and basic elements have been leached from the coal preferentially over silicon and acidic elements.

The above findings are confirmed by the leaching efficiency for the AAEMs, Fe, and Al shown in Figure 4-10a/b. As shown in Figure 4-10a, the elements that are known to be organically associated (per the mechanisms shown in Figure 4-4) were leached with high efficiency (Na & Mg). In most lignite, potassium is primarily present as clays, but has some degree of carboxylic acid salt association, which is consistent with the higher leaching efficiency in the light SGs. In the heavy SGs, the Na and Mg have a higher proportion of clays association, hence their decreased leaching efficiency.

In this sample, as shown in Figure 4-10b, aluminum appears to have a significant fraction as organically associated, as indicated by the moderate leaching efficiency in the light SGs and decreasing with increasing SG. Iron also appears to be partially organically associated, but may also be in the form of some acid-soluble mineral. It is also possible that this oxidized sample contains pyrrhotite or a derivative that would be more susceptible to acid leaching than pyrite.

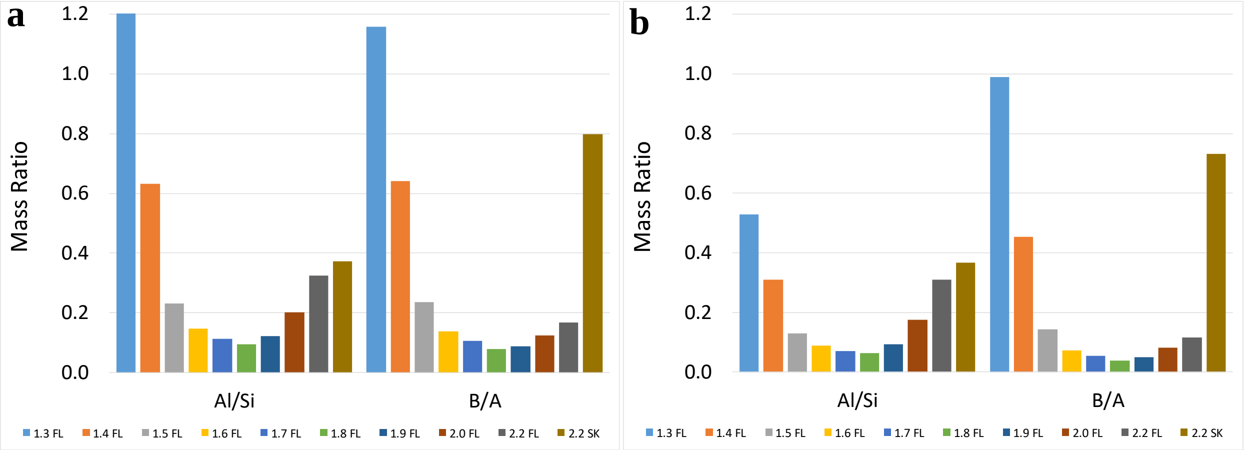


Figure 4-9. *Aluminum to silicon ratio and base to acid ratio for the unleached raw coal (a) and the leached coal (b). B/A = (Ca+Mg+Na+K+Fe)/(Si+Al+Ti)*

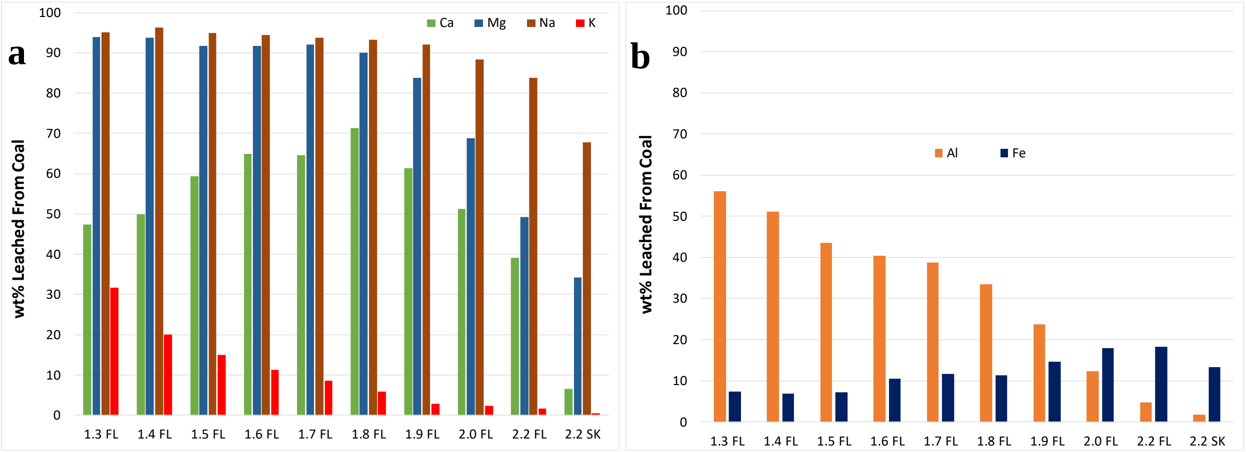


Figure 4-10. *Leaching efficiency for the alkali and alkaline earth metals (a) and aluminum and iron (b).*

To further deduce the mode of occurrence of the major inorganic elements and their behavior during the REE leaching process, Figure 4-11 plots the sulfur-free coal basis concentration (y-axis) versus the ash yield of the sample at each SG. For samples with an organic association, a negative slope should be present. For those with a mineral association, a positive slope should be present. A mixed or flat slope would contain multiple modes of occurrence.

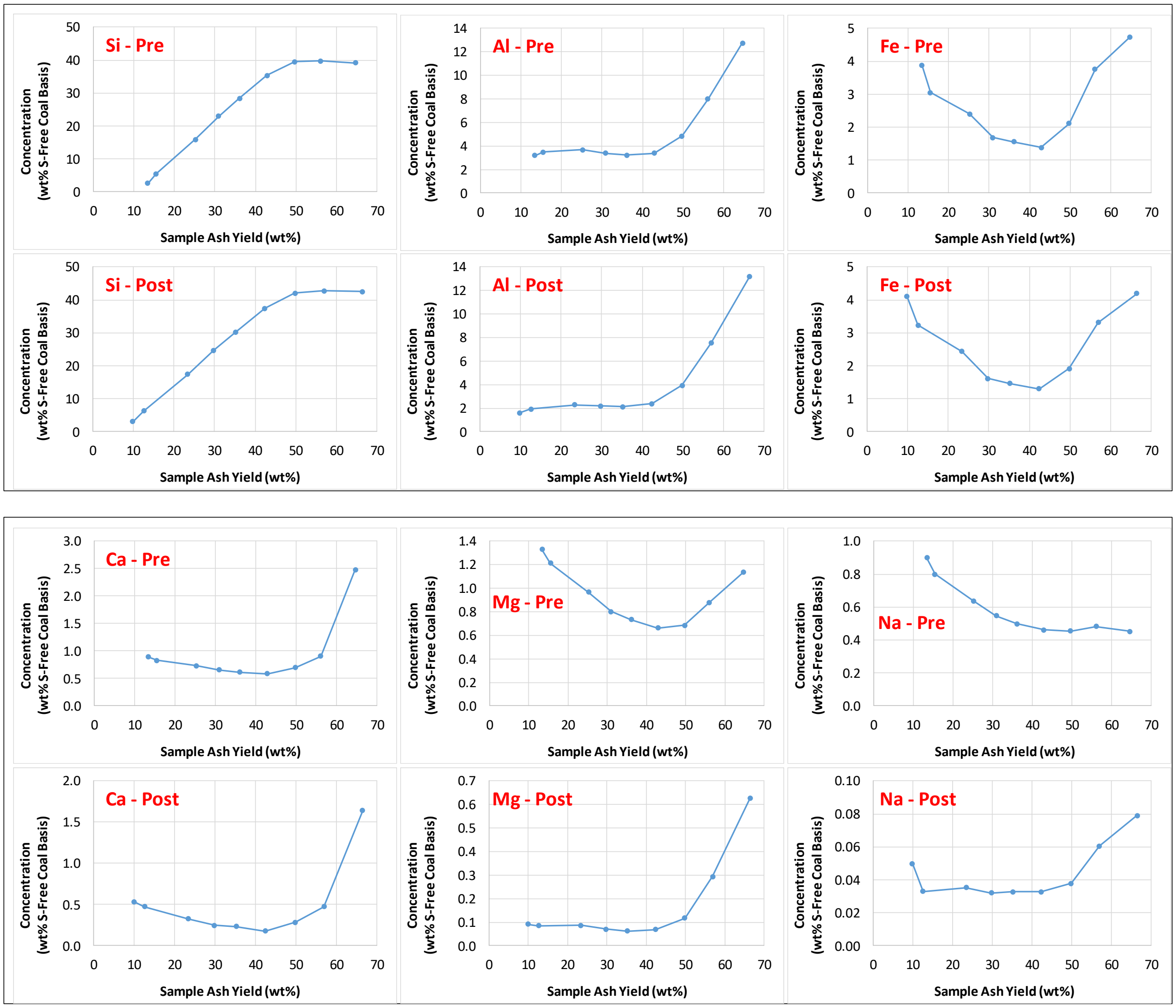


Figure 4-11**.** *Plots of selected inorganic elements concentration versus sample ash yield pre- and post-leaching. Plots with a positive slope indicate mineral-associated elements (i.e. Si). Plots with a negative slope indicate organic-associated elements (i.e. Na-Pre). Combinations of mineral and organic associations are also apparent (i.e. Fe). Comparison of the pre and post leach plots provides indication of which association of each element was leached from the coal.*

The occurrence of Si points toward a strong mineral association. There is also little change between the un-leached and leached samples, which was expected given the lack of solubility of Si in acidic solutions. For Al, there appears to be a flat slope through the intermediate SGs, with a strongly positive slope in the heavy SGs, indicating a mixed organic/inorganic association. There isn't a major change in the shape of the plots despite a reduced magnitude of the concentration in the light SGs. This could be explained by incomplete leaching of the organically associated Al due to insufficient availability of hydrogen ions (per the trivalent oxidation state mechanism in Figure 4-4). Fe appears to also have a mixed organic/inorganic association, with a strongly negative slope in the light SGs and a strongly positive slope in the heavy SGs. When comparing the pre- and post-leach samples, there is little difference in shape or magnitude. As with Al, this could indicate insufficient hydrogen ions, or it could indicate partial digestion of Fe-minerals across multiple SGs.

Both Ca and Mg exhibit mixed associations, likely as organically associated in the light SGs and then clays for Mg and gypsum for Ca in the heavy SGs. Sodium exhibits a plot that shows a strong organic association. Post leaching, both the Mg and Na plots show significant changes in shape of the plots as well as reduced magnitudes indicating that most of the organically associated fractions were leached and the mineral (clay) associated fractions were retained in the coal. While the magnitude of the Ca post-leach sample is decreased from the pre-leach, the shape of the plots is nearly identical. This could indicate that the gypsum present in this lignite sample may be finely dispersed within the coal particles and also present in separate, non-coal particulate. This theory is conceivable since the gypsum was formed from reaction of organic calcium with pyrite oxidation products. A portion of the gypsum may have crystallized within the interior pores of the lignite.

In summary, the following key observations have been made when investigating the behavior of major and minor inorganic species during the REE leaching process:

- Several of the major inorganic species in the Harmon lignite are also likely organically associated per the mechanisms described in Figure 4-4 previously. These include the AAEMs, aluminum and iron.
- While the AAEMs can be segregated from the REEs, the Al and Fe are likely to behave similarly to the REEs, and thus methods must be conceived to be able to segregate the Al and Fe from the REEs somewhere within the overall process (i.e. Figure 4-3).
- This sample exhibits evidence of oxidation, with formation of gypsum in the heavy SG fractions as well as likely finely disseminated gypsum included within the coal particles.
- The oxidation of pyrite has likely transformed it into a state where it is more soluble in the acid solution, thus likely increasing the leaching of iron in the process.

4.4.2.2 Mineral Typing Pre- and Post-Leaching

CCSEM-EDS was used for all samples with SG <2.2. The >2.2 SG was not evaluated as it was observed to be mostly gypsum. As described previously, the CCSEM with EDS is a semi-quantitative approach to measure aggregate percentages of the chemical composition within a coal sample. For this project, the CCSEM-EDS was coupled with a proprietary mineral typing software owned by project partner Microbeam

Technologies, Inc. The full data for the pre- and post-leach coal can be found as Appendix A. However, the major mineral type groupings for the pre- and post-leach coals are provided as Figure 4-12a.

Looking at the pre-leach coal (UL in Figure 4-12a), the major mineral form is quartz, especially in the intermediate SGs. In the light and high SGs there is a higher fraction of clays and gypsum. There is also a significant amount of mixed or unidentified mineral types that consisted of conglomerate mineral grains or mineral types unrecognized by the software. The large amount of gypsum in this sample confirms that it is partially oxidized.

In terms of the mineral type changes after leaching, besides the increasing quartz content, it is difficult to discern any obvious trends. Quartz, being insoluble in acids, is understandably unaffected by the leaching and is thus increased due to part or full digestion of other more soluble mineral types. The mixed particle types are also typically decreased after leaching, indicating that the leaching process – either due to agitation or partial digestion – has resulted in the breakup up the mineral/clay conglomerates. In the case of most of the SGs, the mixed particles appear to be mainly quartz, with lesser amounts of clays and gypsum.

As shown in Figure 4-12b, the decrease in particle size of mineral grains after leaching indicates that partial digestion of some mineral forms is likely to have occurred. It could also indicate that the mixed mineral types identified in Figure 4-12a were broken up during the process.

In summary, however, it appears that the dominant mineral form in this sample is quartz with an uncommonly small fraction of clays (at least based on experience of the UND team investigators). Combined with an efficient leaching process that removes all or a majority of the carboxylic acid-associated inorganic elements, it is plausible that the inorganic content of the upgraded coal byproduct resulting from this process (as in Figure 4-3) may be made up nearly entirely of quartz; this is even more plausible after separating the high SG fractions (i.e. > 1.7 SG as described in Section 4.4.1) that contain a higher percentage of clays and gypsum.

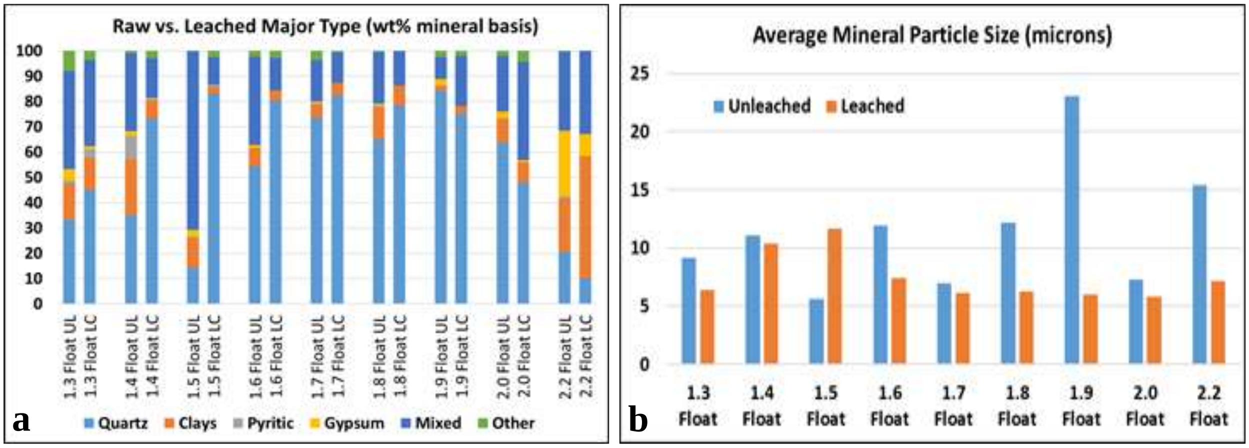


Figure 4-12. ***a*** *- Major mineral types identified by CCSEM-EDS data for the unleached (UL) and leached (LC) coal as a function of the SG fraction. Note that 2.2 Sink was not examined for these tests.* ***b*** *- Average particle size of mineral grains measured by CCSEM before and after leaching. A decrease in size for most SG fractions is an indicator of partial digestion of some mineral forms, and/or a breakup of mixed mineral grains.*

4.4.2.3 REE Leaching Efficiency

In addition to the inorganic species discussed in Sections 4.4.2.1 & 4.4.2.2, the REE leaching efficiency was also examined as a function of SG. As described previously, the theory entering this effort was that REE leaching would be more effective in the coal-rich light SG fractions – following the leaching mechanism described in Figure 4-4. The results for each of the REE are provided in Figure 4-13 and for total REE in Figure 4-14. The results, however, show that the best leaching efficiency was in the intermediate SG fractions. While this was unexpected, it can be explained by referencing the reaction mechanisms shown in Figure 4-4. In order to leach the REE, hydrogen ions have to be available in a sufficiently high concentration to break the organic complex and protonate the carboxyl groups. In the light SG ranges, there is a significantly higher content of competing cations (i.e. organically associated Na, Mg, Ca, Al, Fe) than in the higher SG ranges. This resulted in consumption of the acid during these tests, not leaving a sufficient amount of hydrogen ions available to fully leach the REE. Therefore, it is expected that by providing more hydrogen availability (either through periodic/continuous replenishment or by providing a higher ratio of liquids to coal during leaching), a significant improvement in REE leaching would be overserved in the light SGs.

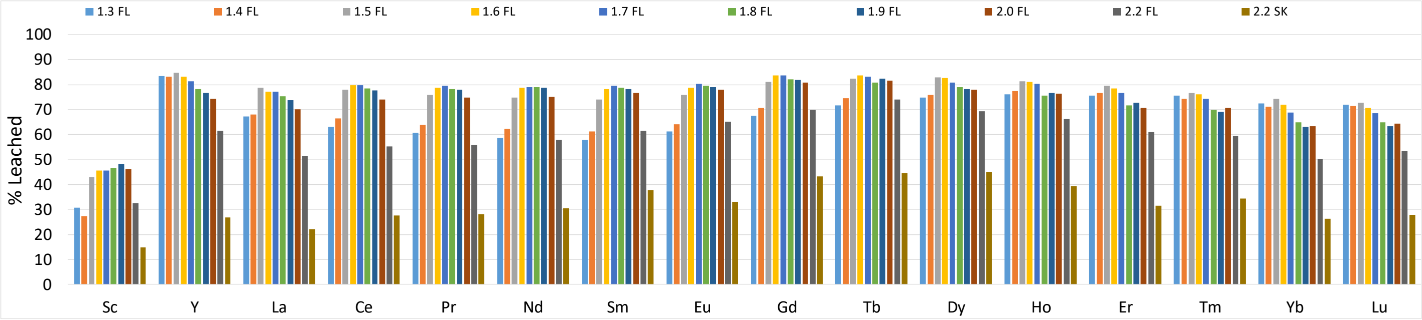


Figure 4-13. *REE leaching efficiency (wt% leached from sample) as a function of specific gravity (increasing left to right for each element). Efficiency was best in the intermediate SG fractions.*

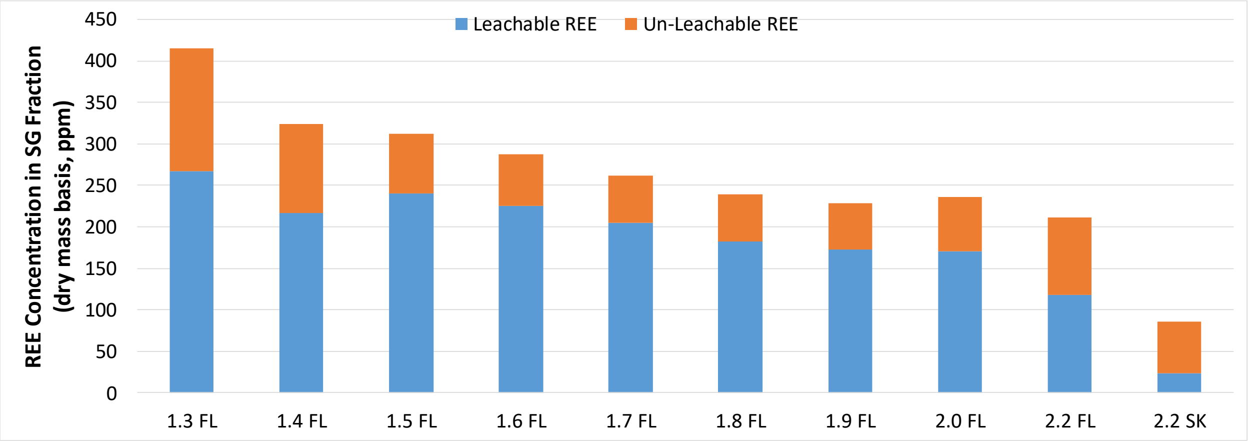


Figure 4-14. *Total REE leaching efficiency given on the basis of leachable (extractable) REE content within the total content of REE in each SG fraction. The highest total leachable REE was in the 1.5-1.6 SG fraction.*

4.4.3 Bulk Sampling and Large-Scale Density Separations

Based on the results described in Section 4.4.1 and 4.4.2, the project team has selected the <1.7 SG fraction of the Harmon lignite coal with the following justification:

- Ability to achieve the 300 ppm REE concentration programmatic target
- High quantity of recoverable REE
- Understanding of the impurities modes of occurrence and behavior during leaching
- Ability to effectively segregate key impurities, namely calcium, from the REE using a two-stage leaching process as depicted in Figure 4-3 and Figure 4-4.
- Ability to take a potential waste coal with very high ash yield (i.e. 30-40wt%) and turn it into a significantly upgraded lignite, with ash yield of 10-15wt% (mainly as quartz), using density

separation combined with the UND leaching process. This process preserves the majority of the energy content of the lignite, allowing the similar BTU's to be recovered as when mined.

After completion of all of the testing on the 130 lb sample of the Harmon lignite, several members of the UND team, one member from Barr Engineering and four members of the NDGS team travelled to Slope County, ND and procured approximately 2.5 tons of the Harmon lignite coal from the top of the exposed outcrop. Some photographs from the sampling trip are provided in Figure 4-15. The coal was manually excavated using shovels and electric chisels and hauled out using 5-gallon buckets. It took about two days to complete the sampling and reclamation work, which needed to be done to meet the standards of the National Forest Service.

Once secured, the coal – in 15 55-gallon drums – was returned to UND for preparation prior to larger-scale density separation. At UND, the coal was partially dried to remove surface moisture, then crushed to approximately -20 mesh, further dried and then finally sieved and re-crushed to 20x100 mesh. The -100 mesh fines were retained, but are not planned to be used during bench-scale testing.

Figure 4-15. *Some photographs of the large-scale sampling trip to collect about 2.5 metric tons of the Harmon lignite coal from an exposed outcrop in Slope County, ND. Top photo – the sampling team photographed by a drone directly above the sampling site. Bottom photo – the sampling team during sampling at the site. The sample was collected by shovels, electric drills and hauled out by 5-gallon buckets.*

Once prepped, the Harmon coal was shipped to Hazen Research Inc., in Golden, CO where it was processed in two stages:

1. Desliming by wet sieving at 100 mesh
2. Density separation by a pilot-scale coal spirals system to an approximate cut point of 1.7 SG

A concentrate, middlings and tailings stream were generated in the first pass through the spirals. The middlings were then re-fed to the spirals and a scavenger concentrate, middlings and tailings fraction were generated. The overall mass balance on a dry basis is in Table 4-6.

Unfortunately, as shown in Table 4-6, the REE concentration of the as received coal was significantly lower than hoped for. During the sampling, the project team selected the location along the outcrop that was most easily accessible by foot, as well as per the recommendation of NDGS on where the highest REE concentrations were likely to be located. However, because of the manual excavation and to ensure safety of the operation, there was only a limited lateral extent along the outcrop that could be sampled from. Further, the NDGS permit from the National Forest Service limited the depth into the face of the outcrop that could be excavated to three feet. To ensure that sufficient mass of coal was excavated, combined, this resulted in the need to excavate an approximate stratigraphic depth of 12-16 inches, rather than the planned ~6 inches. Therefore, a significant amount of lower REE content material from deeper down the seam was mixed with the REE-rich material taken from the top layers, causing dilution to the previously-identified >250 ppm source. This can also be observed in the ash yield of the as received coal, which was about 23wt%. This is compared to about 40wt% for previous samples taken from the top 3-6 inches of this seam (see Figure 4-8).

Table 4-6. *Overall mass balance and REE concentration results for the large-scale density separation of the Harmon lignite coal.*

Coal Fraction	Mass Fraction (wt% of As Rec'd)	Ash Yield (wt%)	Sc	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	TREE (coal)	TREE (ash)
As Received Coal	100	22.8	5.7	26.0	20.1	37.7	4.4	17.0	3.7	0.86	4.6	0.74	4.5	0.88	2.46	0.33	2.04	0.30	131	576
Slimes	4.5	41.9	7.8	24.7	25.4	47.3	5.4	20.1	4.2	1.00	4.7	0.75	4.5	0.85	2.45	0.34	2.12	0.31	152	363
Concentrate	54.4	14.7	5.9	27.4	21.7	41.3	4.8	18.2	4.0	0.93	5.0	0.80	4.9	0.94	2.63	0.35	2.16	0.32	141	961
Tailings	12.3	64.8	3.0	13.0	9.4	19.5	2.4	9.1	2.0	0.49	2.3	0.38	2.3	0.44	1.24	0.16	1.04	0.15	67	103
Scavenger Concentrate	12.5	15.1	5.8	25.5	21.2	41.3	4.7	18.3	4.0	0.91	4.8	0.78	4.7	0.89	2.52	0.33	2.04	0.30	138	914
Scavenger Middlings	12.5	19.3	6.6	30.1	22.3	44.2	5.1	19.4	4.3	0.99	5.2	0.85	5.1	0.98	2.82	0.37	2.35	0.35	151	782
Scavenger Tailings	3.8	30.7	5.8	23.6	18.5	36.4	4.3	16.8	3.6	0.84	4.5	0.72	4.4	0.85	2.38	0.32	1.95	0.28	125	408

Similar to the float-sink data discussed previously in Section 4.4.1, there is an enrichment of the REE in the low ash yield fractions. Based on these results, the primary concentrate, scavenger concentrate and the scavenger middlings streams were blended and stored under argon in sealed 55 gallon drums. However, as this blend only had an approximate REE concentration of 142 ppm on a dry coal basis (919 ppm ash basis), it could not be used as the feedstock for production testing in Task 7 of the project. An alternative location for collection of a large sample which would meet the 300 ppm specification was selected, and is discussed in Section 4.5.

4.5 H Bed Outcrop

The NDGS has previously sampled the outcrop of H Bed lignite at this location as a part of separately-funded sampling efforts [2] [3]. The goal of the NDGS work is to characterize the coal-based REE resources in portions of the State without active mines to provide justification for the potential opening of a new mine. During the sampling effort, the NDGS identified a sample of the H Bed in this location which had an REE concentration over 1,000 ppm on a dry coal basis, and the other samples taken from this location averaged over 300 ppm.

In Phase 1, samples of this same coal (same site and coal bed) were examined and it was shown to provide leaching efficiency of about 90% for all the REE (Sc at about 80%), the highest of all coals tested in Phase 1 and 2 to date. Further, it also contains very high concentration of other leachable metal(loid)s, such as Co, Ge and Ga, which may be able to be recovered/concentrated in the UND process as well, further improving economics.

Despite the high enrichment of REE at this location, it was not chosen as the initial location for the large-scale sampling because of difficulty in accessibility relative to the Harmon outcrop. Due to the sample of coal from the Harmon outcrop not meeting the 300 ppm REE threshold, a sampling trip was planned to this location to collect a large quantity of sample of the H Bed for the bench-scale testing program in Tasks 5 & 7.

A manual excavation effort was undertaken to collect a ~7000-pound sample of H Bed lignite coal from an outcrop in Slope County, ND. In total, 18 55-gal drums of coal were excavated from the outcrop (see Figure 4-16 for photographs). Each drum was separately dried and crushed to -10 mesh, and then split for ICP-MS by a combination of cone and quartering/riffle splitting. The 18 samples from each drum were analyzed for REE concentration using ICP-MS.

Figure 4-16. *Photographs of the sampling site and excavation of the 7000 lbs of REE-rich H Bed coal from Slope County, ND during the week of November 12, 2018.*

Figure 4-17 provides the REE concentration (dry whole coal basis) for each drum. As shown, the drums ranged from 350 to 830 ppm, with a weighted average of 647 ppm, significantly above the programmatic requirement of 300 ppm. Figure 4-18 provides the upper continental crust (UCC)-normalized REE distributions for each drum and shows that the H Bed coal is significantly enriched in the medium molecular weight REE.

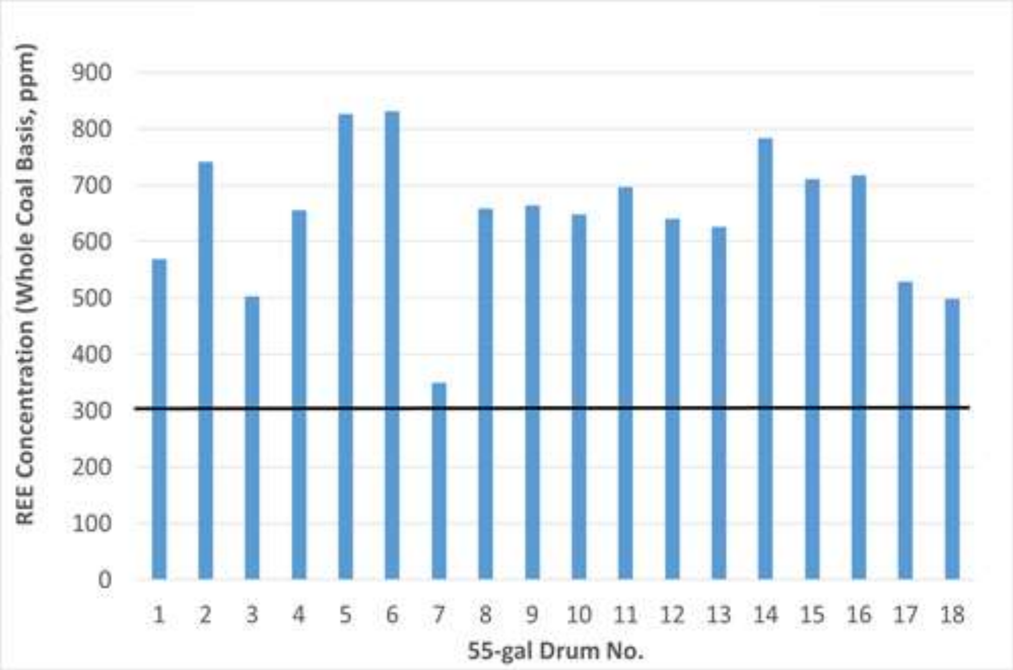


Figure 4-17. *Total REE concentration for each drum of coal collected from an outcrop of the H Bed seam in Slope County, ND.*

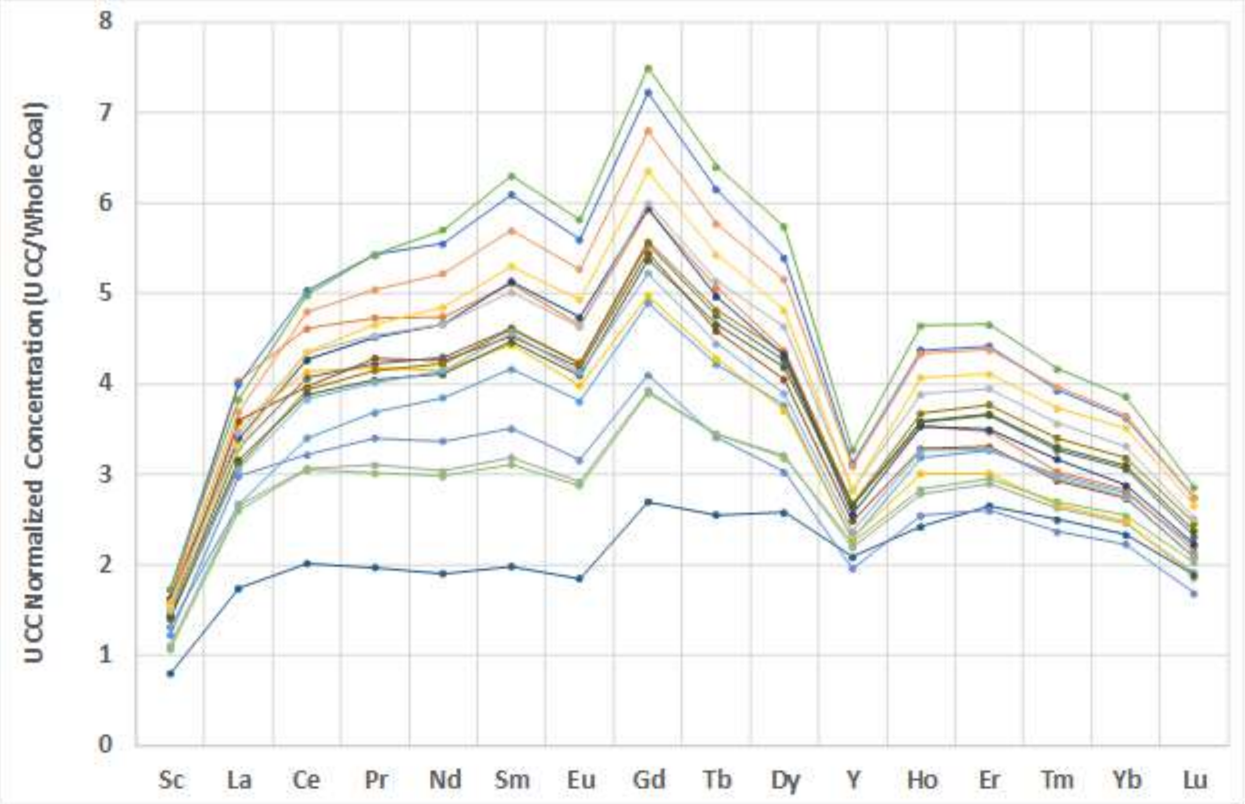


Figure 4-18. *UCC-normalized REE distribution for each of the 18 drums of H Bed coal. There is significant enrichment of the middle molecular weight REE.*

The coal was shipped to Hazen Research in Golden, CO for de-sliming and density separation utilizing the same parameters as with the Harmon coal. Through this process, similar results as to the Harmon lignite were anticipated, namely a significant decrease in ash content with REE enrichment in the concentrate fractions. Figure 4-19 provides a simple flowsheet of the coal processing that was performed at Hazen Research. Based on the average ash content of the H Bed coal (~38wt%, dry basis), a significant enrichment of the REE into the product fractions (primary concentrate, scavenger concentrate, scavenger middlings) was anticipated.

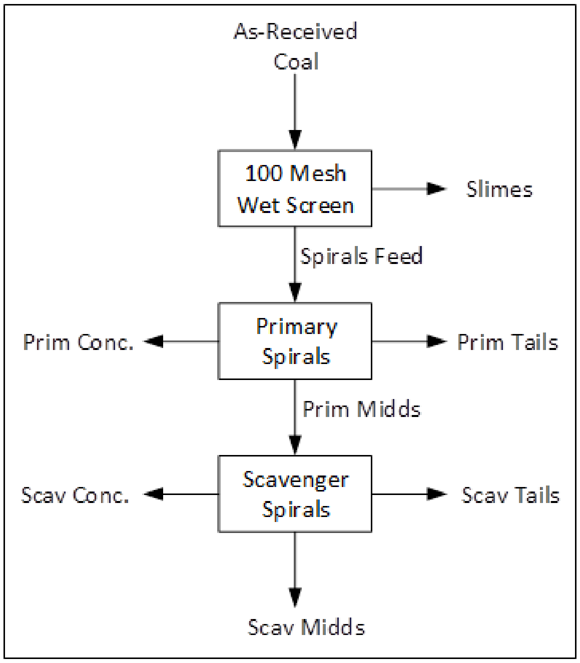


Figure 4-19. *Flowsheet for coal processing conducted on the REE-rich H Bed coal at Hazen Research. The fractions to be combined and tested on the bench-scale test system are anticipated to be: primary concentrate, scavenger concentrate, and scavenger middlings.*

Representative samples were obtained from each split produced from the Hazen Research spiraling process for REE analysis for determination of blend requirements and may be found in Table 4-7. As expected, REE concentrations, particularly on an ash basis (against other inorganic impurities) increased. However, the whole-coal basis REE enrichment was less than expected, though significant ash reductions achieved.

Table 4-7**.** *Results from the spiraling conducted at Hazen Research on the 7000-pound H Bed lignite coal.*

Coal Sample	**Ash Content (wt %)**	**Total REE Content (dry mass basis, ppm)**	**Total REE Content (ash basis, ppm)**	**HREE/LREE**
As Received	35.45	646	1822	0.28
Concentrate	15.09	657	4357	0.30
Middlings	33.33	640	1919	0.28
Tailings	70.31	353	502	0.26
Scavenger Conc	19.5	679	3483	0.30
Scavenger Midds	47.26	630	1333	0.28
Scavenger Tails	59.34	550	927	0.26
Blend	19.34	658	3881	0.30

The blend (Table 4-7) was produced from the combination of the primary concentrate, scavenger concentrate, and scavenger middlings fractions. The composition of the resource as compared to the upper continental crustal average (UCC) is similar to the previous as-received coals, as expected (Figure 4-20).

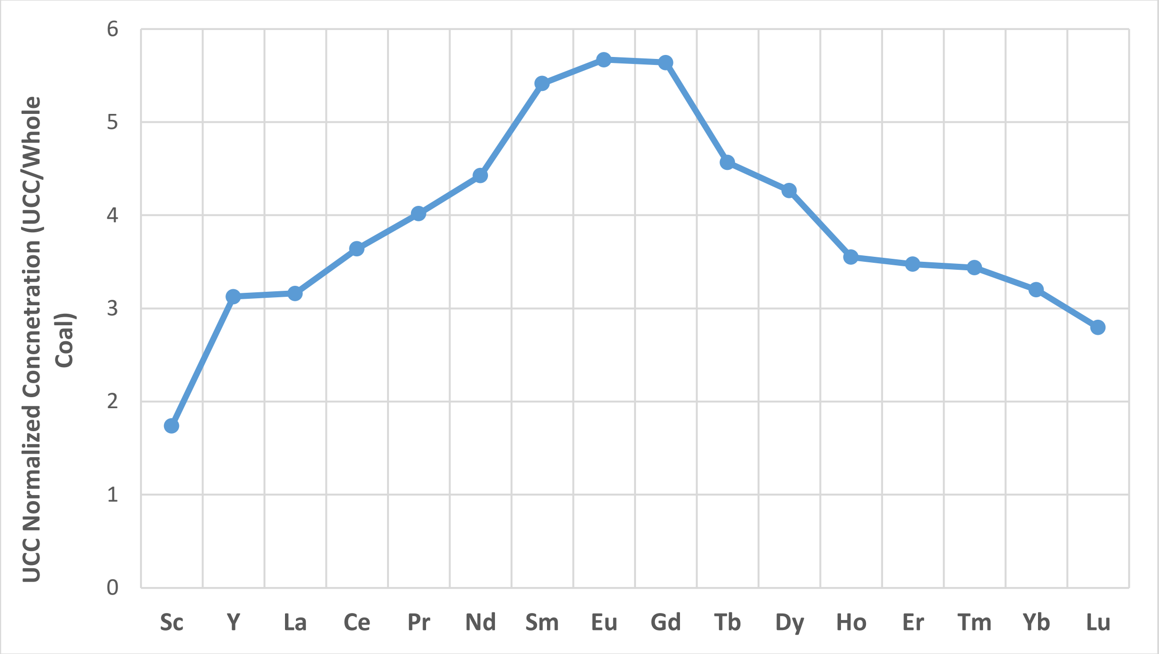


Figure 4-20. *UCC normalized concentration of the blended H Bed gravity separated lignite prepared for testing. Significant enrichment in the MREE (particularly critical Eu) is noteworthy.*

Based on these results, the primary concentrate, scavenger concentrate and the scavenger middlings streams were blended and stored in sealed, argon-purged 55 gallon drums. This blend, with an approximate REE concentration of 658 ppm on a dry coal basis (3,881 ppm ash basis), was used as the feedstock for production testing in Task 7 of the project.

4.6 Analytical Methods

The samples collected were analyzed in a variety of ways to determine bulk chemical composition and modes of REE occurrence. The primary analytical methods used are summarized in Table 4-8, with additional details in the following sections.

Table 4-8. *Analysis methods utiltized in the Phase 2 Effort*

Category	Equipment	Function
Bulk chemical composition	ASTM standard analysis	Proximate analysis; Ultimate analysis; Ash composition
	X-ray Fluorescence	Bulk chemistry; major, minor and trace element
	Inductive Coupled Plasma-Mass Spectrometry	Abundance of trace elements including REE
	Flame atomic absorption spectrometer	Abundance of major elements
Modes of Occurrence	Float-Sink Analysis	Correlations between ash content and REE concentration were used to make qualitative correlations
	CCSEM	Mineralogical analysis of major elements contained in coal samples

The workhorse analytical method used in this project was inductively coupled plasma mass spectrometry (ICP-MS), which was used primarily to measure the abundance of REEs in the samples. Modes of occurrence were determined using a float-sink analysis method. The following sections briefly describe each of the analytical methods used, along with equipment specifications.

4.6.1 Sample Preparation

Prior to analysis, to ensure complete homogenization of collected samples, the sample preparation methodology described below was adopted and maintained throughout the project. Complete homogenization of the samples was accomplished through grinding and/or mixing. During the homogenization of the samples, the materials were ground to -60 mesh to be ready for further sample preparation or analysis. ASTM standard methods (D2234/D2013) were followed. The collected samples were treated through the following steps.

1. Recording in inventory: each sample was assigned a unique identifier, and its sampling date and locations were recorded in the inventory sheet;
2. Drying: the portion of samples to be used for analysis was dried in a convection oven for 12 hours at 70°C;
3. Crushing and homogenization: the dried samples were crushed to -60 mesh size and mechanically mixed;

4. Grinding: the crushed samples were further ground to -200 or -325 mesh to meet the requirement of the analysis method;
5. Further Preparation: additional preparation was performed based on the requirement of the analysis method.

4.6.2 Inductively Coupled Plasma Mass Spectrometry

Inductively coupled plasma mass spectrometry (ICP-MS) is currently the most widely utilized method to determine the concentration of trace elements in solid samples. The method has been described in detail by Bank and others (2016) [4], and has become the standard method for determination of the abundance of REEs in coal and coal-related samples. ICP-MS requires digestion of the solid samples prior to analysis in order to extract all of the REEs into a liquid solution. The digestion procedure is the critical piece for ensuring accurate measurement by ICP-MS. Testing in this project utilized an external lab for ICP-MS analysis. Standard ASTM methods were used for ICP-MS analysis (ASTM D6357).

The ICP-MS measures trace and major element analysis at the part per billion levels. The coal sample is first ashed to remove carbon, then digested in a mixture of HF, HCl, and HNO_3. The acid is boiled off to dryness, and samples are diluted to volume and analyzed by ICP-MS. Liquid samples analyzed were diluted directly and analyzed. Regularly during the project, the accuracy of the ICP-MS measurements was confirmed via analysis of Standard Reference Materials [5] and comparison of the measured versus certified values. At no point in the project did the analysis fall outside of an acceptable accuracy range.

4.6.3 X-ray Fluorescence

Although not used extensively in this project, X-ray fluorescence (XRF) is a method to provide quantitative measurement and qualitative survey scans of the chemical composition of solid samples. UND has two XRF systems that were used in this project, as described below.

Rigaku Supermini 200 XRF: This XRF is a wavelength dispersive bench-top XRF able to provide low ppm detection limits for major, minor, and trace elements. The instrument is equipped with a 12 sample autosampler and can analyze either solids or liquids. The software allows rapid analysis of known and unknown samples. The system provides the ability to perform quantitative analysis and qualitative survey scans to identify the presence of elements.

Bruker Tracer IV Geo handheld XRF: The Tracer IV Geo is equipped with a large area silicon drift detector as well as a vacuum system for the analysis of lighter elements. This portable instrument can be taken to field sites. The flexibility of the system also allows for analysis of bulk samples (e.g., coal core samples, clays and other sediments for major elements) in the field without any sample preparation.

4.6.4 Flame Atomic Absorption Spectrometer

Flame atomic absorption spectrometry (Flame –AAS) is a common technique used for detecting metals present in samples. Flame –AAS was used in Phase 2 to provide quantitative measurements of major elements in liquid samples, such as aluminum and iron.

4.6.5 ASTM Analysis Methods

In addition to the above analytical methods, for some of the samples, standard ASTM measurements were made for proximate (ASTM D3172) and ultimate (ASTM D3176) analysis and ash composition (ASTM D4326-13). However, these were used for a very limited number of samples and were primarily to generate mass balances for laboratory extraction testing. Float-sink analyses were also conducted to identify the mass of sample and the distribution of the elements within the specific gravity fractions.

5 PARAMETRIC TESTING

This chapter details the parametric testing completed to optimize the process conditions and to identify the most efficient configuration. Details on construction of the bench-scale system are also included in this chapter.

5.1 Hagel B and Harmon Parametric Testing

The overall flowsheet for the UND REE recovery process as originally conceived planned is summarized by Figure 5-1. In the first stage of leaching, the goal was to selectively remove mono- and divalent cations (primarily alkali and alkaline earth metals – AAEMs) that are more weakly bound in the lignite than the trivalent lanthanides/REE. This was accomplished by a milder solvent formulation. A second stage of leaching using a stronger solvent formulation then had the goal of selectively removing the organically associated trivalent REE, with concomitant leaching of other metals such as Fe and Al. Once into the liquid solvent phase, the REE would be further concentrated and ultimately precipitated as a mixed REE solid product.

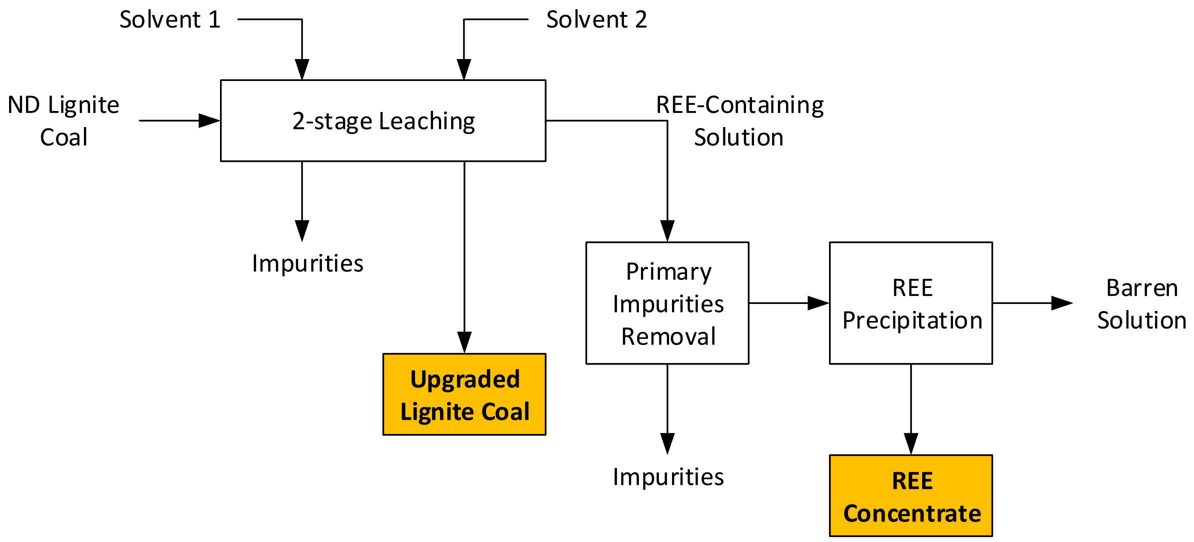


Figure 5-1. *Flowsheet of the originally planned UND REE recovery process for lignite coal.*

5.1.1 Bench-Scale System Procurement and Construction

Task 3 of this Phase 2 project involved the construction of the bench-scale system to be utilized for parametric testing in Task 5. For the bench-scale system, four 55-gallon mixing tanks were procured and installed. in an identical configuration for rapid parametric testing in Task 5. Photographs of the completed test system are provided in Figure 5-2.

The major components installed for the bench-scale system included Buchner funnels and vacuum pumps for the filtration system, diaphragm pumps to feed liquid into the tanks, gas scrubbers, and coal and acid hoppers on top of the tanks. In addition, pH probes and thermocouples were installed in each tank, and piping and valves to feed material from the mixing tanks to the filters. A National Instruments control system was designed for the bench-scale system. Inputs, outputs, and logic arguments were added to the control system, including actuated valves, sensors and pumps. A deionized water production/supply system was installed which could produce up to 100 gallons per day. Further addition of ground loop isolators and additional electrical equipment for improved pH control and measurement were installed.

Meetings were held with the UND Safety Office to ensure that chemical reagents needed for testing were properly stored, handled, and disposed. For completion of shakedown procedures and preparation for operation of the system, Hagel B lignite was mixed with water to ensure the process, including all control and monitoring systems, would operate smoothly before introducing acid to the system. Overall, the system performed as expected during shakedown, with some minor changes made to filtration operation. Identification of pH control challenges with the addition of acid (mainly caused by ground loop faulting from the conductivity of the liquid in the grounded tank), forced the addition of the aforementioned ground loop isolators, enabling Test 13's pH values to be read (as compared with the inability to accurately measure Tests 1-12 during operation.

Testing was planned to be performed in multiple tanks simultaneously, as to reduce the time spent on parametric testing. Based upon labor constraints and challenges with control of multiple systems simultaneously, the system was unable to be run with any more than two tanks at the same time. However, through staggered tests, testing was able to be completed in an expedited fashion.

Figure 5-2. *Photographs of the newly installed bench-scale test system currently in the batch testing configuration for Task 5.*

5.1.2 Hagel B Bench-Scale Stage 1 Leaching Testing

After construction of the bench-scale system, Hagel B lignite was utilized in parametric testing on the bench-scale. This testing focused on testing of the Stage 1 leaching of the 2-stage leaching process shown in Figure 5-1. It was completed using the bench-scale system described in Section 5.1.1, and the coal used in this testing was the Hagel B lignite from Falkirk Mine. Initially 12 tests were completed evaluating the following key parameters:

- Leaching solution composition (reagent 1 and reagent 2)
- Leaching solution reagent concentration (molarity)

- Coal/Liquid ratio (wt:wt)
- Contact time (hours)

One additional test was added to the testing plan after the initial 12 tests were completed, which evaluated a pH-based leaching parameter.

Figure 5-3 displays the results of Ca, Mg and Na leaching from the feed lignite coal as a function of the reagent 1 concentration. Contact time and coal/liquid ratio were constant for these tests. All data are determined on a dry elemental basis and on a whole dry coal basis. As shown in the figure, the leaching percent generally increases with increasing reagent concentration.

The next four tests evaluated four concentrations (same as those used for Reagent 1 in Figure 5-3) of Reagent 2. The results are presented as Figure 5-4. Overall, the results are only slightly lower than those for Reagent 1 with the same concentrations, indicating that the reagent type has minimal impact. Therefore, the cost of reagents can be the primary selecting factor for optimization (Reagent 1 significantly cheaper than Reagent 2).

Figure 5-5 provides results for the leaching efficiency as a function of the contact time. This data was taken for a constant Reagent 1 concentration (2nd lowest from Figure 5-3) and constant coal:liquid ratio (same as Figure 5-3). Interestingly, the data actually shows a decreasing leaching efficiency with contact time. This shows that shorter contact times could be used thus minimizing capital costs (leach tank size).

Figure 5-6 shows the effect of the coal: liquid ratio of leaching efficiency. In these tests, a higher extraction of Ca, Mg, and Na was observed with the lower coal/liquid ratio, while the leaching of the REE was either the same or slightly lower for the test with the lower coal/liquid ratio. The acid concentration of acid type 1 and the contact time were kept constant for these tests. The lower coal/liquid ratio was theorized to provide more moles of H^+ per unit mass of coal during leaching, permitting a prolonged leaching driving force. As these tests pointed out, the driving force for extraction was diminishing without constant acid addition, and pointed towards additional acid-utilization mechanisms for driving force maintenance.

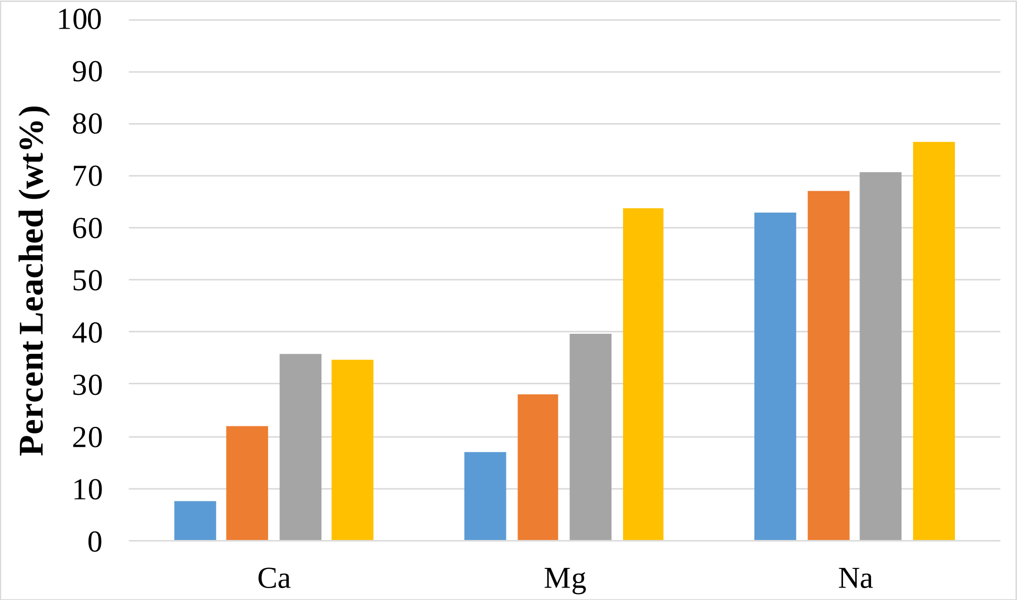


Figure 5-3. *Impurities leaching results as a function of increasing Reagent 1 concentration (left to right).*

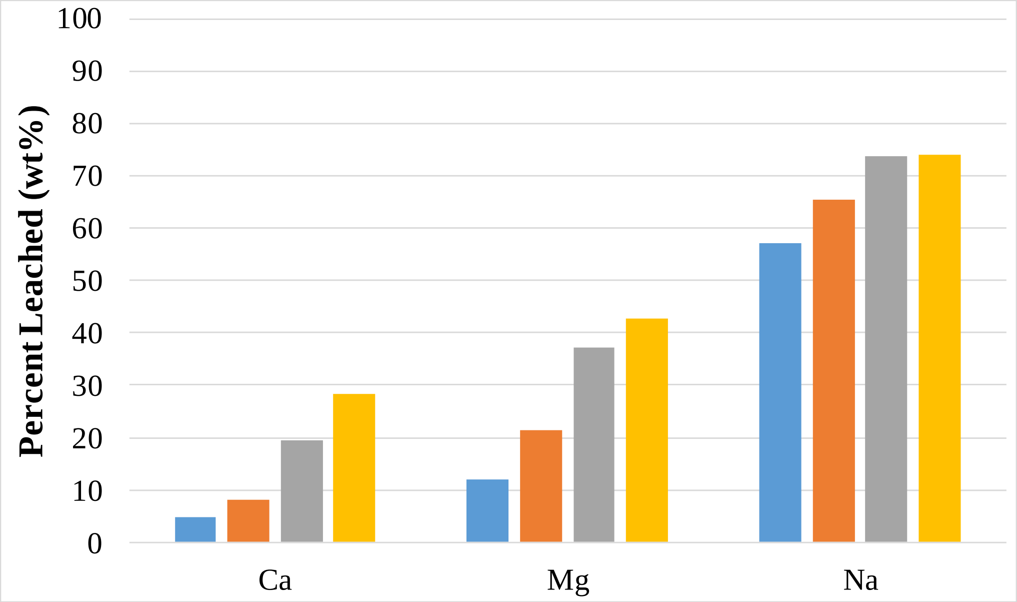


Figure 5-4. *Impurities leaching results as a function of increasing Reagent 2 concentration (left to right).*

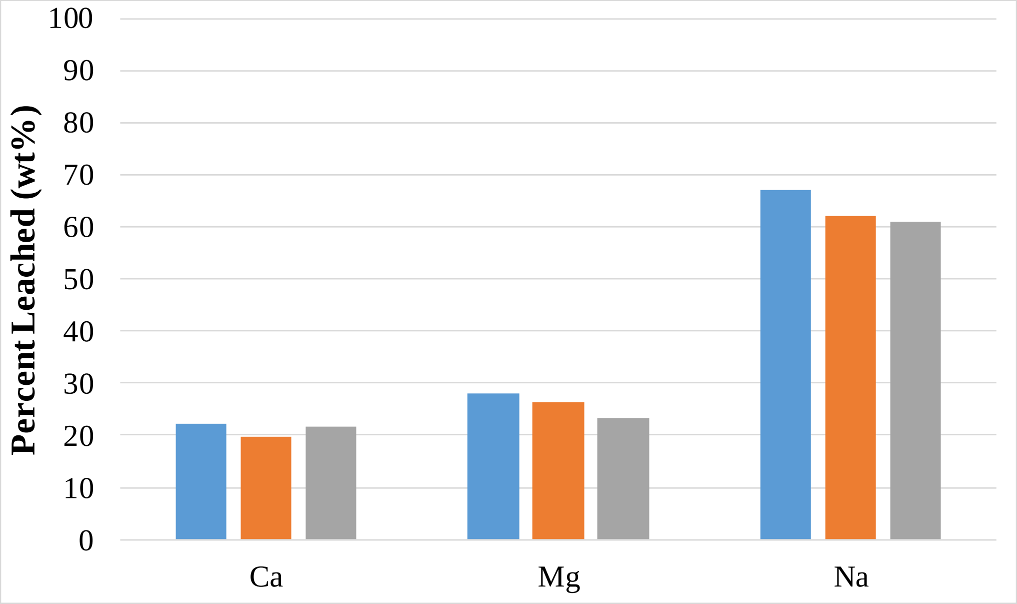


Figure 5-5**.** *Impurities leaching as a function of coal/Reagent 1 contact time (increasing time left to right)*

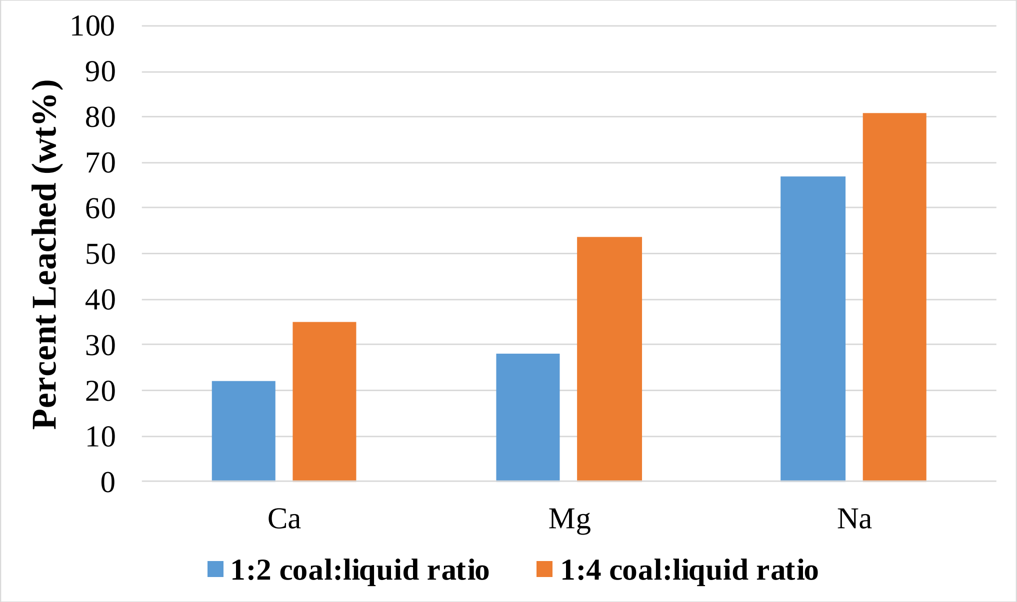


Figure 5-6. *Impurities leaching as a function of coal/liquid ratio (wt/wt) (increasing left to right).*

A pH-based test was performed with periodic acid addition throughout the test to providing more active reagent and prevent complete consumption of H^+ ions. The pH was monitored throughout this test, and is shown in Figure 5-7. A rapid increase in the pH was observed immediately after the coal was added, with subsequent acid additions the rate of increase in pH lessened. As the leachable material was extracted from the coal, the rate of consumption of H^+ ions decreased.

The extraction results of the pH-based pre-leaching test compared to a concentration-based pre-leaching test, which both had the same initial acid concentration, acid type, contact time, and coal/liquid ratio, are shown in Figure 5-8. Extraction of impurities was higher in the pH-based pre-leaching test, due to the additional active reagent which was available and prevented complete consumption of H^+ ions.

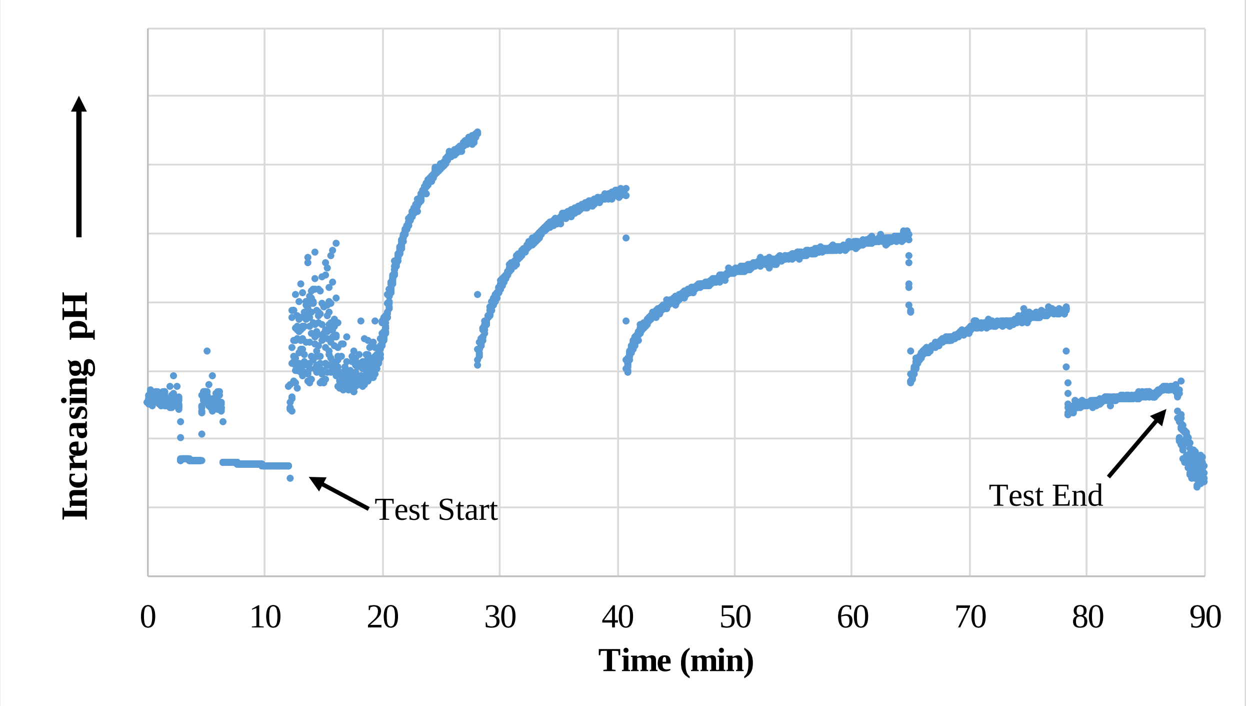


Figure 5-7. *Changes in pH over time during Stage 1 leaching test with periodic acid addition to maintain pH.*

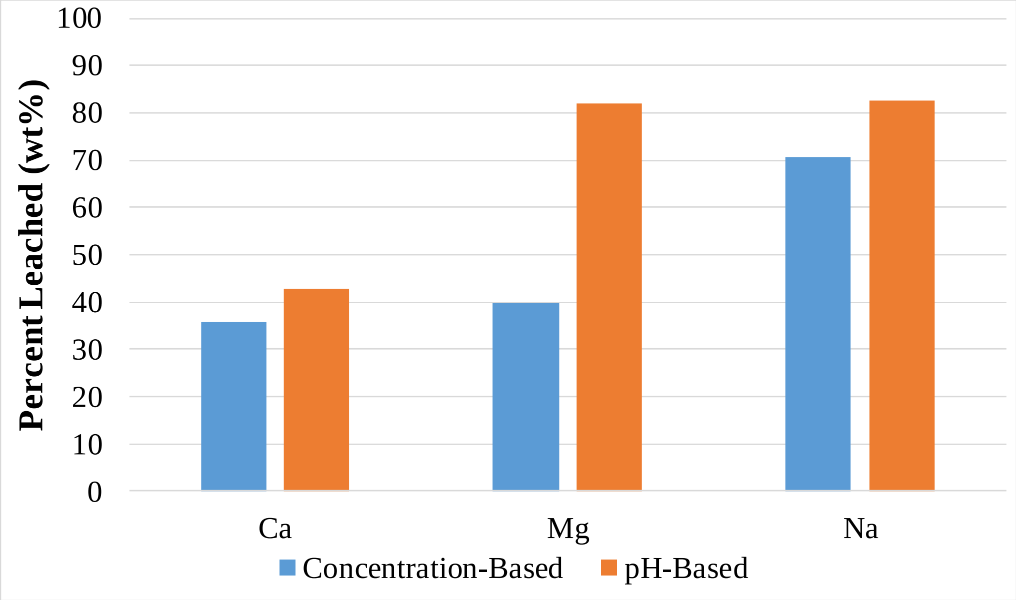


Figure 5-8. *Comparison of impurity leaching results for concentration-based and pH-based leaching.*

5.1.3 Leaching Optimization

As provided in Figure 5-1, a two-stage leaching process was evaluated. The UND solvent, being an aqueous acidic solution, was tested over a range of pH conditions to determine the leachability of select (important and representative) cations. The goal of this testing was to determine the combination of pH/contact time at which effective segregation of the AAEMs from the REE could be achieved. Both equilibrium and kinetic tests were completed. For equilibrium tests, fresh solvent was continuously added to maintain a constant pH during each test, measured through use of immersed pH probes. Equilibrium was presumed to occur at the point when pH stabilization occurred. For kinetics-based testing, samples of the slurry were periodically taken at selected intervals to determine the kinetics of mono-, di-, and trivalent cations, independently. All data discussed below, unless otherwise noted was completed using the same type of acidic solution.

5.1.3.1 Acid Consumption Tests

In a first series of tests, the acid consumption for the two coal types tested on the bench-scale test system (Hagel B and Harmon lignites) was determined as a function of time in a pH range relevant to the Stage 1 leaching (see Figure 5-1). Results are provided in Figure 5-9.

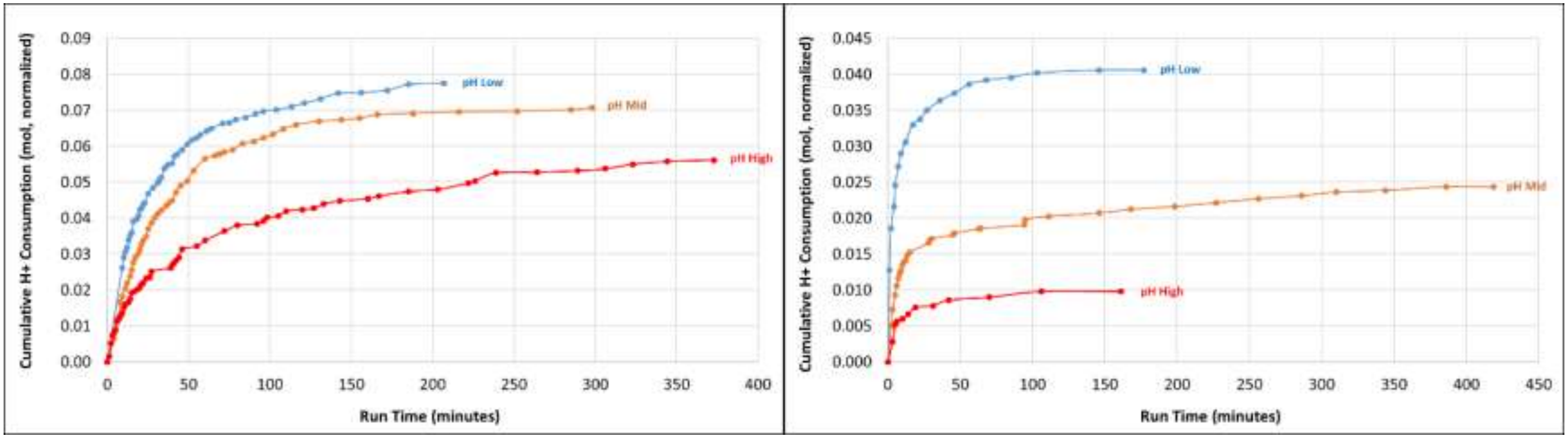


Figure 5-9. *Acid consumption during Stage 1 leaching for the Hagel B (left) and Harmon (right) lignite coals. Low, mid and high pH are the same for each coal type. pH was maintained at a constant value throughout the tests via periodic acid replenishment.*

For both coal types, the acid consumption is initially rapid and then plateaus to zero/low values over time. For the Harmon coal, the acid consumption reached plateau points at a more rapid rate than with the Hagel B feedstock. Additionally, the Harmon coal required considerably less acid per mass than the Hagel B coal. This is consistent with previously reported data that shows that the Harmon coal contains lower concentrations of AAEMs, which are the primary acid consumers under the pH conditions examined.

Of note is the significant increase in acid consumption that occurred at the low pH for the Harmon coal, which was not observed for the Hagel B coal. This suggests that the leaching of the trivalent cations was initiated under lower pH conditions and did not occur at the mid and high pH conditions. These data also point to an equilibrium limitation, rather than a kinetic limitation, in terms of the acid consumption (increase in acid consumption with decrease in equilibrium pH).

A similar set of tests as those summarized by Figure 5-9 were completed under pH conditions relevant for the Stage 2 leaching (See Figure 5-1). However, for these tests, only the Harmon coal was tested. Results are provided in Figure 5-10 for three pH settings (lower pH than those provided in Figure 5-9). The results can be directly compared with Figure 5-9 (right), and clearly show that lower pH (higher acid concentration) results in higher acid consumption. This again points towards equilibrium being the primary driving factor in leachability of inorganic species from the lignite coal, rather than a kinetic-based influence such as mineral dissolution.

As with the Stage 1 leaching results discussed previously, equilibrium leaching was reached within 20 minutes of contact time. The additional acid consumption that occurred during these tests, as compared to the previous Stage 1 leaching tests, may be attributed to the leaching of higher-concentration trivalent elements, such as Al and Fe.

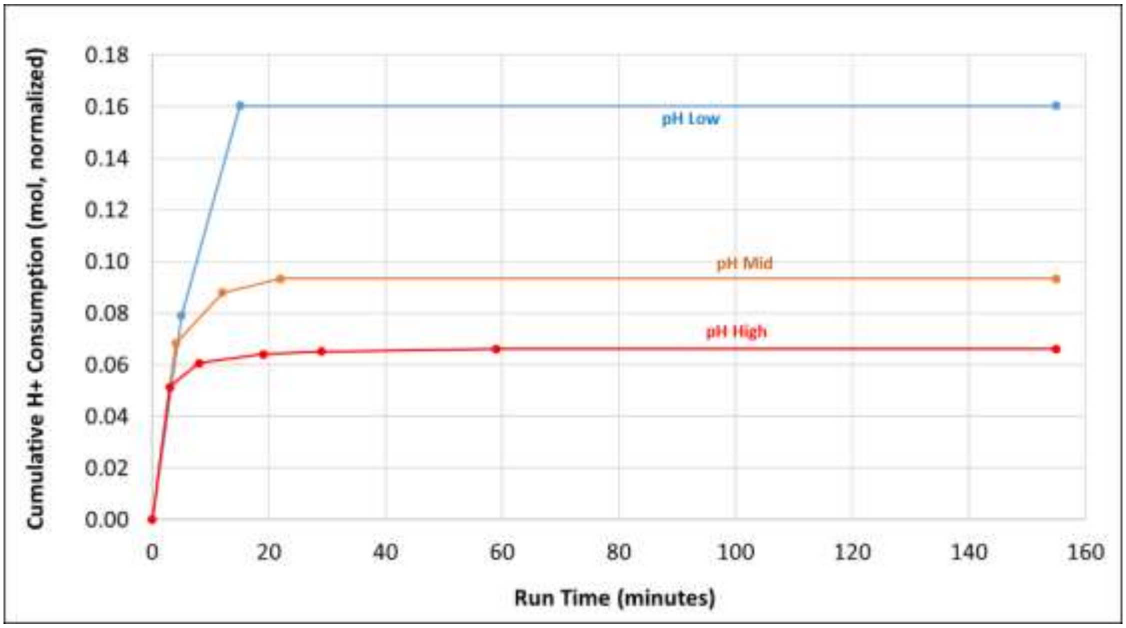


Figure 5-10. *Acid consumption during Stage 2 leaching of the Harmon lignite coal. pH was maintained at a constant value throughout the tests via periodic acid replenishment. Comparison with* Figure 5-9 *(higher pH than in this figure) shows that lower equilibrium pH resulted in higher acid consumption.*

5.1.3.2 Kinetics Tests

While it is fairly clear from the previous data that equilibrium, rather than kinetics, is the limiting factor in leaching efficiency from the lignite, tests were also completed to measure the leaching efficiency of select cations as a function of time to confirm. For these tests, analysis was performed using UND's flame atomic absorption spectrometer (Flame-AAS). Magnesium was used as the analog for all divalent (organically associated) cations, while Al was used as the analog for trivalent cations (REE). This was done for simplicity, as the Flame-AAS is unable to measure the REE directly. Results are provided in Figure 5-11 for the same pH conditions as shown in Figure 5-10 (Stage 2 leaching conditions).

The results in Figure 5-11 confirm the very fast leaching kinetics. Magnesium leaching is complete within about 5 minutes of leaching, while the Al leaching is slightly slower, with complete leaching by about 30-40 minutes. The leaching efficiency (proportional to concentration in mg/L in the liquid phase) of the Al is also more dependent on pH than the Mg under the pH conditions of interest for REE extraction, pointing towards an equilibrium distribution based upon ionic valence.

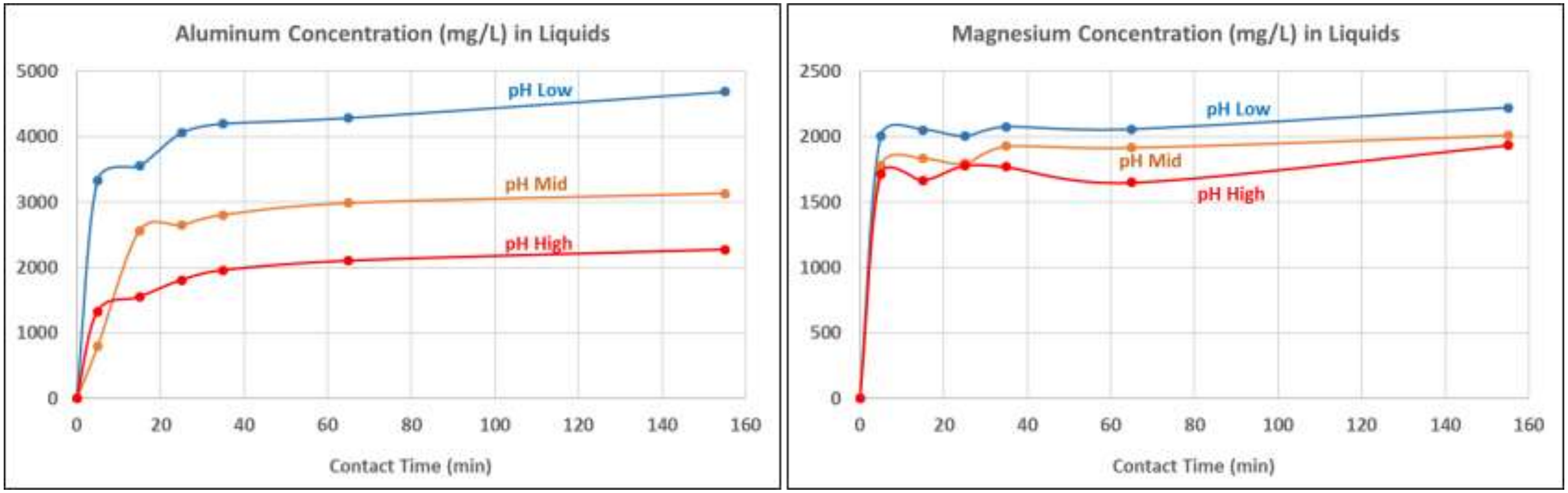


Figure 5-11. *Kinetics of leaching for trivalent cations (Al as REE analog) and divalent cations (Mg as analog) as a function of pH for Stage 2 leaching conditions. pH values are same as used in* Figure 5-10.

5.1.3.3 *Equilibrium Tests*

The leaching efficiency of select cations as a function of pH, over a range covering both Stage 1 and Stage 2 leaching is provided in Figure 5-12. In this figure, Nd represents the lightest molecular weight (MW) REE, Gd represents the middle MW REE, and Er represents the highest MW REE. A selection of impurities of note, including Ca, Na, Mg, Al and Fe, were chosen to determine optimal pH-targets for high extractability of the REE with minimal co-extraction.

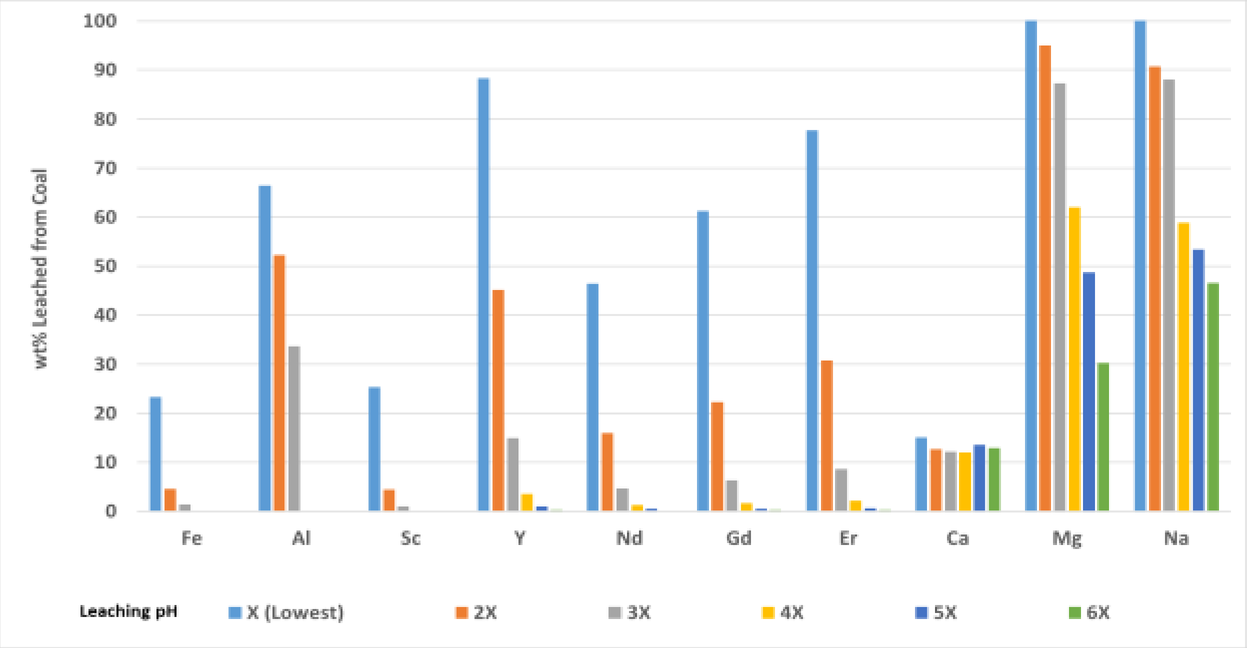


Figure 5-12. *Equilibrium leaching efficiency of select cations under a range of pH consisting of both Stage 1 and Stage 2 leaching conditions. pH shown as multiples of the lowest pH (same as low pH in* Figure 5-10*). The raw coal was the feed for each test. Note: data for Fe, Al and Sc not available for pH 4X, 5X or 6X. However, based on the trend, leaching should be very low or zero for each.*

As shown in Figure 5-12, the leaching efficiency for Mg and Na was high, even at the highest pH tested. Essentially all of the Mg and Na contained in the feed coal was leached at the lowest pH. However, the data shows that there is no clear plateau; leaching efficiency continued to increase with decreasing pH. The REE were found to have similar leaching performance, with the LREE and Sc at a lower extraction than Y or the HREE. Additionally, Al showed similar extraction at the lower pH values, with higher extractability at higher pH. Fe was the lowest extractable element, with less than 5% at all pH values except the lowest.

5.1.3.4 *Summary of Leaching Optimization*

As presented previously in Figure 5-1, the original process utilized two stages of leaching in order to segregate the REEs from the AAEMs. However, these data indicate that efficient segregation is not possible, especially for Ca. Since Ca is the primary competing cation in subsequent leachate processing using oxalic acid precipitation (discussed in next stages of this report), the project team has decided to forego the separate leaching stages, with a one-step leaching approach conducted for all further testing.

Finally, the kinetics of the leaching process are rapid, with 30-40 minutes appearing sufficient to achieve near-complete leaching of trivalent cations for a given pH set point. However, acid replenishment is needed to maintain a constant (desired) pH throughout the duration.

5.1.4 One-Step Leachate Processing Optimization

Once the REE (and other inorganic elements) are leached from the coal into the acidic solution, further processing is required to reject impurities, thus increasing the concentration of REE as well as potentially recovering other valuable products. In this task, two general leachate processing routes have been examined: 1) pH-based precipitation, and 2) oxalic acid precipitation

5.1.4.1 pH-Based Precipitation

Removal of Fe and Al were determined as essential for improving overall process flow, and a method for removal through pH-adjustment from the leachate was identified. A series of tests was completed with two types of base – $Ca(OH)_2$ and NaOH – to identify REE and impurity separation at multiple pH levels. A summary of the results for $Ca(OH)_2$- and for NaOH- based precipitation are presented in Figure 5-13 and Figure 5-14, respectively. The results clearly show that there are significant differences in pH at which each of the elements precipitates. When using $Ca(OH)_2$, there are significant losses of the REE throughout the pH ranges. This is presumably due to encapsulation or surface adsorption on the precipitate that forms. Because of this loss, $Ca(OH)_2$-based precipitation was determined as an uneconomical means to achieve concentration of the REE.

Using NaOH, the majority of Fe precipitates at pH <4, while Al precipitates between pH 4-5. There are differences in the solubility of the LREE vs. HREE. HREE have significant precipitation between pH 4-5, while the LREE have very little. However, the LREE have more significant precipitation with the Fe at pH <4. Sc becomes insoluble between pH 4-5, in the same region as Al. The majority of the REE become insoluble by pH 7. In general, for the NaOH-based precipitation, there is potential to produce two products:

1. High purity Al product (>95wt% oxide basis), with enrichment in Sc and HREE of a pH of ~4-5
2. REE concentrate (~25wt% oxide basis) in a pH range of 5-7.
3. An Fe-rich impurities precipitate is produced in the pH range of <4.

While the NaOH-based precipitation method is able to exceed the programmatic target for REE concentration (2wt% elemental basis), the reagent consumption and associated operating costs for such an approach are significant, and unlikely to be economical. An alternative approach is needed. By using oxalic acid-based precipitation of the REE, neutralization past the Fe-rich impurity window is not needed, and thus has the potential to achieve the high REE concentration while limiting reagent consumption costs.

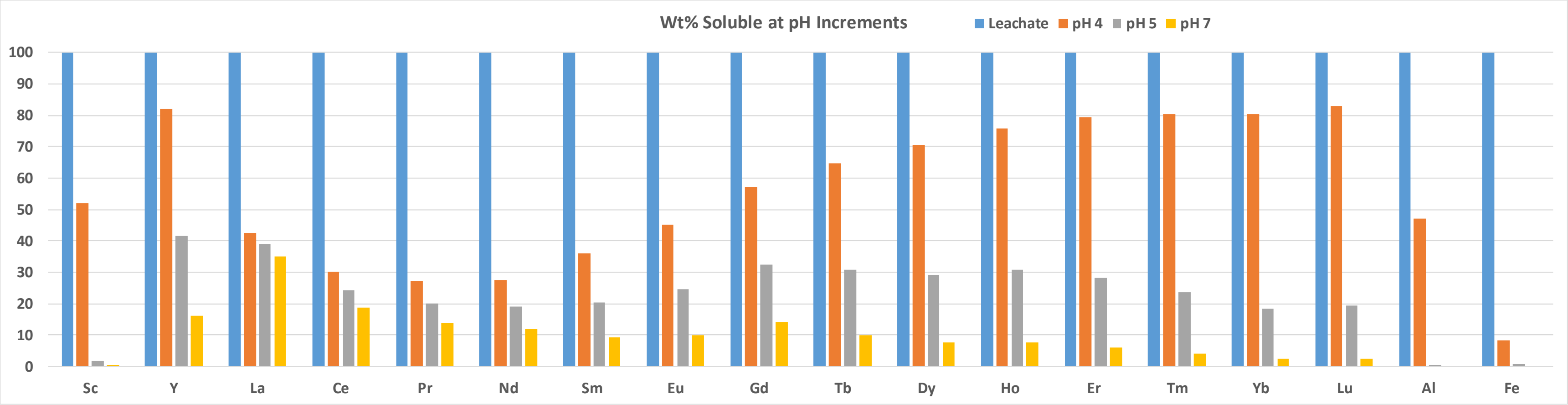


Figure 5-13. *Staged precipitation results when using $Ca(OH)_2$ as the neutralizing agent.*

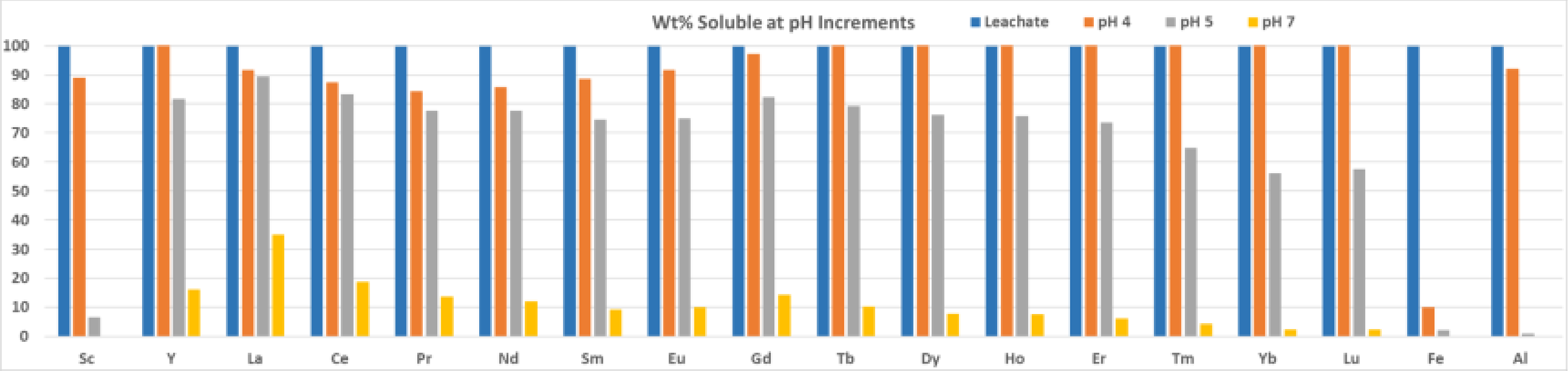


Figure 5-14. *Staged precipitation results when using NaOH as the neutralizing agent.*

5.1.4.2 Oxalic Acid-based REE Precipitation

As discussed in the previous section, the pH-based REE precipitation is unlikely to be economical due to the large amounts of NaOH needed to effect precipitation of the REE in the pH window of 5-7. The oxalic acid precipitation method has potential to provide benefits because it can precipitate the REE at significantly lower pH, thus eliminating the need for complete neutralization of the leachate using expensive base such as NaOH (neutralization of barren solution can be completed using cheaper base).

The general procedure investigated for the oxalic acid precipitation is summarized below:

- Single stage leaching of the lignite to generate an REE-containing leachate
- Partial neutralization of the leachate using NaOH or Na_2CO_3 to pH ~3.5 to generate an Fe-rich impurities precipitate, while leaving the REE and Al soluble
- Add oxalic acid with co-addition of NaOH to precipitate the REEs at pH ~2
- As noted previously, Ca is the primary competing cation. Thus, the precipitate product will contain primarily REE and Ca oxalates

Using the above approach, with NaOH as the neutralization agent, the oxalic acid precipitation produces a solid oxalate product with the cation distribution (roughly equivalent to oxide basis concentrations) shown in Figure 5-15. These data show that Ca is the dominant cation, unsurprising given the large concentration difference in the feedstock. Ca makes up about 87wt% of the cation mass, while the REE make up about 9 wt%. Other cations include Mg, Na, Ge, Ga, Th, and U. Based on Na and Mg-oxalate solubility, these are likely present only if encapsulated or as surface residue. The yield of REE recovered into the oxalate product was essentially 100%, as the REE concentration in the barren solution was undetectable by ICP-MS.

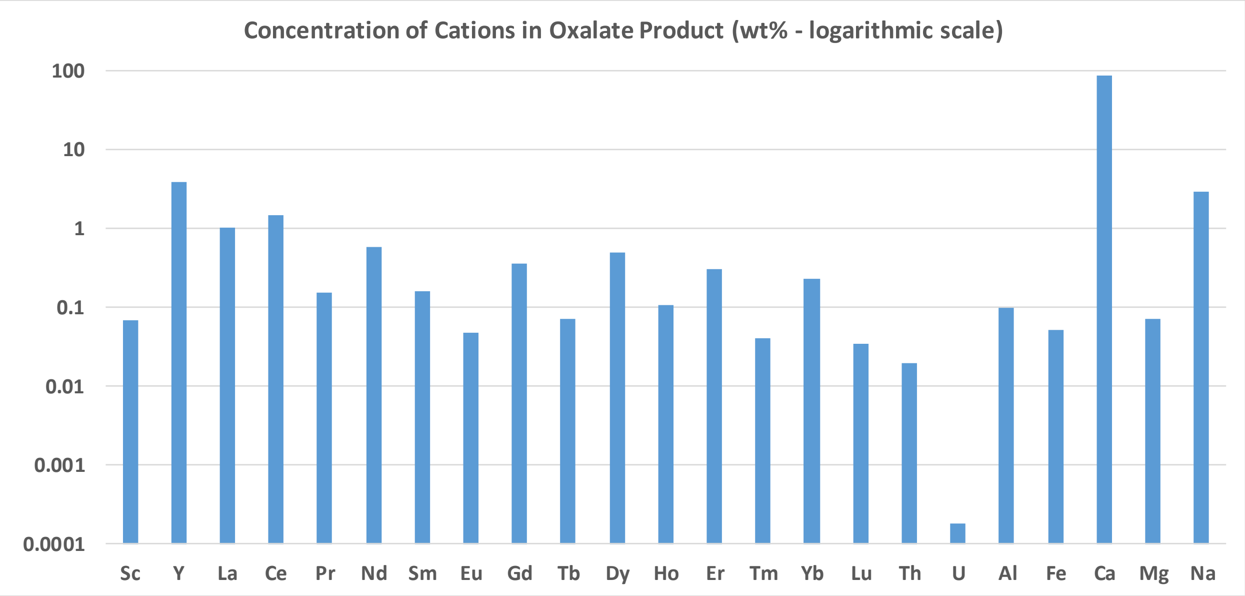


Figure 5-15**.** *Concentration of cations in the oxalate precipitation product produced from Harmon coal when using NaOH as the neutralization reagent. Y-axis on logarithmic scale.*

When estimating reagent consumption and costs associated with the oxalic acid-based precipitation approach, the economics look much more feasible compared to the pH-based precipitation approach. Therefore, an overall process has been established that combines the key steps shown in Figure 5-16.

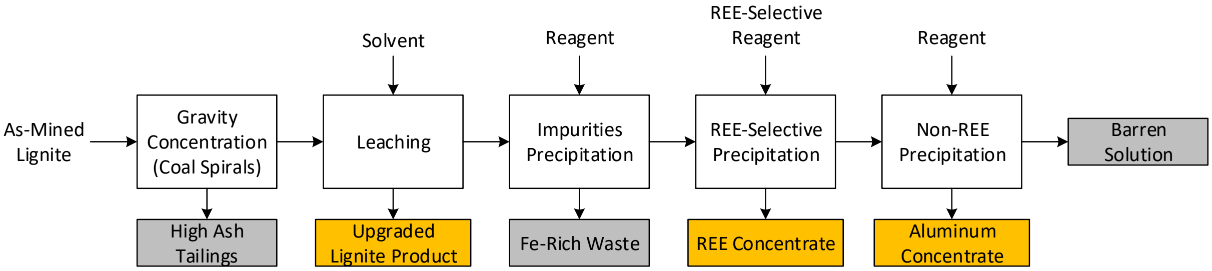


Figure 5-16. *Simplified block flow diagram of the major unit operations for the REE recovery process.*

5.1.4.3 Alternative Base Options for Impurity Removal Stage

After establishing the process shown in Figure 5-16, additional optimization into the downstream PLS liquids processing was conducted. This included the type of base utilized for impurity removal for more cost-effective options, pH values for each base utilized, and concentration of the REE-selective reagent (oxalic acid) required for complete REE recovery. These will each be explained in further detail below.

Using the optimized leaching conditions for the Harmon coal identified, optimization studies for REE recovery and economics were considered for the PLS processes. Initial pricing from vendors demonstrated that NaOH, while a highly effective base, proved to be a major expense for the process. Cheaper alternatives were considered, including $Ca(OH)_2$, $Mg(OH)_2$, and Na_2CO_3. Initial testing of the interactions between impurity precipitation with minimal REE loss, final REE oxalate purity, and total cost of the reagent were considered. Figure 5-17 shows the wt% loss of REE (not desired) to the impurity removal step as a function of base composition.

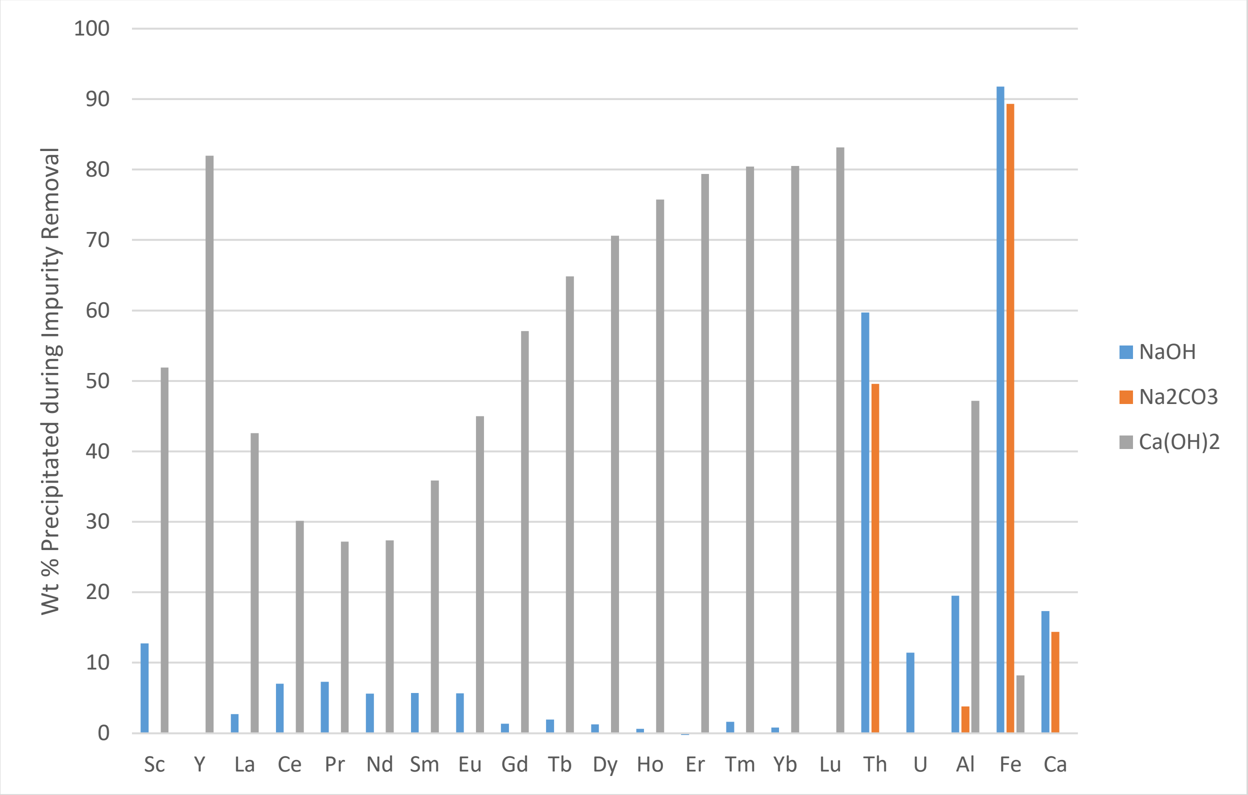


Figure 5-17**.** *REE fractionation into impurity removal stream as a function of base composition. Ca and Th/U not measured for $Ca(OH)_2$ experiments.*

Using the results shown in Figure 5-17, $Ca(OH)_2$ was removed as a possible base due to large losses of REE and Sc in waste streams and ineffective removal of Fe from the PLS. This was unexpected from initial literature searches, but can be explained through REE encapsulation and adsorption onto rapidly precipitating substances in the solution (i.e. gypsum). Use of $Mg(OH)_2$ resulted in a similar trend of less magnitude; however, $Mg(OH)_2$ substantially decreased the purity of REE in the subsequent oxalate precipitation step, and was removed from consideration.

For the two bases remaining (Na_2CO_3 and NaOH), oxalate precipitation tests were conducted to determine possible impacts of basic anions on the final precipitant. Figure 5-18 demonstrates the results of these tests.

From Figure 5-18, the Na_2CO_3 resulted in higher recovery of most REE with the notable exclusion of Sc, while also reducing Th and Ca precipitation into the oxalate product. Additionally, the Sc not precipitated with the oxalate product remains in the solution, and may be extracted with a potential Al product, allowing a more complete recovery. Given the lack of REE loss in the impurity removal step (Figure 5-17), highly promising REE recovery (Figure 5-18), high purity product, and lower cost of Na_2CO_3 as compared with NaOH, the base expected to be of most value to the process is Na_2CO_3.

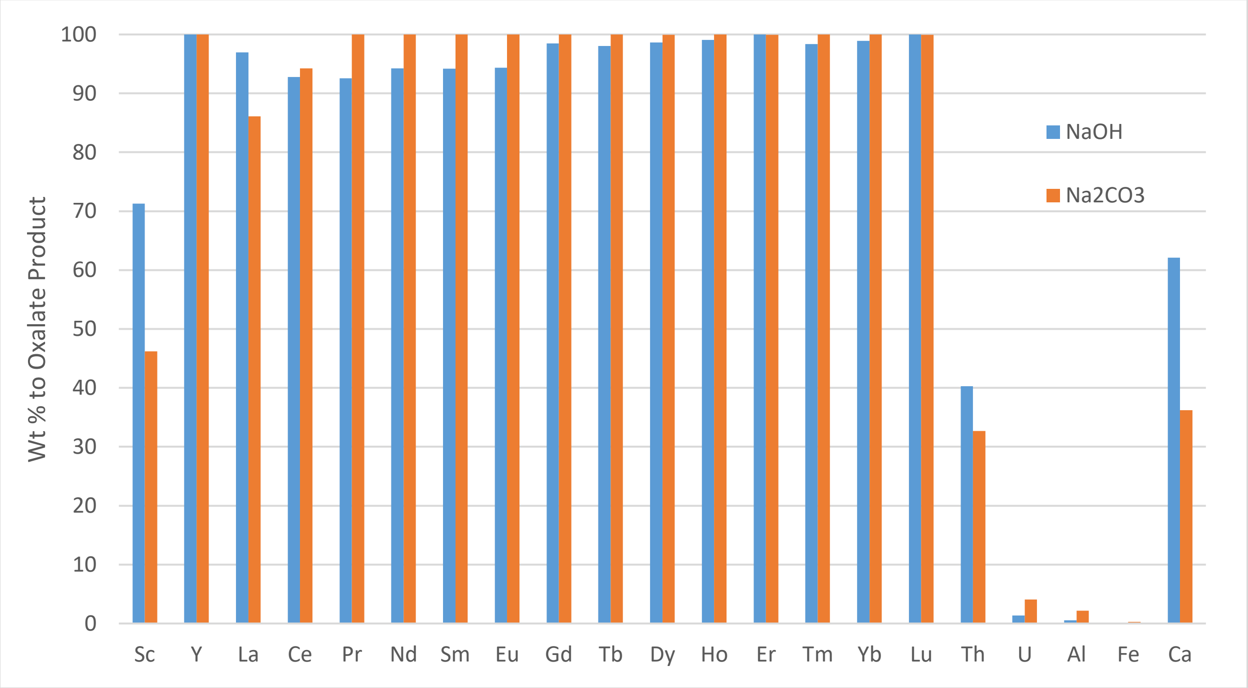


Figure 5-18**.** *REE fractionation by weight percent from the leachate into the oxalate product*

When estimating reagent consumption and costs associated with the oxalic acid-based precipitation approach, the economics look much more feasible compared to a pH-based/staged neutralization precipitation approach. Therefore, an overall process that combines the following key steps has been established.

1. Lignite leaching with an acidic solution of pH low enough to ensure high REE leaching efficiency
2. Partial neutralization of the leachate with Na_2CO_3 to precipitate Fe-rich impurity while leaving the REE and Al in solution
3. Oxalic acid addition with co-addition of Na_2CO_3 to precipitate REE-Ca-rich oxalate at pH ~2
4. Neutralization of barren solution with Na_2CO_3 to precipitate Al-rich product (while leaving alkali and alkaline earth metals in solution)

5. Roasting (~800°C) of the REE-Ca-oxalate precipitate to decompose the oxalate into oxides

5.2 H Bed Parametric Testing

5.2.1 Lab-Scale Testing of As-Received H Bed Lignite

This testing was completed using the as-received H Bed lignite, this was done to reduce the testing load (and therefore reduce the overall mass) of the physically beneficiated lignite. Leaching procedures developed using Harmon coals were applied to the H Bed samples. The procedures involve testing with multiple pH values, and with kinetics testing using Al as an analog for trivalent elements. The results of these leaching tests are shown in Figure 5-19. As determined through economic factors, the second highest acid concentration was selected, due to similar leaching performance as the more concentrated solution with considerably lower costs associated (acid and subsequent base consumption). Additionally, to ensure >95% of equilibrium leaching, an hour of leaching time was given (see Figure 5-20 for kinetics data).

Utilizing the optimized leaching conditions, impurity removal experiments were performed involving addition of the selected base from the optimized Harmon samples to multiple pH values. The results from these experiments are summarized in Figure 5-21. Despite higher Fe removal efficiencies at higher pH values than 3, the lack of all other precipitation of REE and Sc at this pH was favorable.

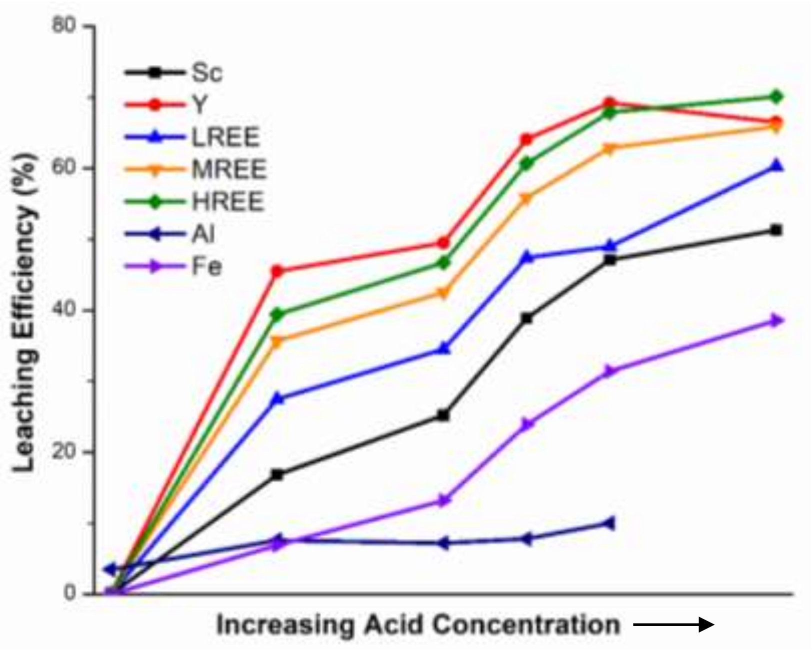


Figure 5-19. *Leaching efficiency vs acid concentration for as-received H Bed lignite.*

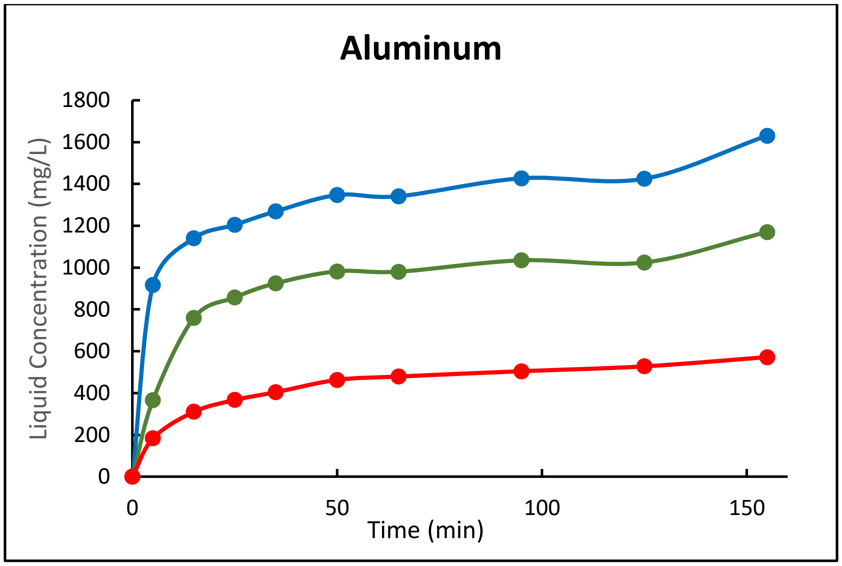


Figure 5-20**.** *Leaching kinetics (through association with Al) in the as-received H Bed lignite.*

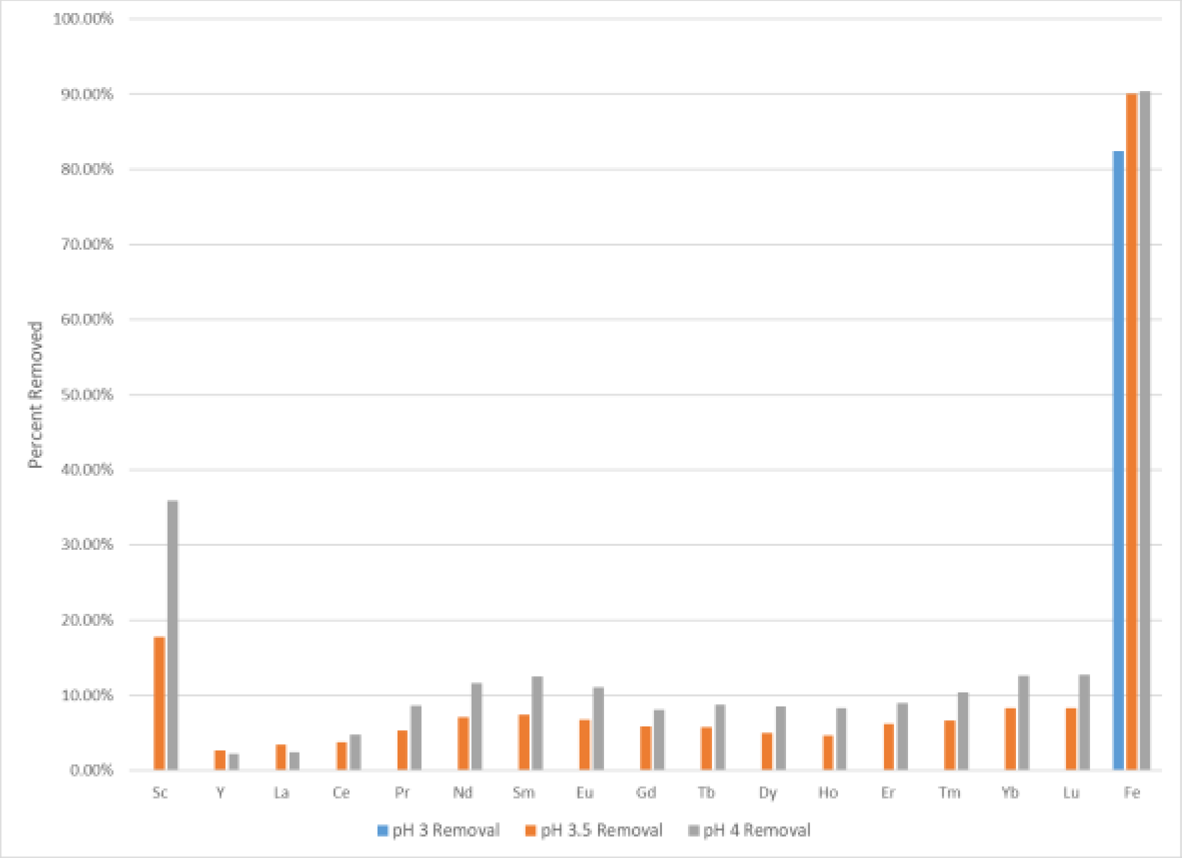


Figure 5-21**.** *Removal of REE, Sc and Fe during base addition impurity removal processes.*

Testing of selective REE precipitation conditions was conducted utilizing varying amounts of oxalic acid to determine optimum points of concentration and yield. At a lower oxalate loading, a substantial purity and yield of REE, particularly MREE including many of the magnetic CREE, were precipitated at >85% and >70%, respectively. The following middle oxalate product was found to precipitate all other REE and Sc with greater than 90% recovery. The results of these findings are found in Figure 5-22.

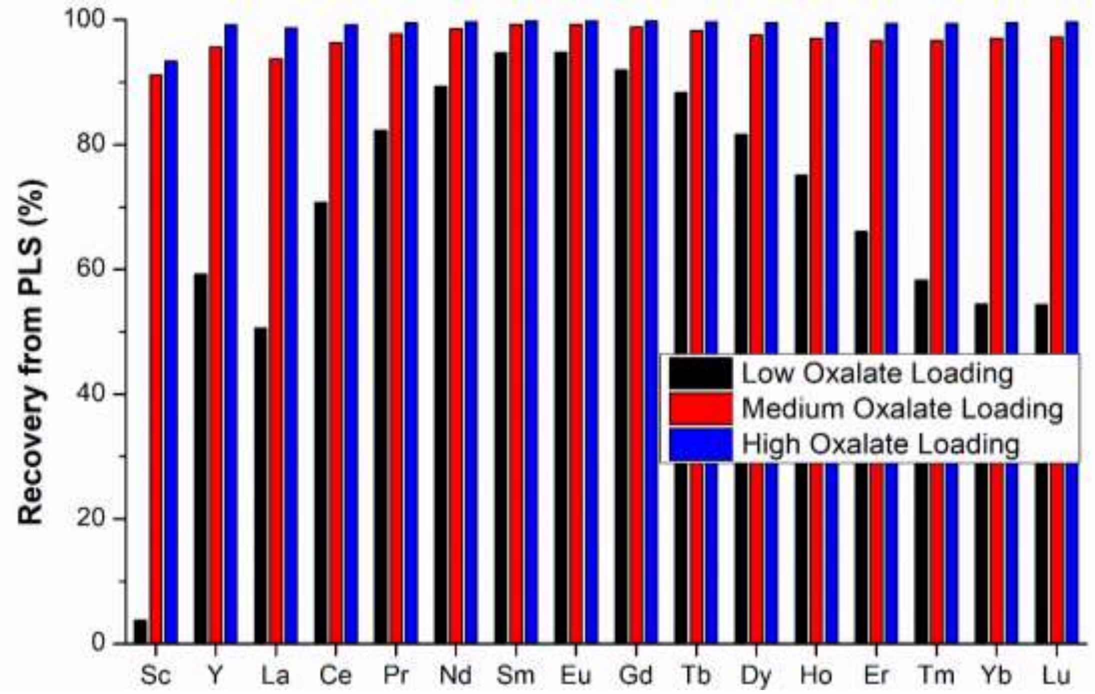


Figure 5-22**.** *Recoveries of REE and Sc from PLS using varying loading of oxalate. Two products are envisioned, a low oxalate loading and medium oxalate loading product.*

5.2.2 H Bed Bench-Scale Parametric Testing

The overall UND process is summarized by the process schematic provided in Figure 5-23. With the completion of physical preparation and separation of the H Bed lignite feedstock utilized as the feedstock for this project, batch-wise parametric testing was conducted on the bench-scale equipment.

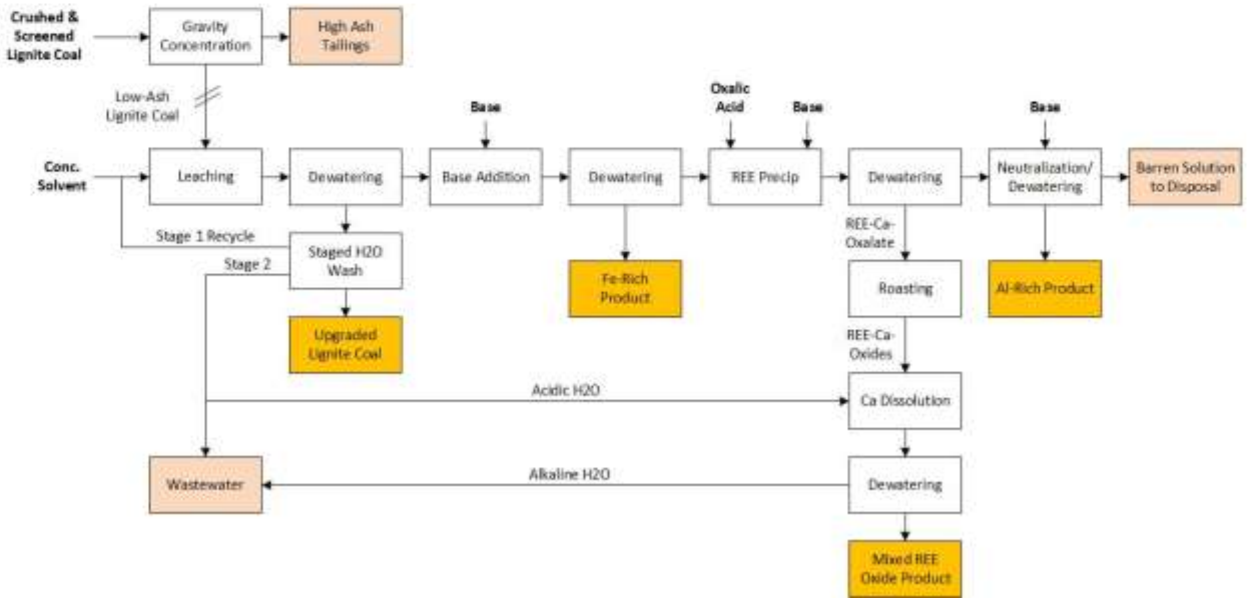


Figure 5-23. *Process schematic of major unit operations for Phase 2 testing.*

5.2.2.1 Leaching

Previous parametric testing of leaching conditions for lignites tested during the project identified pH of the leaching process as a significant variable for selectivity and recovery. Additionally, slurry density and residence time of the leaching unit operation have been identified as key factors for process economics, and have been investigated. Parametric tests on the physically separated H Bed lignite was limited to pH control, as previous tests on Harmon and non-separated H Bed lignites had demonstrated optimal points of operation for residence time and slurry density. Leaching results based upon 3 pH values (low, medium, high) may be found in Figure 5-24.

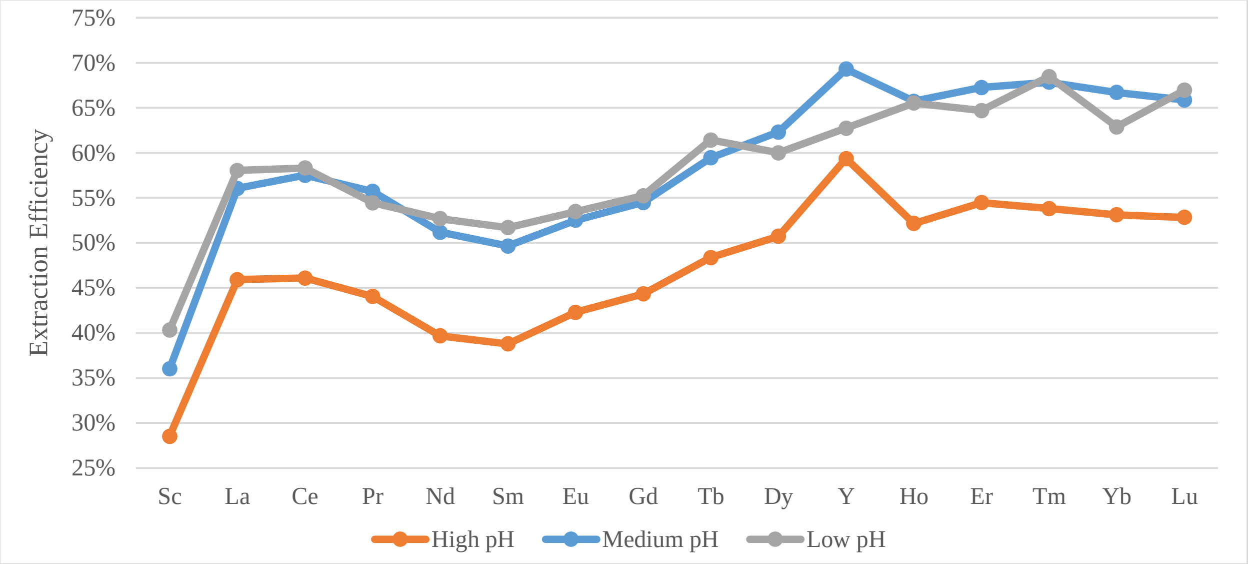


Figure 5-24. *Leaching efficiency of REE vs pH of leachate.*

Control over leaching pH was conducted utilizing continuous concentrated acid addition through a dosing peristaltic pump. Acidic leaching consumes acid over time due to replacement of inorganics on coal functional groups, and must be replaced to maintain a driving force gradient. Based upon the results, the medium pH was chosen due to the lack of significant increase in leaching at the lower pH, but the significant reduction in acid consumption associated with the test (up to 30%).

Leaching residence time has been found to have little effect on leaching of REEs over 45 minutes as demonstrated in previous reports. This time correlates well with the results from the batch leaching tests conducted, with pH stabilization of the solution near the 45-minute mark (Figure 5-25). Slurry density was determined to have a minimal impact on leachability of the REE under controlled pH conditions in previous tests. Additionally, minimized liquid/solid ratios enabled higher concentrations and better performance in downstream leachate processing, so a high solids loading was utilized for operation.

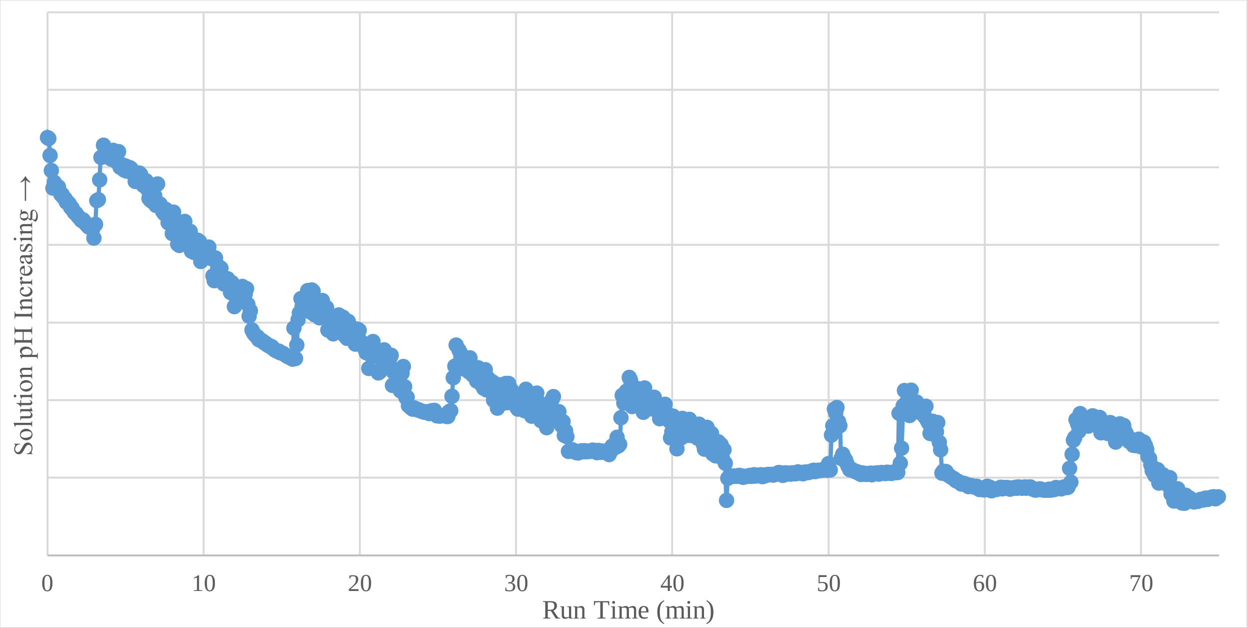


Figure 5-25. *Time of leaching marked by pH change.*

5.2.2.2 Impurity Removal

Impurity removal parametric testing utilized the chosen optimal condition from the leaching parameters, and was conducted utilizing the previously discovered ideal base and at pH values near the optimal point (pH 3.5) expected. These tests were operated similarly to the leaching tests, with continuous base addition as a function of pH control. Residence time of the operation was evaluated using the response of crucial variables, including pH, and was determined to be near 2 hours for 95% of equilibrium removal. Removal efficiencies of each REE, Fe, Th, and U were measured using ICP-MS, with the lower pH value (3) being chosen for minimal REE loss, high Fe rejection, and high NORM rejection while maintaining non-hazardous levels. (Figure 5-26).

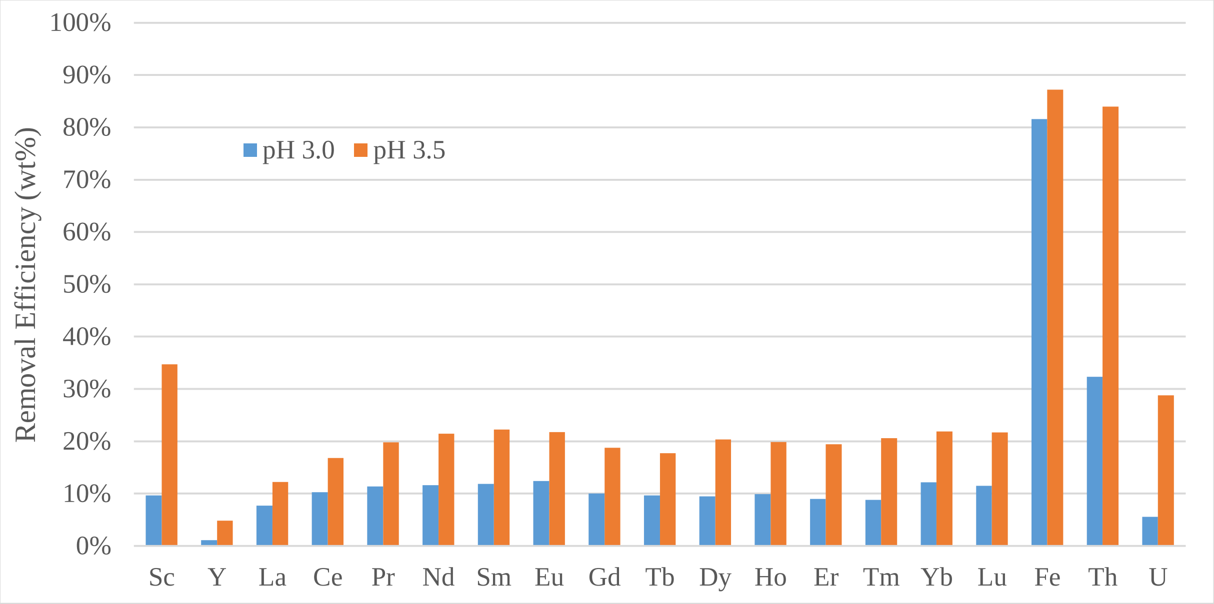


Figure 5-26. *Removal efficiency of deleterious ions from UND leachate.*

From this step, minimal losses (<10%) of the REE were accounted for, while >80% of the Fe removed. This substantially improves economics relating to REE precipitation, primarily due to the minimized complexation penalties incurred with high Fe content. Additionally, Th removal was modest (>30%), while maintaining product levels below hazardous requirements (< 500 ppm as per 10 CFR 40.13(c)). Thorium commonly associates with REE during precipitation processes, and may result in nuisance concentrations from up-cycling. The removal of a portion of this deleterious element in a non-hazardous form (below radioactivity limits) with potential salability as iron ore as a significant advantage.

5.2.2.3 REE Precipitation

Research conducted previously before and during the project indicated that oxalic acid could be a highly cost-effective method of selectively precipitating the REE from the Fe-depleted leachate. Previous work on this project demonstrated the complexation challenges associated with other trivalent ions, namely Fe and Al, which requires additional use of reagent to ensure super-saturation of REE-oxalates and effective precipitation. In addition to complexation challenges, co-precipitation of certain ions, namely Ca, Th, and U, remain a significant challenge involving product purity and regulatory compliance.

Precipitation for REE-oxalates has been determined to occur most effectively at a pH of approximately 2, acting as one control variable. However, significant selectivity of the REE precipitation is achieved through variance of the oxalate loading contained in the solution, with lower oxalate loading, resulting in higher product purities with minimal additional processing costs. However, reduced oxalate loadings reduce the total recovery potential of a number of REE, forcing tradeoffs.

Preliminary parametric testing was conducted during previous quarters to determine, if economically feasible, a single operating parameter for the precipitation to maximize economic potential. However, conduction of this testing pointed towards the development of two REE products, one of significantly higher purity (lower loading), and one with maximal recovery (higher loading).

Bench-scale parametric testing followed this two-product operational scheme, with each pregnant leach solution (PLS) subjected to two oxalate treatments, a lower and higher concentration respectively. The second of the two tests utilized an increased oxalate loading as compared with the first for each treatment. This method enabled a more complete picture of the purity and recovery of each product generated during this process. Recovery and product purity data for each concentration may be found in Table 5-1.

Table 5-1. *Purity of REE products and recovery from the PLS.*

Product Name	Product Purity (Oxide Basis)	Average REE Recovery (from PLS)
Low Ox-1	68.2%	59.2%
High Ox-1	5.63%	33.6%
Low Ox-2	56.4%	73.3%
High Ox-2	1.60%[a]	11.9%

[a] Low purity due to significant recovery of REE into previous product tested.

From this data, we chose products Low-Ox1 and High Ox-2 to maximize purity of valuable REE and total recovery. Significant fractionation of the REE within the two product streams occurred, with expected benefits related to both products in downstream processing (Figure 5-27). Substantial concentration of the magnetic REE (Pr, Nd, Eu, Tb, Dy) over the low value lightest REE (La & Ce) offer substantial value to this product to prospective refining options. Further, the second product, containing high levels of Sc and low levels of other significant value targets allows for rapid and cheap potential separation of Sc, improving value.

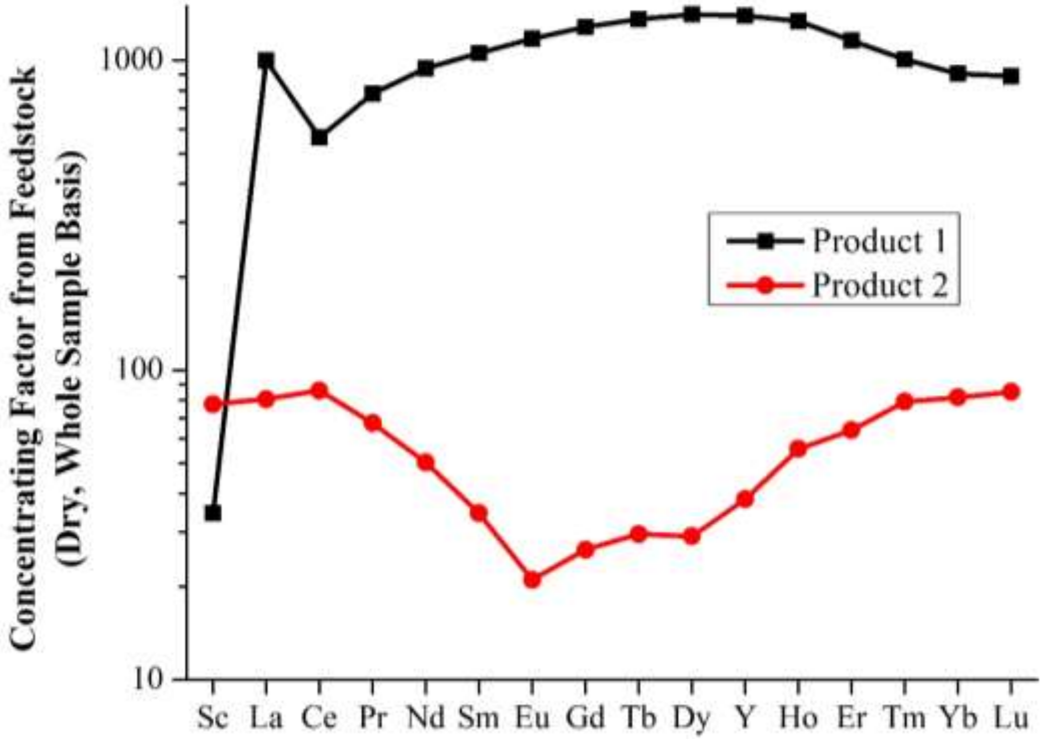


Figure 5-27**.** *Concentrating factors of REE within both products. Note the minimal concentration of Sc into the first product, primarily recovered at higher relative REE purity in second product.*

Thorium and Uranium levels have been tested in each of the REE products generated from the selective precipitation process, with all levels being within minimum requirements stated in 10 CFR 40.13(c), specifically the REE materials and metals clause (<0.25% ThO_2 on whole sample basis) [7]. The reduction in potential hazards associated with production, shipping, and end-life considerations are expected to significantly improve viability of the process.

5.2.2.4 Aluminum Precipitation

The final major unit operation of the process is marked through targeted neutralization of the REE-depleted liquor for a potential high-value Al product generated. This product is considered to be generated at minimal additional processing cost, primarily due to the requirement of neutralization with a base required for wastewater treatment. The Al product generated has been verified to be of at least 60% Al_2O_3 content, with up to 90% Al recovery from the liquor at the highest pH value chosen. Additionally, this product also remains within tolerances for Th and U, saving potential hazardous purification/transportation costs.

6 CONTINUOUS TESTING – PRODUCTION TESTS

This chapter includes details on bench-scale system modifications required for semi-continuous testing operation, and discusses the results of the semi-continuous testing.

6.1 Bench-Scale System Modifications for Continuous Tests

This section details the modifications made to the bench-scale system constructed in Task 3 to prepare for semi-continuous operation for Task 7 tests. A diagram of the semi-continuous system with all modifications can be seen in Figure 6-1. Photographs of the as-installed modified semi-continuous system are provided in Figure 6-2. The previous system design for the bench-scale mixing tanks had each tank operating independently of each other, while this design connected the tanks and allowed for flow between them.

Modifications made to the prior batch-type system included new piping, valves, and pumps to allow for flow between mixing tanks. Two screw feeders were added to the system to allow for continuous feed of solids into Tanks 3 and 4; the first screw feeder being used for oxalic acid addition, and the second used to feed coal and sodium carbonate.

Additionally, the vacuum filtration systems which had previously been used for filtration of solids during earlier testing was removed and replaced by a new filtration system. The modifications to the filtration system included a surge tank and slurry pump which could feed the in-line filters or a filter press. The two in-line filters were setup to allow for continuous operation in a duplex configuration, with one filter being in use while the other was cleaned and prepped for use. The filter press for this system had a capacity of 4 cubic feet, and was sized to hold approximately 100 kg of coal (wet).

Safety precautions including pressure relief valves, automatic shutoffs of valves and mixers, and flow line purging mechanisms have been installed to reduce potential risks. Manual operation of the unit has been limited as much as reasonably possible, with efforts to reduce potential operator/environmental factors incorporating error into results. Additional inputs, outputs, and logic arguments were added to the National Instruments control system, including a number of actuated valves, sensors and pumps. Logic including pressure relief, automatic filter exchange, and valve cycling for slurry discharge were developed and installed.

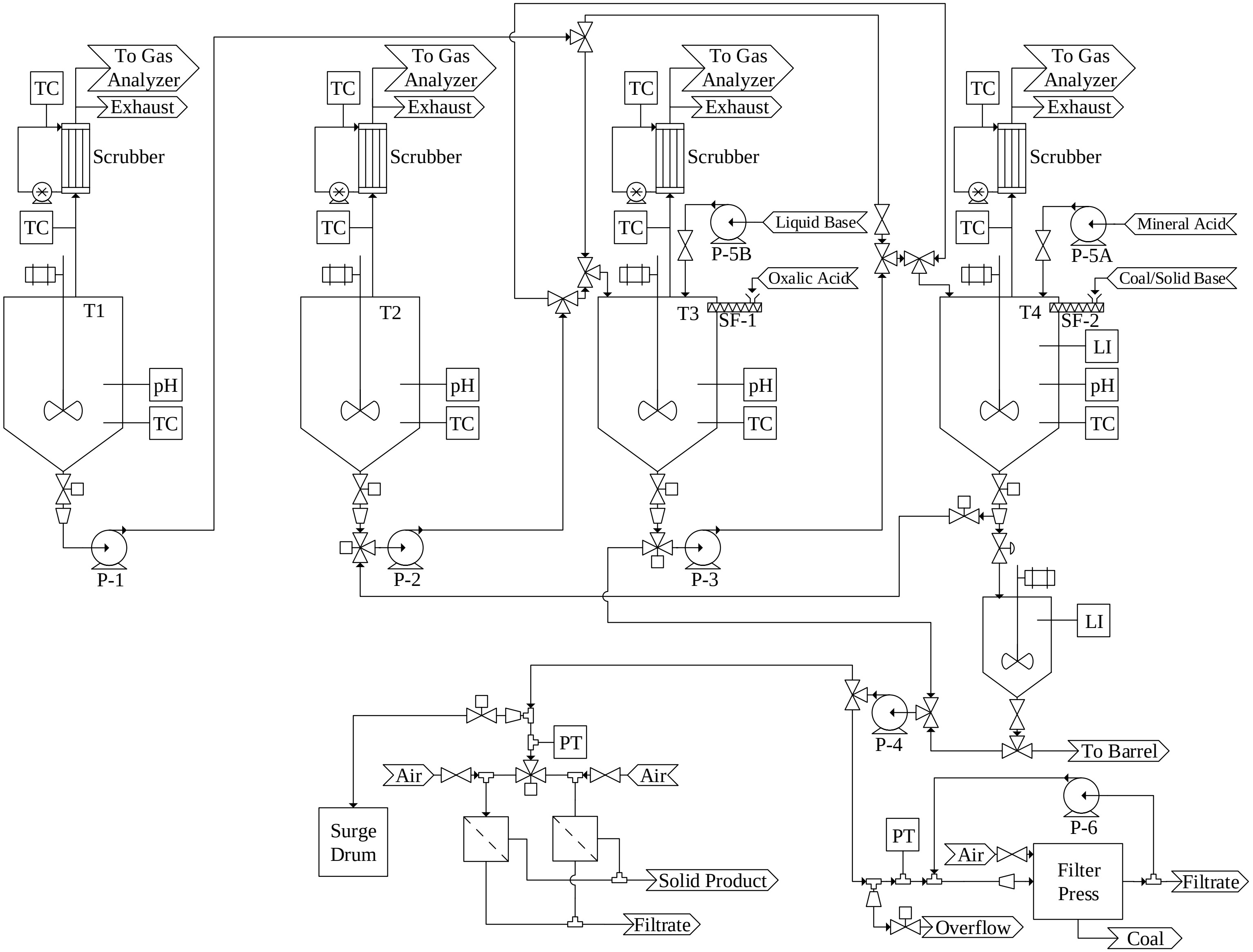


Figure 6-1. *Piping and instrumentation diagram for the as-installed semi-continuous REE extraction system.*

Figure 6-2. *Semi-continuous bench-scale system as installed.*

The pumps and screw feeders were calibrated before operation of the system to determine appropriate flow and feed rates for the process. For completion of shakedown procedures and preparation for operation of the system, an off-spec feedstock (Harmon lignite) was utilized to ensure the process, including all control and monitoring systems, would operate smoothly to limit potential waste of high-REE feedstock. This high-fidelity shakedown test was conducted using the parametric values for the H Bed lignite, and therefore was not representative of possible Harmon lignite results (parameters may vary between coal seams).

During the semi-continuous unit shakedown tests, modifications to expected standard operating procedures were made involving filtration steps. Feeding of the filter press with coal –water slurries at the slurry density planned for leaching developed solid coal plugs in the filter press prior to filling, preventing additional flow. Optimal filter pressure operation requires complete filling of the press to enable the maximum dewatering efficiency. To resolve this problem, filter press discharge liquid was recirculated in-line with the incoming leachate slurry to increase flow velocity and lower apparent slurry density at the press entrance, as shown on the PID diagram (Figure 6-1).

For control of pH-based setpoints with addition of concentrated acids/bases, feedback control loops were established. Control parameters including on/off control and PID controls were utilized for both solid and liquid feeds to the system. Evaluation of time delays associated with mixing, measurement, and dispensing of the pH adjustment chemicals was evaluated and included in control logic.

A total system and process shakedown test using <300 ppm coal gathered previously in the project was used to ensure PID control effectiveness and safe operation of the system under actual conditions (with acids, bases, coal, etc.). This test was completed satisfactorily, with an outline of each unit operation's testing method found below:

1. Leaching – During leaching tests, coal was fed via screwfeeder (SF-2) into the mixing tank (T4) with wash water generated from prior tests (P2) and concentrated mineral acid (P5A). Liquid/solid ratios were controlled through metering of the screwfeeder and pumps, determined through calibration and controlled via 4-20 mA output signals. Acid addition was controlled through a feedback control loop based upon measured pH of the slurry, with immersed pH probe measurement. Cycling valves below the leaching tank fed into a surge tank (T5), also mixed, without pH control, prior to feeding the positive-displacement hose slurry pump (P4), also controllable. In-line between the slurry pump and the filter press, a y-section of pipe was placed to allow liquid recirculation from the cleaned filter press discharge and the filter press inlet (from P6). Continuous flows into and out of equipment continued until filter press pressure met requirements, at which point flows were stopped. Leachate was cleaned

through recirculation through the dense cake, and liquids were removed through air blowdown of the press. Leachate for recirculation (35 gallons) was set aside for the next leaching test, with multiple leaching tests performed each week to generate sufficient liquid volume for downstream applications.

2. Impurity Removal – Cleaned leachate combined from the multiple leaching tests was continuously pumped into and out of a mixing tank (T4) at low mixing speeds, where continuous, controlled addition of the solid base was conducted through PID control over a screwfeeder (SF-2). Solids developed during this process were challenging to filter, with gravity settling resulting in an effective dewatering mechanism. The slurry produced from this process was allowed to settle in a barrel for some time, before the clean liquid on the top was pumped through pressure-filters for polishing.
3. REE Precipitation – The cleaned, filtered liquid following the impurity removal step was fed into a mixing tank and combined with set flowrates of oxalic acid (SF-1), depending on the concentration of interest. The oxalate screwfeeder was set at the beginning of the test and controlled as needed through on/off control, depending on pump variability. The mixture was allowed to mix for a short time, prior to being pumped into another tank for pH adjustment. The secondary tank utilized the same base screwfeeder/PID controller setup, albeit with alternate PID tuning parameters and setpoint. Solids generated during this were filtered on pressure filters pumped through the slurry pump (for ease of plumbing). Following completion of primary REE precipitation, secondary product precipitation occurred via the same metric, at different oxalic acid concentrations.
4. Aluminum Recovery – Filtered, REE-depleted liquids were pumped into the tank with the solid base equipment setup (screwfeeder/PID), and flow was pH controlled to setpoints. Resultant mixtures were pumped into a separate tank, where liquid base was used to complete the neutralization for product generation. Similar to the impurity removal, Al solids were also allowed to settle in barrels over time, with the thick slurries recovered from the bottom filtered for product quantification.

Overall, the system performed as expected with the necessary changes to filtration operation determined through preliminary system shakedown. Control loops for pH control of unit operations were developed and executed satisfactorily with the low-REE feedstock.

6.2 Semi-Continuous Testing Results

This section contains details the results of the testing completed on the semi-continuous bench-scale testing completed using the H Bed coal. Chemical usage through each week of testing is shown in Table 6-1.

Table 6-1**.** *Chemical consumption by week during semi-continuous testing.*

Chemical	**Week 1**	**Week 2**	**Week 3**	**Week 4**
Conc. Leaching Acid	70.7 g/kg coal	63.1 g/kg coal	54.6 g/kg coal	72.1 g/kg coal
Sodium Carbonate	70.5 g/L solution	66.1 g/L solution	66.4 g/L solution	75.9 g/L solution
Sodium Hydroxide	9.5 g/L solution	13.2 g/L solution	11.7 g/L solution	10.6 g/L solution
Oxalic Acid	44.2 g/L solution	40.1 g/L solution	36.3 g/L solution	42.5 g/L solution

6.2.1 Leaching

Production testing began with semi-batch leachate generation tests required for recirculation for optimal filter press operation. Each leachate generation "batch" was performed on a shortened filter press (reduced number of filter plates) to enable adequate volume for recirculating leachate generated at that time while filling the press to design pressures. A number of these tests were required to generate 35 gallons (total liquid volume of the filter press) of the cleaned leachate for semi-continuous testing of the process.

Semi-continuous test "batches" were operated over the course of a week, and involved the use of ~200 kg of coal each week. During leaching tests, coal feed rates of 25 kg/hr were used, with some variation due to moisture changes in the coal. The coal feed rate was observed to fluctuate as the moisture content of the coal changed, with high moisture coals having lower feed rates than the high moisture coals (Figure 6-3). In Figure 6-3d the initial coal being fed had a high moisture content, then at about minute 140, a lower moisture content coal was added to the screwfeeder, and significant change in feed rate was observed.

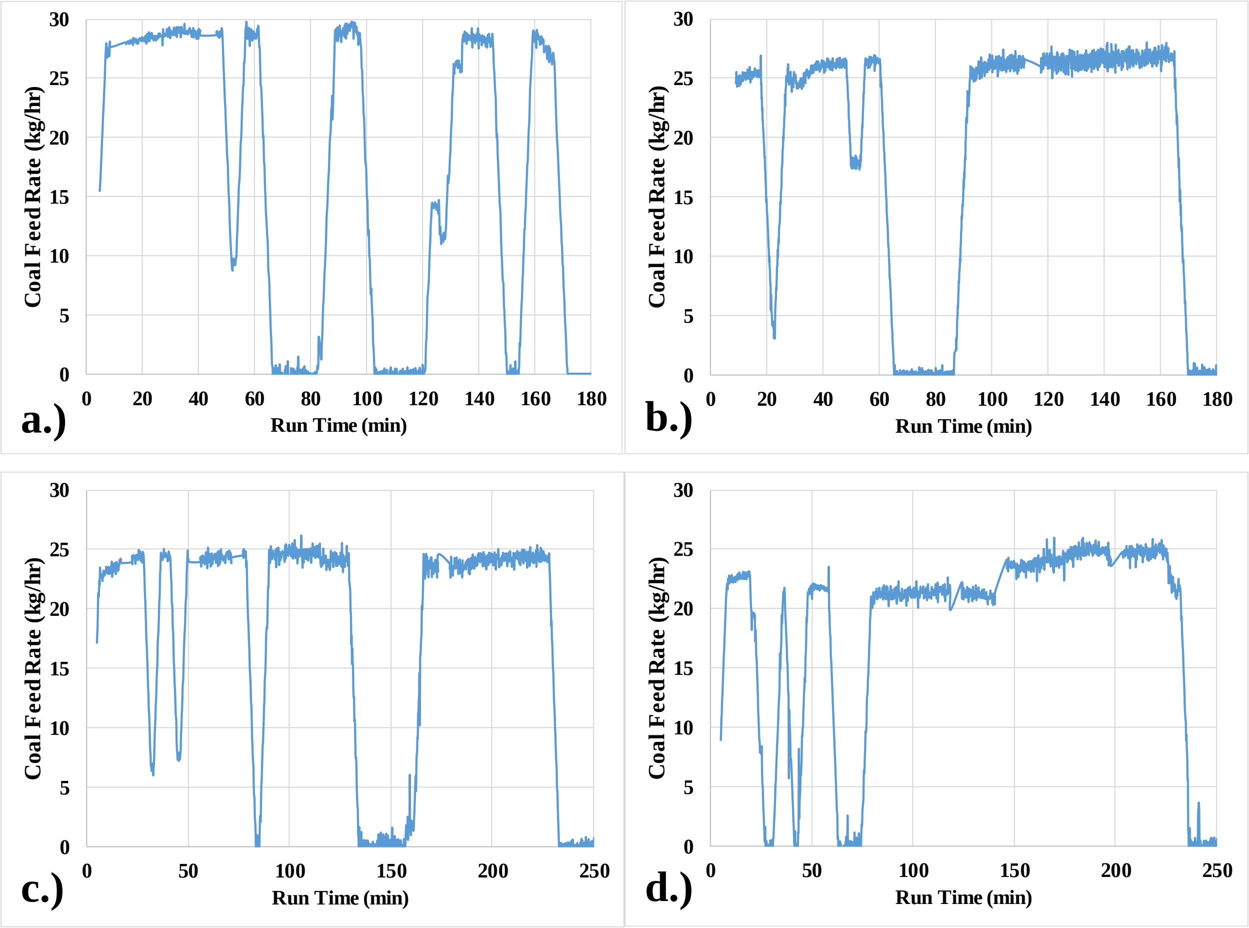


Figure 6-3. *Coal feed rates during various leaching tests. a.) Week 4, Leaching Test 2, coal moisture = 29.4%; b.) Week 2, Leaching Test 2, coal moisture = 31.1%; c.) Week 3, Leaching Test 2, coal moisture = 32.4%; d.) Week 2, Leaching Test 1, coal moisture 1 = 34.1%, coal moisture 2 = 31.8%.*

Acid feed rate controls operated as expected, and the pump turned on and off as necessary to maintain the desired pH during leaching. Figure 6-4 shows the pH maintaining the desired value while the feed rate of acid is varied to stabilize.

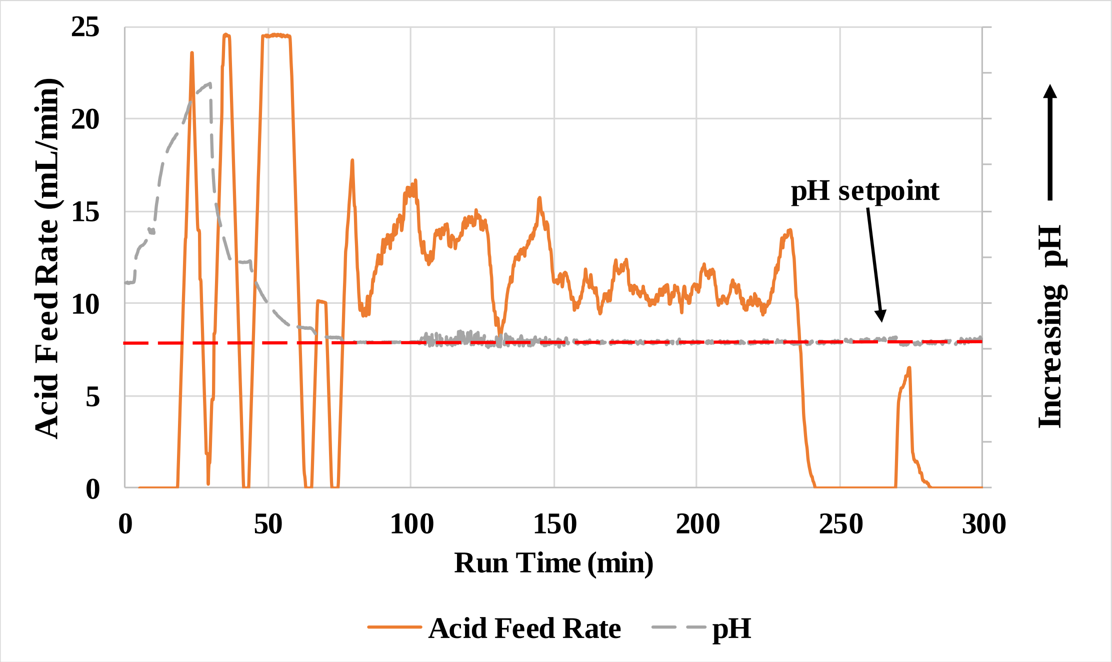


Figure 6-4. *Acid feed rate and pH reading during leaching.*

Increasing concentrations of specific ions in the coal water washing stream were seen in Weeks 1 through 3 are graphed in Figure 6-5 as a function of time, demonstrating this up-cycling hypothesis (logarithmic axis). Concentrations in Week 4 decreased slightly, however this is likely due to a lower leaching efficiency of REE from the coal. For Weeks 1-3, REE and other basic, tri and divalent metals (Co, Ga) show increasing concentrations with the recycle stream, but do not concentrate higher valence materials, including Th and U. This is likely explained through the reaching of a solution equilibrium at the pH levels of interest, allowing recapture of the tetravalent ions into the organic matrix. Furthermore, this equilibrium point of tetravalent materials including the deleterious Th and U, while continuing increases in REE concentration, point to a still unsteadied solution profile, with likely higher REE extraction expected during continued testing. Because of the significant addition of a recycle stream (the wash water step), weekly reductions in acid consumption and overall REE extraction rates were noted (Figure 6-6 and Table 6-1).

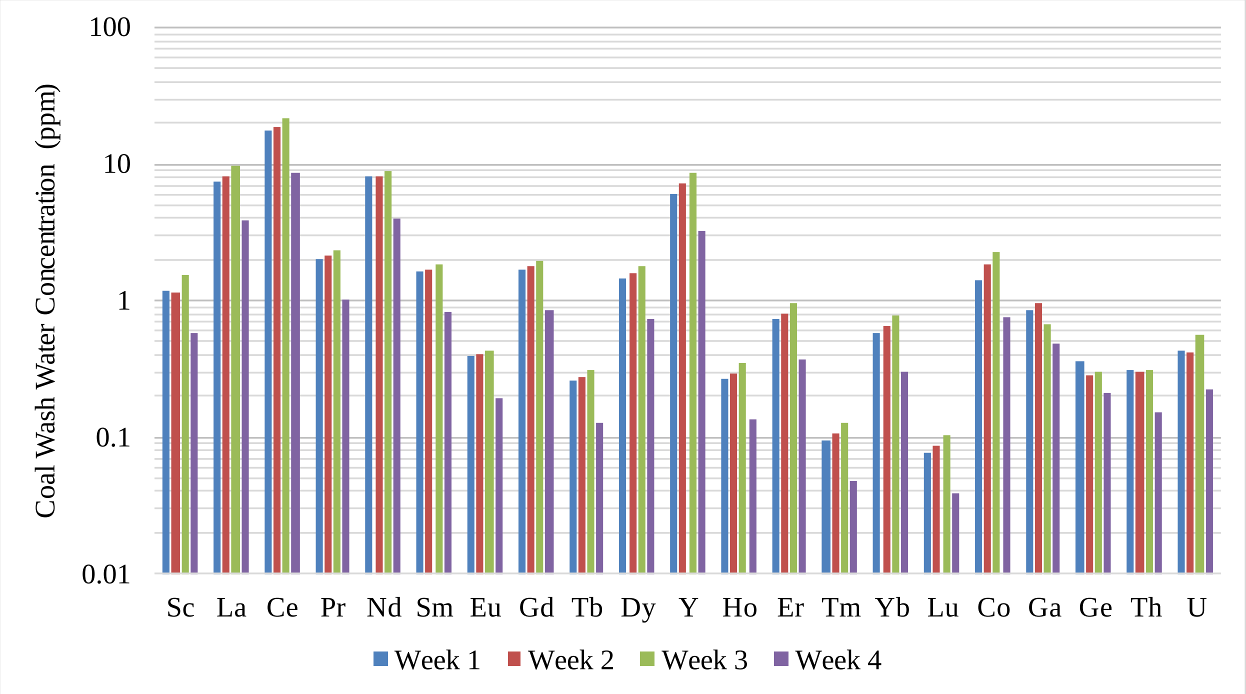


Figure 6-5. *Concentrations of selected ions within the recycling coal water washing liquids.*

The addition of a second coal water wash step in Week 4 (Figure 6-6 – Week 4-Test 2) recovered 5% more REE from the coal compared to a single water wash step (Figure 6-6 – Week 4-Test 1) by exchanging the pore water remaining. Future testing will utilize this second wash to increase recoveries.

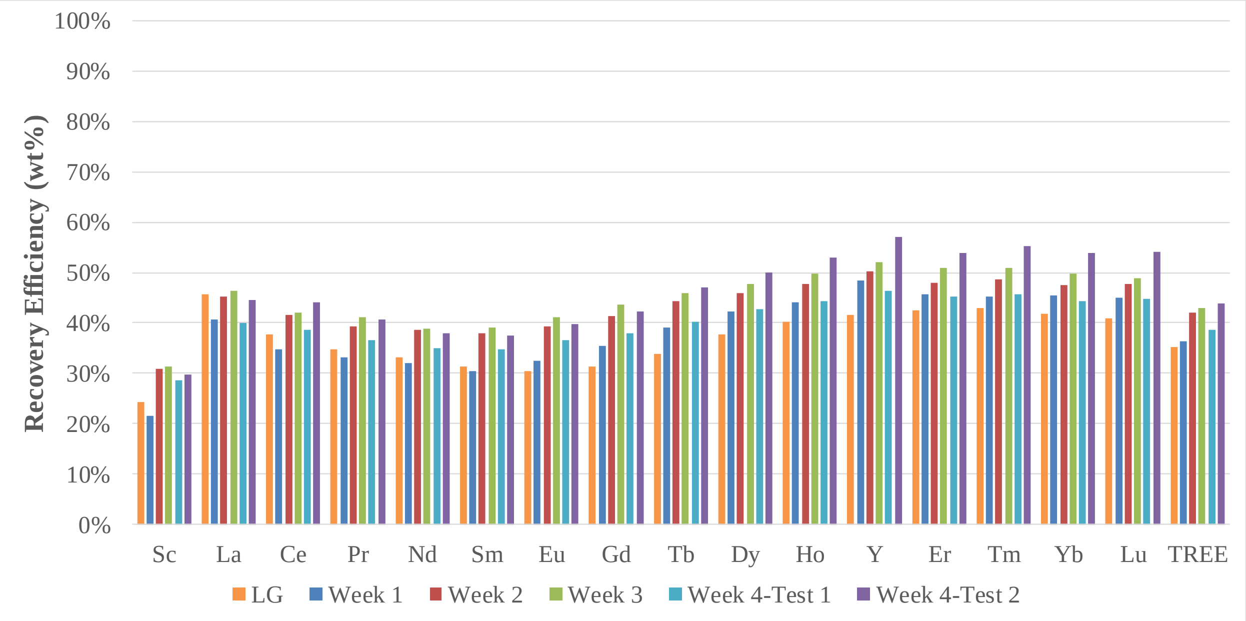


Figure 6-6. *REE and CM leaching efficiency by element, week.*

6.2.2 Impurity Removal

The control scheme used for sodium carbonate addition controlled the feed rate to maintain the desired pH throughout the test (Figure 6-7). Extractions of over 70% of iron were achieved for Weeks 1, 2, and 4 (Figure 6-8). However, Week 3 had only 60% extraction of iron and approximately 15% loss of total REE. The poor performance in Week 3 is the result of equipment issues, with the control valve under the tank malfunctioning, which required manual control of the valve and a residence time which was 50% shorter than the desired residence time. The shorter residence time did not give sufficient time for the solution to reach equilibrium, resulting in the losses of REE and lower extraction of iron observed in Week 3. The other weeks of testing all had <5% loss of REE.

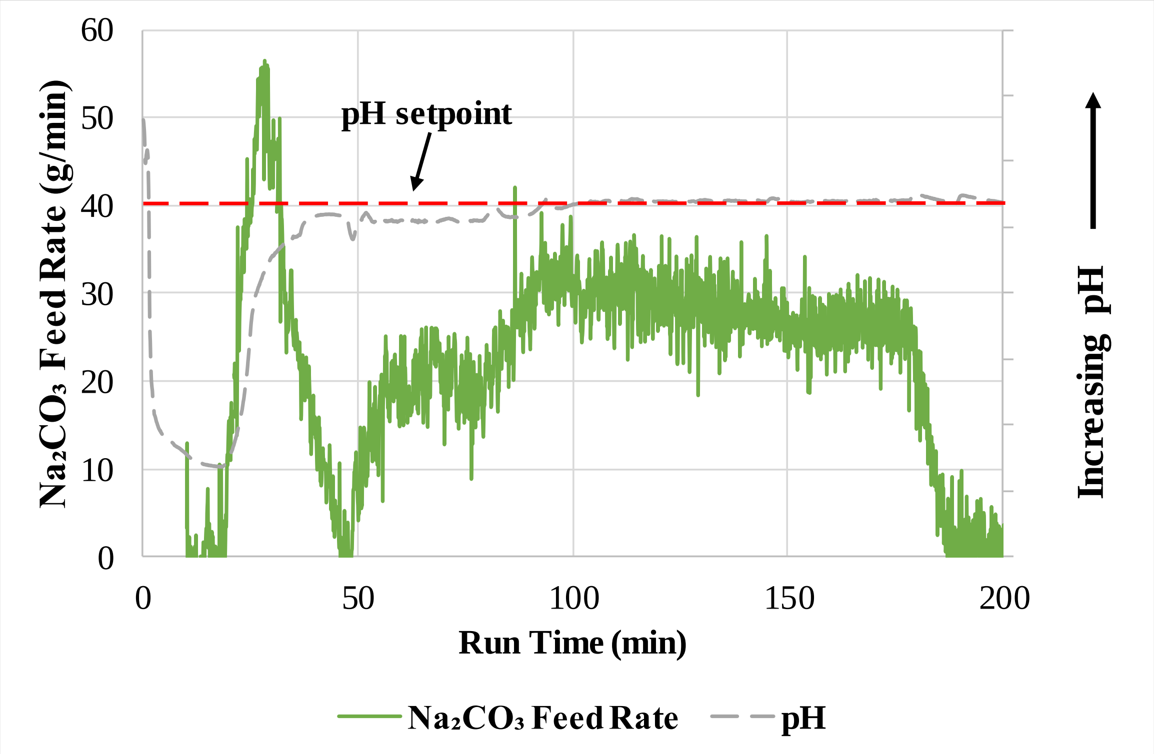


Figure 6-7. *Cumulative feed of sodium carbonate and pH reading during impurity removal.*

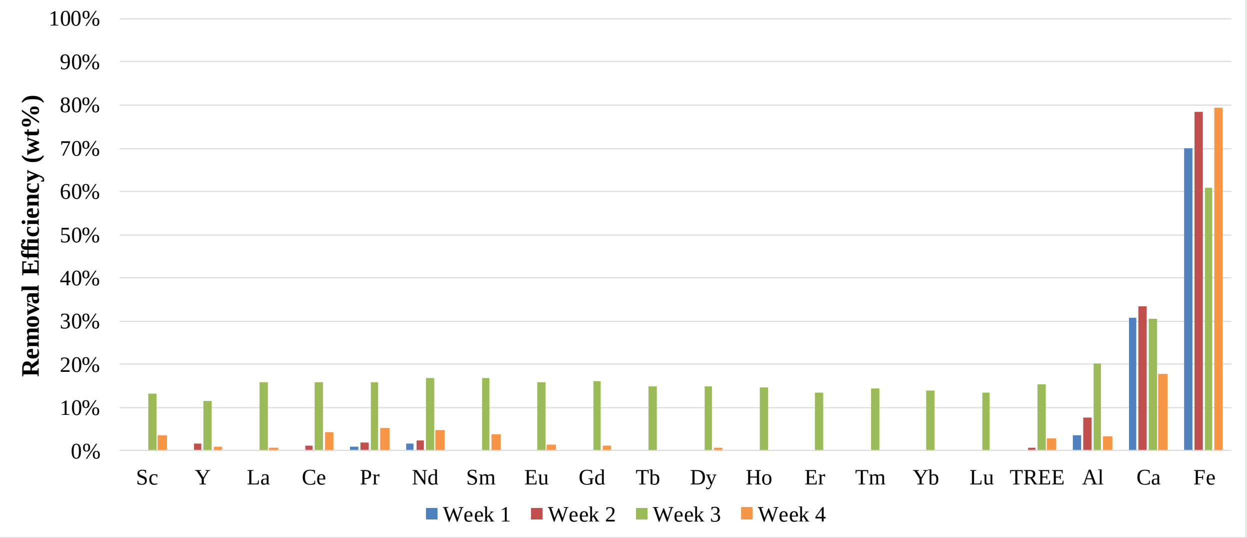


Figure 6-8**.** *Extraction of selected elements during impurity removal.*

6.2.3 REE Precipitation

Preliminary analysis of the products generated during continuous testing to this point has shown lower REE concentrations in the high-purity concentrate than expected (~54% rather than ~65%, Table 6-2.) This reduction was determined to be the result of additional mineral formation through the process of filtration, and can be engineered against in further tests. Declining oxalic acid use in Weeks 1 through 3 is due to incorrect pump calibration, with Week 3 reaching the desired loading of the material (Table 6-1). The determined system challenge and the deviation from previous analysis are as follows:

- Oxalic acid concentrations in Weeks 1-2 were higher than anticipated due to inaccurate calibrations of pumps. This was the result of calibration without full pressure drop evaluations taken into consideration, resulting in slower liquid flows than expected.
- Filtration occurred using pressure filtration through a filter cloth, rather than vacuum as previously conducted. When reaching critical pressures for the filters, a filter exchange was made and air purged through the remaining lines to dry the cake.
- Concentrations of REE and other co-precipitants and complexing agents for oxalic acid increased from week-to-week, resulting in potential changes in expected concentrations needed for effective separation.

Table 6-2**.** *Preliminary elemental analysis of the REE concentrated developed during weeks 1-3 of semi-continuous testing (oxide basis).*

Sample	Total REE	Critical REE	NORM (Th + U)
Week 1 HPC[1]	40.3%	16.0%	0.06%
Week 1 LPC[2]	3.5%	1.4%	0.04%
Week 2 HPC	32.3%	13.1%	0.11%
Week 2 LPC	4.1%	1.7%	0.07%
Week 3 HPC	27.0%	11.5%	0.11%
Week 3 LPC	8.6%	3.3%	0.04%
Week 4 HPC	54.4%	26.7%	0.26%
Wek 4 LPC	7.5%	2.9%	0.07%

[1] *HPC – High Purity Concentrate*

[2] *LPC – Low Purity Concentrate*

The mineral deposit found with the REE concentrates was is likely the result of the air purging without prior cake washing with DI water. Residual liquids were dried onto the cake, and as a result any dissolved solids from the liquid are deposited onto the collected concentrate. This mineral deposit was most pronounced on samples with the smallest filter cake (largest liquid/solid ratio remaining in the line up to the filter, most pronounced on Weeks 2 and 3, where mass recovered from the filters was reduced due to more controlled addition of precipitant). Improved filtration schemes, including immediate cake washing, are planned for further activities and will be incorporated into technology scale-up. Removing this mineral impurity prior to filtering and drying of the concentrate is expected to return the concentration of REE in the concentrate to levels seen in previous tests.

The NORM concentration in the Week 4 HPC solid (Table 6-2) was higher than previous samples and is likely the result of the lower leaching pH used in Week 4, which extracted a higher percentage of NORM from the coal than previous weeks. This concentration of NORM changes processes for handling of the solid, and future leaching will not be conducted at the lower pH to keep the NORM concentration low.

During the REE precipitation testing, a control loop was employed to maintain the pH for precipitation of REE through control of the feed rate of sodium carbonate. The control loop was able to successfully maintain the desired pH as shown in Figure 6-9.

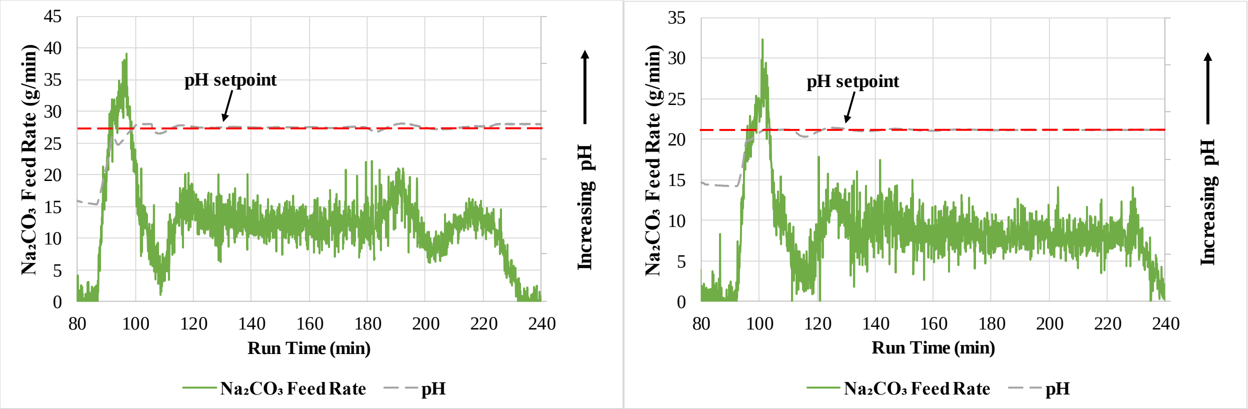


Figure 6-9. *Cumulative feed of sodium carbonate and pH reading during primary REE product precipitation (left) and secondary REE product precipitation (right).*

6.2.4 Aluminum Precipitation

The final major unit operation of the process is marked through targeted neutralization of the REE-depleted liquor for a potential high-value Al product generated. Extraction of over 70% was achieved in Weeks 2 and 3, while Week 1 and 4 extracted less with only 40% and 62% extracted respectively. Additionally, this product also remains within tolerances for Th and U, saving potential hazardous purification/transportation costs.

Maintenance of the desired pH values during testing was conducted through a control loop which varied the feeds of sodium carbonate and sodium hydroxide. The feed rates and pH values are shown in Figure 6-10.

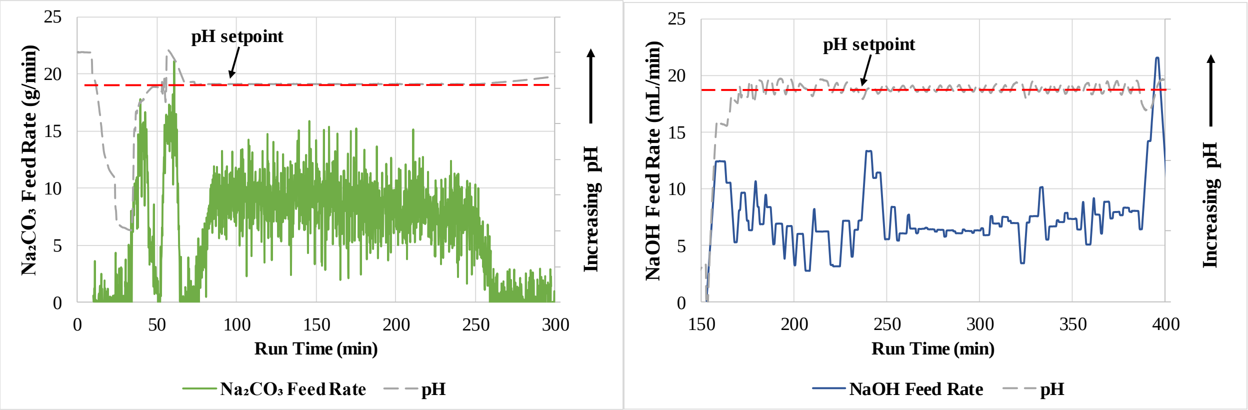


Figure 6-10. *Cumulative feed of reagents during aluminum precipitation for sodium carbonate (left) and sodium hydroxide (right).*

7 SUMMARY OF PHASE 2 TESTING REPORT AND TECHNICAL AND ECONOMIC ANALYSIS REPORT

This chapter contains the summaries of the Phase 2 Testing Report and the Technical and Economic Analysis Report. Additional details for each of these reports can be found in Appendix B and Appendix C respectively.

7.1 Phase 2 Testing Report

The Phase 2 testing plan was developed based on the results of testing completed in Phase 1, which indicated an organic association of REE in North Dakota lignite. Additionally, in Phase 1 extraction of REE from lignite was achieved with a simple and environmentally benign process, which utilized dilute mineral acids. Based on conclusions made from Phase 1 testing results, Phase 2 testing was accomplished in two stages, 1) parametric evaluation of each of the process unit operations using batch tests, and 2) processing approximately 1000 kg of lignite coal under optimized conditions in continuous flow operation. The parametric evaluations were conducted at both the laboratory and bench-scale, with the semi-continuous testing conducted solely at the bench-scale utilizing equipment installed in Tasks 3 and 6.

As part of the testing completed in Phase 2, physical concentration methods utilizing float-sink density separations were employed on a sample collected by the North Dakota Geological Survey from an outcrop of Harmon lignite to determine the potential benefit to the process economics. Float/sink analysis was conducted on multiple size fractions (4x20 US Mesh, 20x40, and 40x60), and REE concentration was measured for each fraction (Figure 7-1). As shown in Figure 7-1, REE concentrations show a marked affinity towards the organic-based fractions on a whole coal basis. The organic association of REE in lignite enables coal cleaning technologies to simultaneously improve REE concentrations and improve value of the resultant coal.

By separating the high density, high ash material from the lighter specific gravity fractions, significant concentration of REE may be achieved. By selecting a cutpoint of 1.7 specific gravity for the Harmon coal (Figure 7-2), 80% of the REE within the overall coal was retained, a coal feedstock > 300 ppm was achieved, and the ash content of the leached coal was reduced by 12 percentage points. This was chosen to maximize potential cost-savings for REE processing, while retaining a sizable fraction of the coal (70%) for recovery of mining costs (through upgraded product sale). Additionally, the removal of dilute-acid-soluble mineral matter in the high specific gravity fractions improved potential liquid-phase concentrations of REE vs other contaminants, decreasing concentration/purification costs.

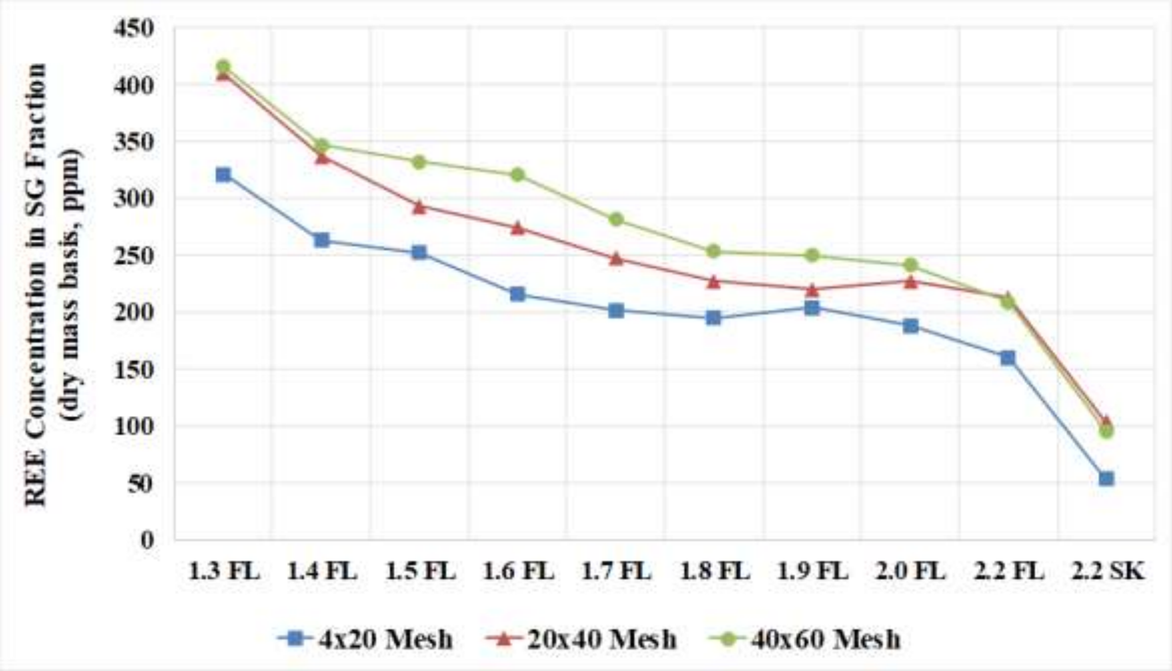


Figure 7-1. *Total REE concentration on a dry, whole coal basis by specific gravity fraction and coal size.*

Figure 7-2. *Cumulative coal, ash, and REE composition and mass by specific gravity fraction.*

Initial testing completed in Phase 2 utilized a 2-stage leaching approach, the first stage being a pre-leaching step which had the purpose of extracting materials from the coal that interfere with REE leaching, such as the alkali and alkaline earth metals. The second stage in the process had the purpose of extracting REE.

From the float-sink analysis of the Harmon coal and previous testing in Phase 1 of the project, evidence points towards REE complexation within organic structures, such as with the humic and fulvic acids indicative of low rank coals [6]. However, the forms of the alkali and alkaline earth metals, while believed to have organic associations, were unclear as to whether mineral encapsulation, organic complexation, or ion-adsorbed behaviors dominated these elements (Na, Mg, Ca). Testing to identify this source was conducted using two different reagents under various concentrations, ammonium acetate and a dilute mineral acid. The ammonium acetate extractions showed very poor results at all concentrations, with near zero extraction of all elements analyzed with the exception of calcium, which had extractions less than 10% for all concentrations. This was likely due to an organic complexation of the alkali and alkaline earth metals. Comparatively, the results for the dilute mineral acid had higher extraction efficiencies of the alkali and alkaline earth metals, but also extracted some REE at higher concentration. Additional testing with the dilute mineral acid was required to determine if optimization would improve results.

Further parametric tests were completed at the bench-scale to evaluate the efficacy and optimize conditions of the initial stage of the 2-stage leaching approach, which would extract impurities from the coal. Several factors were evaluated to determine the effect on pre-leaching efficiencies, including mineral acid type, acid concentration, starting pH, contact time, and slurry density. A pH-based leaching mechanism was also evaluated in this testing matrix to be compared to the concentration-based mechanism which had been utilized previously. The pH-based control mechanism required acid addition throughout the test, which prevented the complete consumption of H^+ ions which occurred during concentration-based testing. By maintaining the leaching driving force, additional material could be leached from the coal.

Figure 7-3 shows the results of two pre-leaching tests, both with the same acid type, contact time, slurry density, initial pH and acid concentration. During the pH-based test, acid was added periodically throughout the test to maintain the pH of the slurry, whereas the concentration-based test had no acid addition during the test. The pH-based mechanism had higher extraction of all of the elements analyzed, both REE (Nd, Gd, Er) and the impurities (Ca, Mg, Na). It was expected that future testing to optimize conditions could minimize REE loss, and this pH-based leaching mechanism was adopted for future leaching tests.

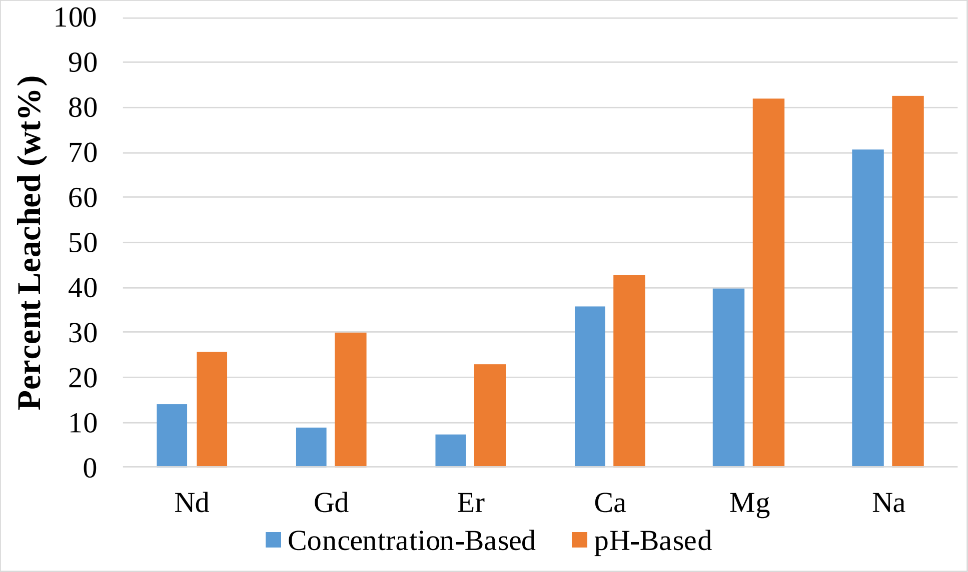


Figure 7-3. *Results for concentration-based and pH-based pre-leaching tests with the same initial acid concentration.*

The leaching efficiency of select cations as a function of pH, over a range covering both Stage 1 and Stage 2 leaching is provided in Figure 7-4. As shown in the figure, the leaching efficiency for Mg and Na was high, even at the highest pH, and with essentially all of the Mg and Na leached at the lowest pH. For Mg and Na, the data shows that leaching efficiency continued to increase with decreasing pH. For Ca, the leaching efficiency was consistently low across all pH values. For Fe and Al, significant leaching did not initiate until the lower pH, with Al being easier to leach than Fe. For the REE, significant leaching was also not present until the low pH conditions, as was expected. Similar to testing of other lignites, the HREE and Y were more easily leached than the LREE and Sc.

As it is the primary diluent in the REE products generated in the process, the removal of calcium was a priority during the Stage 1 leaching. The low removal efficiencies of calcium at all pH values shown in Figure 7-4 were not advantageous as compared with the REE loss, and as a result the 2-stage leaching was proved to not be an effective approach for impurity removal. For all future tests a single-stage leaching approach was used.

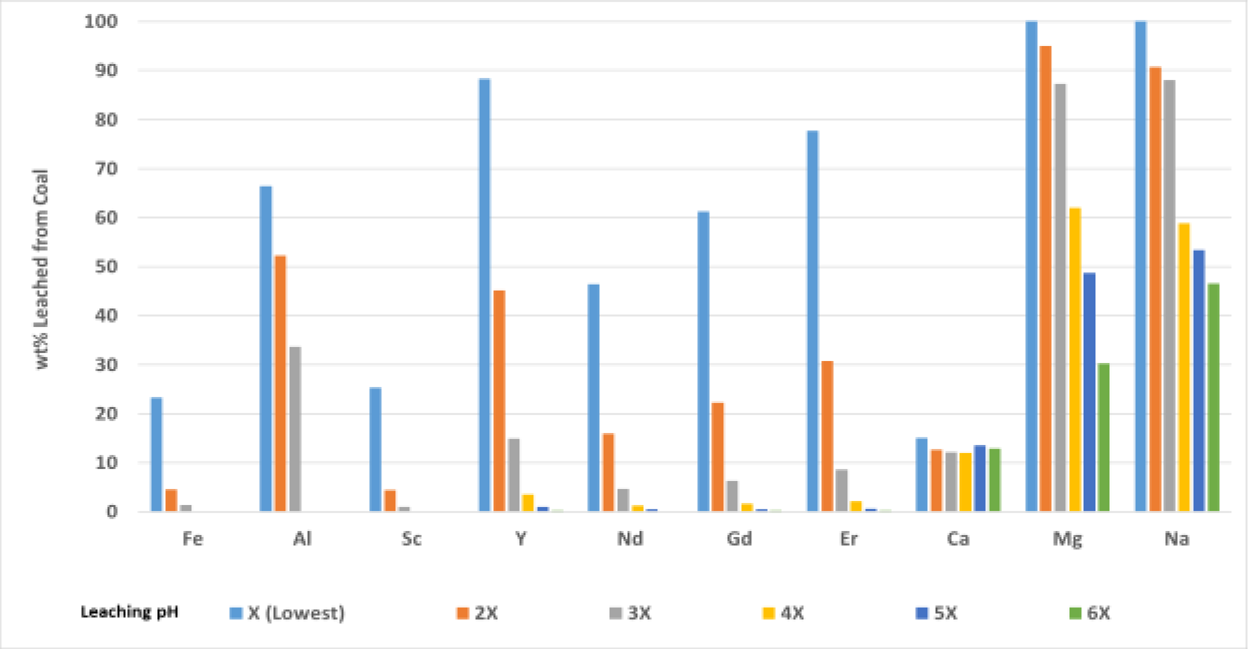


Figure 7-4. *Equilibrium leaching efficiency of select cations under a range of pH consisting of both Stage 1 and Stage 2 leaching conditions. pH shown as multiples of the lowest pH. Note: data for Fe, Al and Sc not available for pH 4X, 5X or 6X. However, based on the trend, leaching should be very low or zero for each.*

Utilization of semi-continuous acid addition was expected to provide significantly improved leaching kinetics (due to the maintenance of driving force associated with maintaining H^+ concentration). As shown in Figure 7-5 for the H Bed lignite, kinetics of leaching of a trivalent ions (Fe used as tracer for the REE) was rapid, with 80-90% of equilibrium leaching occurring within the first 15-30 minutes. Fe was chosen as the tracer for this experiment, as the pH values in question and the residence time utilized were unlikely to dissolve iron-based minerals expected in the coal, such as pyrite.

As shown and compared with static-leaching conducted in Phase 1, leaching kinetics under constant driving force conditions (pH) are minimally affected by the pH value in question, with a non-mineral dissolution mechanism predicted. The improved kinetics, particularly the faster kinetics noted here as compared to that observed in Phase 1 [4], resulted in reduction from 14-hour residence time to a 45-minute residence time for similar extraction performance.

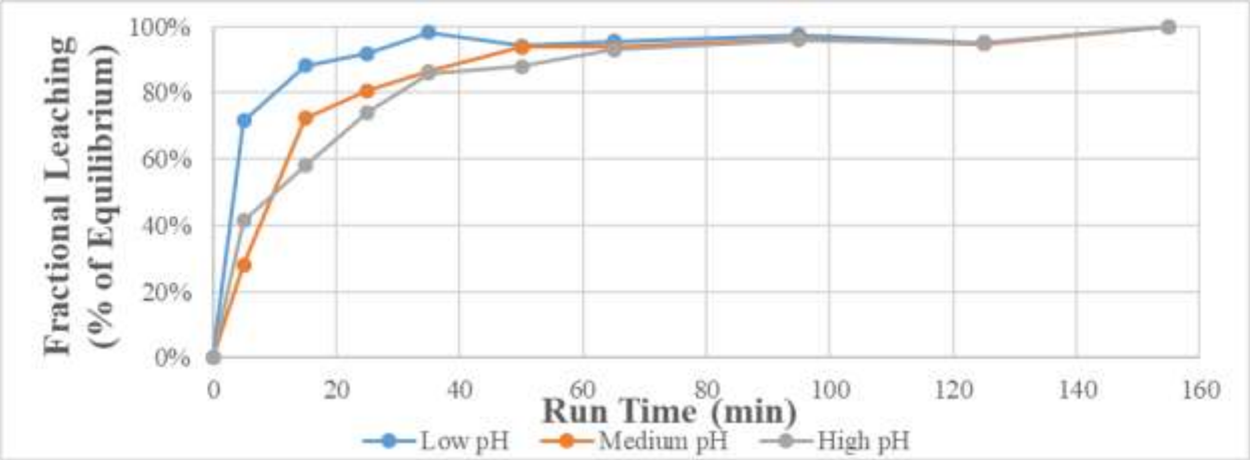


Figure 7-5. *Leaching kinetics (Fe) for H Bed lignite at three pH values.*

After testing leaching parameters, the unit operations and conditions for processing of the pregnant leach solution were evaluated. Two general processing routes were examined: 1) pH-based precipitation, and 2) oxalic acid precipitation. While significant recovery of the REE was possible utilizing pH-based precipitation mechanisms, and with relative high purity, significant precipitation of a valuable REE, Sc, occurred during a pH level at which another major impurity precipitated (Al). This would result in a very low concentration of Sc, and a potential challenging recovery process for the valuable material. In addition, reagent consumption and associated operating costs would be significant with this approach, and unlikely to be economical.

Testing of oxalic acid based precipitation methods found evidence towards Fe^{3+} and Al^{3+} complexation of the oxalate ion, which caused excess oxalic acid to be required to precipitate the REE. Based on this, the amount of oxalic acid required for REE precipitation would vary with changes in the concentration of iron and aluminum in the lignite, and their subsequent leaching recoveries into the liquid phase. Additionally, calcium was identified as an impurity of significant concern, as it was the only low-value impurity of note contained in the REE-oxalate solids produced. High recoveries of REE were achieved with the oxalic acid method.

Based on the results of the parametric testing, an overall process was establish that combined the key steps show in Figure 7-6.

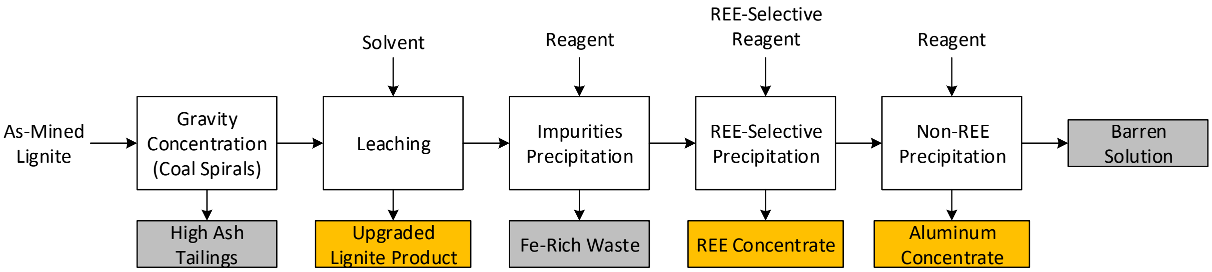


Figure 7-6. *Simplified block flow diagram of the major unit operations for the REE recovery process.*

After finalizing the process unit operations, parametric testing was conducted using the H Bed lignite sample to determine the optimal conditions required for production testing. The coal used in this testing was collected from an outcrop of the H Bed in Slope County, North Dakota. Approximately 7000 lbs were collected, then dried and crushed before been sent to Hazen Research where physical density separation methods were used to improve the REE content in the feedstock and also decrease the ash content. The fractions generated in the density separation process are shown in Table 7-1. The concentrate, scavenger concentrate, and scavenger middlings were blended to create the upgraded feedstock (highlighted in green in Table 1).

Table 7-1. *Abundance of REE from H Bed sample spiral fractions. Orange highlighting indicates fractions combined to create the upgraded blended coal, which is highlighted in green.*

Sample ID	Mass Fraction (wt% of Feed)	Ash Content (wt%)	Total REE (ppm)	Total REE, ash basis (ppm)	HREE/ LREE
Raw Coal	100	35.5	646	1822	0.28
Concentrate	35.6	15.1	657	4357	0.30
Scavenger Concentrate	8.2	19.5	679	3483	0.30
Scavenger Middlings	5.4	47.3	630	1333	0.28
Scavenger Tailings	2.1	59.3	550	927	0.26
Tailings	12.0	70.3	353	502	0.26
Fines	36.7	47.4	826	1743	0.26
Blend	49.2	19.3	658	3881	0.3

Parametric testing of the upgraded H Bed feedstock was completed using the process unit operations described in Figure 7-6. The following conditions were selected based on the results of the parametric testing:

1. Lignite leaching with an acidic solution of pH low enough to ensure high REE leaching efficiency

2. Partial neutralization of the leachate with Na_2CO_3 at a pH of 3 to precipitate Fe-rich impurity while leaving the REE and Al in solution
3. Oxalic acid addition with co-addition of Na_2CO_3 to precipitate primary REE-rich oxalate
4. Oxalic acid addition with co-addition of Na_2CO_3 to precipitate secondary REE-rich oxalate
5. Neutralization of barren solution (Na_2CO_3 to a pH of 6, then NaOH to a pH of 9) to precipitate Al-rich product (while leaving alkali and alkaline earth metals in solution)
6. Roasting (~800°C) of the REE-Ca-oxalate precipitate to decompose the oxalate into oxides

The production testing using the H Bed lignite was completed using the optimized process conditions selected in parametric testing. The REE extracted from the coal during leaching was lower than expected, with the highest recovery at 43% in Week 3 (Figure 7-7). This was theorized to be a result of poor dewatering efficiency, a challenge associated with the significant pore volume and structures within lignite. REE extraction from the coal continued to improve throughout testing, with the exception of Week 4, where extraction efficiency decreased slightly. Testing in Week 4 was plagued with very low dewatering efficiency, a potential side-effect of equipment challenges in metering pump flow. The acid consumption is also shown to be decreasing from Week 1 through Week 3 (Figure 7-7). This is a trend which would likely be continued with additional testing, due to the recycling of the water used to wash the coal after leaching. The increase in acid consumption in Week 4 is due to a lower pH setpoint being used for leaching in Week 4.

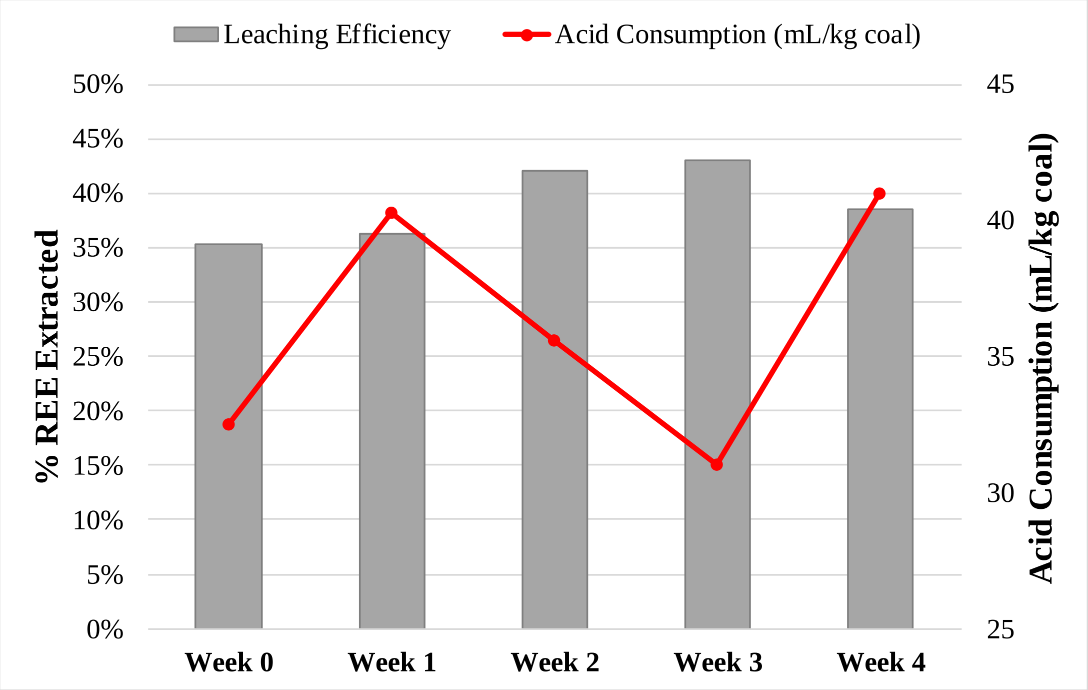


Figure 7-7. *Overall REE extraction from the coal and acid consumption during leaching tests.*

The primary focus of the impurity removal step in the process is the removal of iron. During production testing over 70% removal of iron was observed for Weeks 1, 2, and 4, with less than 5% loss in total REE. Equipment issues in Week 3 of testing resulted in a shorter than desired residence time in this processing step, resulting in lower removal of iron and high loss of REE. This proved that a longer residence time is required for this step, and that at the longer residence time high extraction of iron with minimal REE loss is achievable.

The concentration of REE in the products generated during testing are presented in Table 7-2. In Week 4 a concentration of 54.4wt% REE was achieved in the primary product (on an oxide basis), and the Week 3 secondary product had a concentration of 8.6%.

Table 7-2. *REE concentration for all REE products produced during continuous testing.*

Test	Primary Product REE Concentration (wt%, oxide basis)	Secondary Product REE Concentration (wt%, oxide basis)
Week 1	40.3%	3.5%
Week 2	32.3%	4.1%
Week 3	27.0%	8.6%
Week 4	54.4%	7.5%

Aluminum recovery from the remaining pregnant leach solution was over 60% for all testing weeks, with the exception of Week 1 where only 40% recovery was observed. As this step is considered an optional processing step, these recoveries and purities were not determined to generate an economic unit operation, and lead to exclusion of aluminum recovery as a processing step for this coal. Future testing of the process may result in further optimization which may make this step more economic, and may have separate economics as compared with additional coals.

The results of the testing completed in this Phase 2 project demonstrated that extraction of REE from lignite is technically feasible, with a simple process for generating concentrates in excess of 50% REO's. Additionally, the organic association of REE in lignite provides a distinct advantage, which allows for extraction of REE with dilute acid at mild conditions, particularly in a pH-controlled mechanism. After extraction from the coal, a simple set of process unit operations can be utilized to recover and produce a product with high concentration of REE. An additional aluminum concentrate product may also be produced in this process.

7.2 Technical and Economic Analysis Report

The scope and basis for the technical and economic feasibility analysis was derived from the results of the work conducted in the Phase 2 project. The objective of this study was to determine the technical and economic feasibility of extracting and concentrating REE from North Dakota lignite coal-related feedstocks. The technical and economic feasibility was evaluated for the extraction process developed by UND, which was tested on the bench-scale in semi-continuous operation in Task 7 of the Phase 2 project. The UND REE extraction process involves a mild acid leach at ambient temperature of the pre-combustion coal to extract the REE, Y and Sc, and other valuable elements. The pregnant leach solution (PLS) is pH adjusted to remove impurities (i.e. iron) before the REE extraction step where REE's and critical minerals (CM) are precipitated using oxalic acid and sodium carbonate. The remaining PLS may then be processed to recover aluminum by base addition to the barren solution. For this study, it was assumed a commercial refiner would purchase the concentrated REE product and process the concentration for final separation.

The overall concept for commercial implementation of this REE recovery process is to combine the REE recovery with an additional value-added process, utilizing the higher value of the resultant pre-combustion lignite. The resulting residual coal from the leaching process has a lower ash content and higher heating value and can be beneficially utilized in other processes such as activated carbon production co-located at a combined heat and power plant, or at a humic acid production facility.

Testing completed in Task 7 of this Phase 2 project was the design basis for this technical and economic feasibility analysis. Selectively mined coal sourced from the H Bed seam of the Harmon-Hanson coal zone in North Dakota (650 ppm REE+Y and Sc, whole coal dry basis and 1,350 ppm REE+Y and Sc, ash basis) was assumed to be purchased. Due to unique association of REEs with ND lignite coals, a mild leaching process has been developed to extract organically-bound REEs directly from the raw coal. A simple process is then utilized for processing of the pregnant leach solution, where impurities are extracted prior to precipitation of rare earth element concentrate products, followed by recovery of aluminum from the solution.

The activated carbon and humic acid cases evaluated in this study were completed assuming different plant capacities in order to optimize each alternative. The activated carbon production case assumed a coal feed rate of 10,000 lb/hr, and the humic acid case assumed 40,000 lb/hr of H Bed coal was used.

The environmental impact was considered during the approach of the system configuration. Many of the gases and byproduct solids generated from the process are considered to be saleable products, thus reducing waste streams discharging from the plant. The energy footprint was also significantly reduced by recirculating viable sources of waste heat throughout the process, such as for coal drying after REE extraction. The process is simple, environmentally benign, and low cost, and is based on industrially proven mineral extraction methods widely utilized. Some of the advantages of this technology are summarized below:

- Mild leaching of the raw coal at low/ambient temperature – environmentally benign processing
- Minimal NORM extraction from the coal – low up-cycling risks
- Minimal production of waste
- REEs can be leached directly from the raw coal, permitting added-value use following REE extraction

The mass balances for this process were determined based on the bench-scale production testing in Task 7 of this Phase 2 project. Using the appropriate coal feed rates for both the activated carbon and humic acid cases, the consumption of chemical reagents such as the dilute mineral acid used for leaching, sodium carbonate, sodium hydroxide, and oxalic acid were calculated for the REE recovery process. Leaching efficiency and masses of products produced, based upon testing in Task 7, were also factored into the design and mass balances. For the production of syngas and activated carbon and for the production of humic acid, processing requirements and production rates of products were also calculated and included in the technical and economic feasibility analysis.

For the technical and economic analysis, the market implications were evaluated for introducing new sources of domestic production of REE, yttrium and scandium, as well as other metals that have a large impact on the economics of the proposed plants. For elements such as REE and yttrium, the proposed production rates would account for a very small fraction of overall domestic consumption, and it would not be expected to have any significant impact resulting from the introduction of this new domestic production source besides reduction in reliance on imports. Production rates of germanium and scandium would account for a larger fraction of their respective markets, and would likely have a slightly larger impact on the market. However, the increased supply could allow for growth in the market and expansion in utilization of these materials.

The estimated cost for the proposed process is considered to be a Class 5 estimate, as described by AACE International, Cost Estimate Classification System with an expected accuracy range of -20% to -50% (low) and +30% to +100% (high) [7]. A payable revenue for the REE oxides and select target elements was estimated using published market values. Additional payable revenue is generated from the sale of activated carbon and a fuel source of syngas produced from the carbonation and activation process that displaces the use of natural gas for the Valley City State University (VCSU) steam plant. In the case of the humic acid production, the humic acid and the fuel value of the resultant humic-depleted lignite are viewed as sources of revenue. The payback analysis used each of these components to estimate a simple payback and an IRR, ROI and NPV over 10 and 20 years.

Capital costs were calculated using cost estimate resources, vendor quotes, and engineering judgement based on industry experience. The equipment was sized assuming a plant overall feed rate of 10,000 dry lb/hr of coal for activated carbon and 40,000 dry lb/hr of coal for humic acid. The major equipment required for the process was considered for each processing step, including coal preparation, leaching, impurity removal, REE precipitation, aluminum recovery, carbonization and activation, and humic acid production. The total estimated project cost for the case including the activated carbon production was $36.8 million, which includes additional cost for installation, site work, and site electrical and controls as a percentage of the total equipment cost. Also, an engineering, legal, and administrative amount is included as a percentage of the total construction cost. In the case of humic acid production, the total estimated project cost is $50.7 million.

Operating costs were also calculated using cost estimate resources, vendor quotes, and engineering judgment based on industry experience, and include power, fuel, maintenance, raw material cost, and operator cost. The total estimated operating cost is \$9.98 million per year with the production of activated carbon and \$69.1 million per year with the production of humic acid.

The market prices used assume the final sale product to be REE/target element oxides. This study has evaluated the economics of producing/purifying all of the REEs, plus Y, Sc, Ga, Ge and select base metals (Co, Cu, Mn, Zn). The H Bed coal projects a total of 28,700 lb/yr of REE/target element oxides and about 400 lb/yr of base metals. For the humic acid production case, approximately 115,000 lb/yr of REE/target element oxides and 1,600 lb/yr would be produced. The calculated value of the finished REE and other element oxides products produced at the refinery is deduced by assuming a refining cost per ton of REE/target element and base metal produced. These were set at \$500 per ton of REE, Y, Sc, Ga, Ge (as oxide) and \$500 per ton of base metal (Co, Cu, Mn, Zn). These costs are on a per element basis.

The carbonation and activation process produces activated carbon at a rate of 8,454 ton/yr, assuming a sale price of \$1,500 per ton, activated carbon sales would total \$12.68 million per year. An additional revenue source from the syngas, which is a byproduct of the carbonation and activation process, would total about \$2.1 million per year. The total sales (REE, base metals, activated carbon, and syngas) for this case would be \$17.2 million per year before operating expenses.

During humic acid extraction, a portion of the resultant coal remains, leaving a higher BTU/lb fuel source, with a potential annual revenue of about \$2.5 million. The humic acid extraction is calculated to yield 33,600 ton/year of humic acid, totaling \$67.2 million per year. The total sales (REE, base metals, and humic acid) per year is \$79.3 million before operating expenses.

Each cost and revenue component previously discussed was used to estimate ROI, IRR, and simple payback, which are shown in Table 7-3.

Table 7-3. *Payback Analysis Summary*

Item	Activated Carbon	Humic Acid
CAPEX	($36,800,000)	($50,700,000)
OPEX	($9,980,000)	($69,100,000)
REE and Base Metal Payable Amount per year	$2,500,000	$9,600,000
Upgraded Coal Payable Amount	$12,700,000	$67,200,000
Fuel Credit	$2,100,000	$2,500,000
Net Annual Revenue per year	$5,100,000	$10,400,000
Simple Payback (years)	5.1	4.9
IRR (10 years)	15%	16%
ROI (10 years)	10%	11%
NPV (10 years) @12% discount rate	$4,200,000	$8,200,000
IRR (20 years)	19%	20%
ROI (20 years)	15%	16%
NPV (20 years) @12% discount rate	$17,400,000	$27,200,000
CAPEX/annual dry ton feed	$900	$300
OPEX/annual dry ton feed	$240	$410
Net Revenue/annual dry ton feed	$173	$62

A sensitivity analysis was also completed which evaluated the sensitivity to changes in capital cost, sale price of upgraded coal product, recovery of REE and CM, price of REE, and changes in the operating cost. The economic/sensitivity analysis indicates that the two most impactful metrics for profitability of the combined REE/carbon processing plant include the price of the upgraded carbon product (activated carbon/humic acid), and the OPEX of the REE processing facility, clearly highlighting the importance of the secondary product. However, as these markets are perceived to be more stable as compared with the REE, these fluctuations are deemed unlikely. The sensitivity analysis also showed the relative stability of the process towards fluctuations within the REE markets.

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PHASE 1 FINAL TECHICAL REPORT

SUBMITTED TO

U.S. Department of Energy
National Energy Technology Laboratory

SUBMITTED UNDER FUNDING OPPORTUNITY ANNOUNCEMENT

DE-FOA-0001202

INVESTIGATION OF RARE EARTH ELEMENT EXTRACTION FROM NORTH DAKOTA COAL-RELATED FEEDSTOCKS

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TABLE OF CONTENTS

1 EXECUTIVE SUMMARY

The rare earth elements consist of the lanthanide series of elements with atomic numbers from 57-71 and also include yttrium and scandium. Due to their unique properties, rare earth elements are crucial materials in an incredible array of consumer goods, energy system components and military defense applications. However, the global production and entire value chain for rare earth elements is dominated by China, with the U.S. currently 100% import reliant for these critical materials. Traditional mineral ores including previously mined deposits in the U.S., however, have several challenges. Chief among these is that the content of the most critical and valuable of the rare earths are deficient, making mining uneconomical. Further, the supply of these most critical rare earths is nearly 100% produced in China from a single resource that is only projected to last another 10 to 20 years. The U.S. currently considers the rare earths market an issue of national security. It is imperative that alternative domestic sources of rare earths be identified and methods developed to produce them. Recently, coal and coal byproducts have been identified as one of these promising alternative resources. This report details a Phase 1 evaluation of the technical and economic feasibility of rare earth element recovery from North Dakota lignite coal and lignite-related feedstocks.

There were four major goals of this study: i) identify lignite or lignite-related feedstocks with total rare earth element content above 300 parts per million, a threshold dictated by DOE as the minimum for economic viability, ii) determine the geochemistry of the feedstocks and understand the forms and modes of occurrence of the rare earth elements, information necessary to inform the development of extraction and concentration methods, iii) identify processing methods to concentrate the rare earth elements from the feedstocks to a target of two weight percent, a value that would be sufficient to leverage existing separation and refining methods developed for the traditional mineral ore industry, and iv) develop a process that is economically viable and environmentally benign.

To achieve these overall goals, the research scope was broken down into three main efforts: i) sampling and characterization of potential feedstocks, ii) laboratory-scale development and testing of rare earth element extraction and concentration methods, and iii) process design and technical and economic feasibility evaluation.

In total, nearly 200 unique samples were collected, and several locations were identified that exceeded the 300 ppm total rare earth elements target. The results showed that on a whole sample basis, the rare earths are typically most concentrated in the clay-rich sediments associated with the coal seams, but on an ash basis in certain locations within certain coal seams the content is significantly higher, an unexpected finding given prior research. At Falkirk Mine near Underwood, North Dakota three coal seams were found to have elevated levels of rare earths, ranging from about 300 to 600 ppm on an ash basis. Additionally, exceptionally high rare earths content was found in samples collected from several outcropping of the Harmon-Hansen coal zone in western/southwestern North Dakota that contained as high as 2300 ppm on an ash basis and over 600 ppm on a dry whole coal basis. The results dictated that extraction and concentration methods be developed for these rare earth element-rich coals, instead of the mineral-rich sediments. This effort also found that that at a commercial-scale, due to non-uniformity of the rare earths content stratigraphically in the coal seams, selective mining practices will be needed to target specific locations within the seams. The bulk mining and blending practices as Falkirk Mine result in a relatively low total rare earths content in the feed coal entering the Coal Creek Power Station adjacent to the mine.

Characterization of the coal samples identified that the predominant modes of rare earths occurrence in the lignite coals are associations with the organic matter, primarily as coordination complexes and a lesser amount as ion-exchangeable cations on oxygen functional groups. Overall it appears that about 80-95% of rare earths content in North Dakota lignite is organically associated, and not present in mineral forms, which due to the weak organic bonding, presented a unique opportunity for extraction.

The process developed for extraction of rare earths was applied to the raw lignite coals instead of fly ash or other byproducts being investigated extensively in the literature. Rather, the process uses a leaching process to selectively strip the organically associated rare earths from the lignite with very high efficiency of about 70-90% at equilibrium contact times. Although the extraction kinetics are quite fast given commercial leaching operations, there is some tradeoff between extraction efficiency and contact time. However, at shorter contact time there is improved rare earths selectivity that results in a more concentrated product due to limiting extraction of unwanted impurities. There is also a significant difference in the extraction kinetics for the more valuable heavier molecular weight rare earths, which are much faster than the light rare earths. The testing showed that in a one-step process consisting of leaching for two hours with a selected solvent, a rare earth concentrate of about 1.4 weight percent rare earths could be achieved with about 70% total rare earths extraction, while also producing a residual coal byproduct that has superior qualities to the feed coal, such as reduced ash content. In a modified leaching approach, a 2.0wt% REE concentrate could be achieved in a single processing step, but with only about 36% total REE extraction. At 90% REE recovery, the solvent produced a 0.8wt% REE concentration. Higher REE concentrations could be achieved by a number of hydrometallurgical approaches to selectively precipitate impurities from the leachate.

The process developed in this project is simple, highly effective, low cost and novel. The process is environmentally benign and was demonstrated to be economically viable at the current market conditions. The process can be advantageously integrated with any number of coal utilization processes to augment economics, lower costs and maximize efficiency and synergies. The techno-economic analysis evaluated a configuration of rare earths extraction combined with activated carbon production co-located at a combined heat and power facility, and was shown to have highly attractive economics even at small scales representing a first-of-a-kind demonstration system.

2 INTRODUCTION

The University of North Dakota has partnered with Barr Engineering and Pacific Northwest National Laboratory to determine the technical and economic feasibility of concentrating rare earth elements from North Dakota lignite coal and lignite coal-related feedstocks. This report details the work accomplished in Phase 1 at the time of submission of the Phase 2 renewal application.

The overall goal of the Phase 1 project was to develop a high performance, economically viable and environmentally benign technology to recovery and concentrate rare earth elements from North Dakota lignite, associated sediments, and a lignite drying reject stream. In order to meet this goal, the project team identified the following specific objectives at the project onset:

- Develop sampling protocols and obtain representative samples of lignite, associated roof and floor materials, and coal drying reject streams
- Determine the abundance and forms of rare earth elements and relevant material properties on a particle-by-particle basis
- Determine the potential to concentrate REEs through physical beneficiation methods such as gravity separation, fine coal cleaning technologies and novel separation technologies based on size and density of REE-bearing components in the samples
- Identify the optimum methods to separate and concentrate the REE to 2 percent by weight. The resulting total concentration of mixed REEs in the final product from the proposed recovery process should be determined on a dry basis for solid material, as measured by elemental analysis
- Perform a technical and economic analysis of the optimum methods
- Develop a design of a bench scale system to concentrate the REEs

2.1 Scope of Work

The scope of work was broken down into five main tasks which are summarized below, with results, discussion and conclusions presented in detail in later sections of this report.

- *Task 1 – Project management and planning*: This task included work elements required to maintain and revise the Project Management Plan and to manage and report on activities in the accordance with the plan, as well as to ensure coordination and planning of the project with DOE/NETL and other project participants and sponsors.

- *Task 2 – Sampling and characterization of proposed feedstocks*: This task included sampling of feedstocks consisting of lignite coal, roof/floor/partings sediments associated with the lignite streams, as well as samples from the Coal Creek Station power plant and its DryFining™ lignite drying/beneficiation process. Characterization methods were aimed at understanding the bulk chemistry of the samples as well as the forms and modes of occurrence of the REEs and other important elements. This task also included laboratory-scale extraction/concentration testing of selected feedstocks to concentrate REEs to a target of 2% by weight.

- *Task 3 – Technical and economic feasibility study*: Based on the results of Task 2, a technical and economic feasibility assessment (TEA) was completed by Barr Engineering that developed the design and determined the economic merits of a commercial-scale REE concentration facility.
- *Task 4 – Laboratory-scale testing for determination of bench-scale design parameters*: To effectively develop the design of the bench-scale test system to be constructed and testing in a subsequent Phase 2 project, some additional laboratory-scale parametric testing was completed that established sizing and operating window.
- *Task 5 – Bench-scale system design*: Based on the results of Tasks 2 and 4, the design of a bench-scale test system was prepared for a scale of approximately 10 kg/hr of feedstock throughput.
- *Task 6 – Phase 1 summary report*: This document is the deliverable for this task.

This report contains detailed results of Tasks 2 and 4. A separate report for Task 3 was previously submitted. The Phase 1 design report for Task 5 was also submitted previously.

In this report, Chapter 2 contains the results of sampling and characterization (Task 2) and Chapter 3 contains the results of laboratory-scale extraction/concentration testing (Task 2 and Task 4).

3 SAMPLING AND CHARACTERIZATION

This chapter contains details of the sampling and characterization efforts aimed at identifying North Dakota coal-related feedstocks that are enriched in REEs, as well as in understanding the geochemistry of the materials and the modes of REE occurrence.

3.1 Sampling Efforts

This section describes the sampling efforts to collect representative samples of North Dakota lignite coal and coal byproducts associated with North American Coal Corporation's (NAcoal) Falkirk Mine and the Great River Energy (GRE) Coal Creek Station power plant, including its coal beneficiation system based on the DryFining™ technology. The Falkirk Mine and the Coal Creek Station are both located near Underwood, North Dakota. The Coal Creek station fires lignite coal from Falkirk mine. The DryFining™ technology reduces coal moisture content and beneficiates coal by separating undesirable constituents, such as sulfur, mercury and minerals. The separated undesirable components end up in the reject stream, which was initially expected to contain elevated levels of REE compared to the raw coal feed. The efforts involved obtaining samples from the mine, the DryFining™ process and other sample locations within the power plant. Additional samples were also obtained from the Coyote Creek Mine, near Zap, North Dakota; the Harmon-Hansen coal zone, near Amidon, North Dakota; the Milton R. Young Station, near Center, North Dakota; the Antelope Valley Station, near Beulah, North Dakota; and the Freedom Mine, near Beulah, North Dakota.

There are three major coal zones in North Dakota: i) Hagel, ii) Beulah-Zap, and iii) Harmon-Hanson. The majority of work was focused on the Hagel, but samples were also collected from the other two zones. The Harmon-Hansen zone was found to be peculiarly enriched in REE in one location sampled. Figure 1 shows an overall map of the coal producing regions in North Dakota. Figure 2 shows a map of the Hagel coal zone, and Figure 3 shows a map of the Harmon-Hansen coal zone. The Harmon-Hansen is the only of the three that is not currently being mined, with its last mine, the Gascoyne Mine, having closed in 1997.

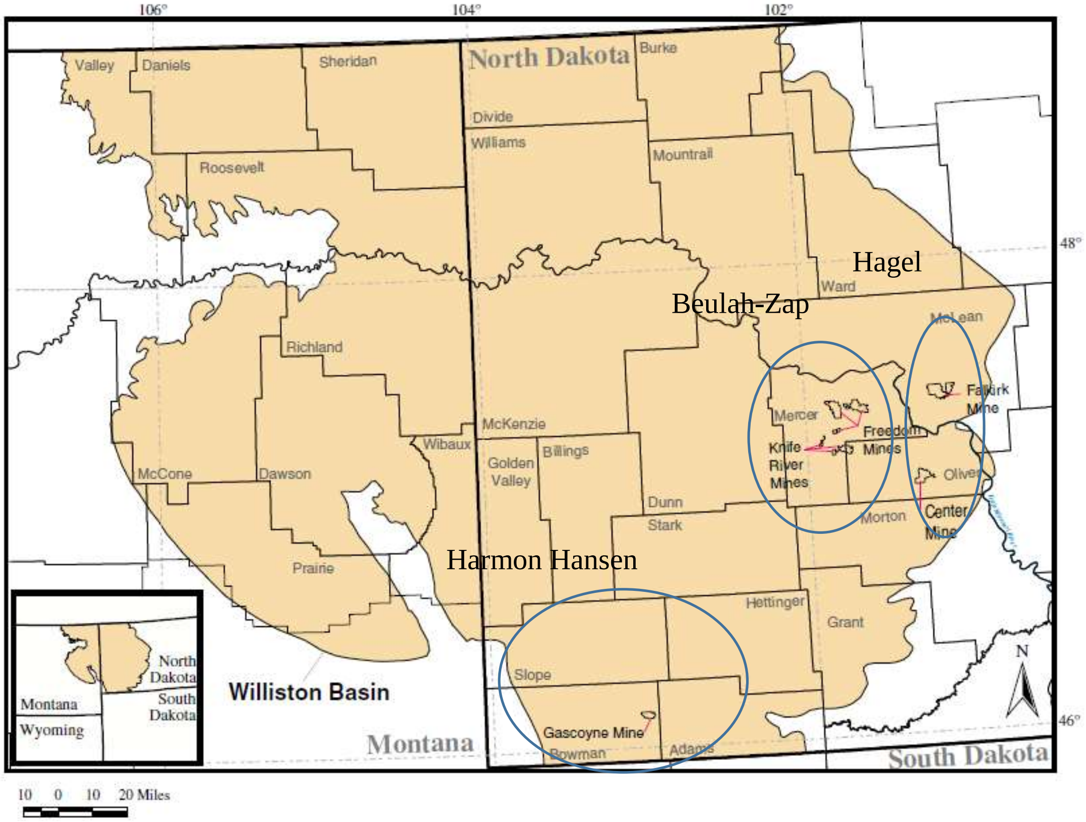


Figure 1. Map of the Williston Basin and coal zones in North Dakota [1]

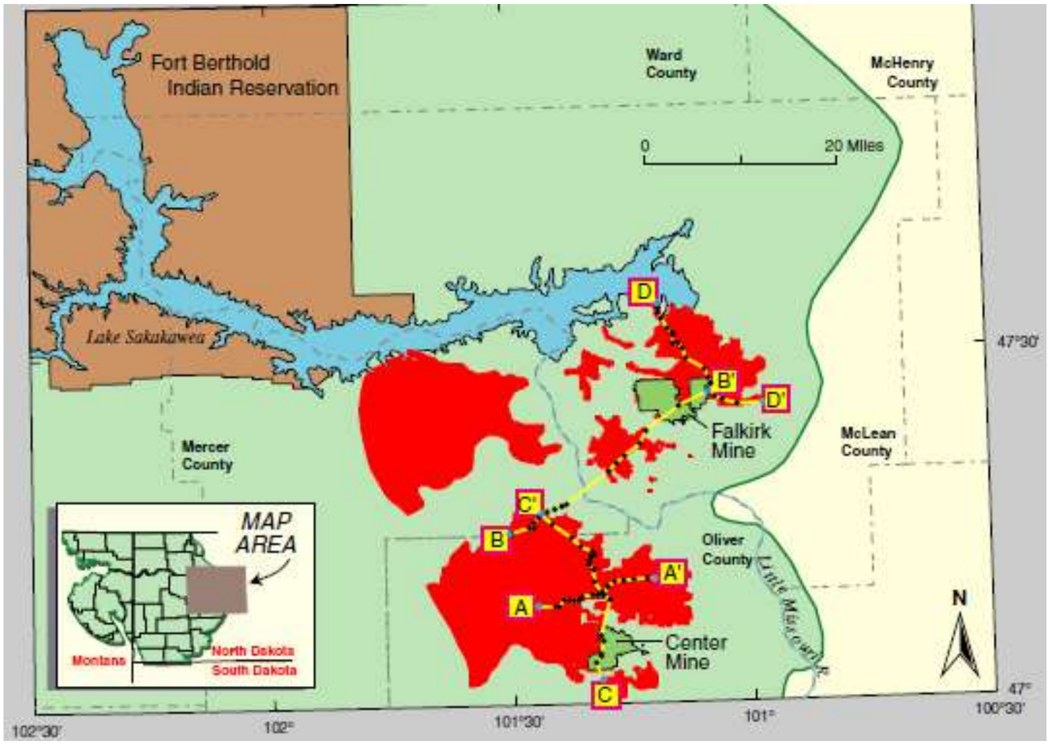


Figure 2. Map of the Hagel Coal Zone - samples collected mainly from Falkirk Mine [1]

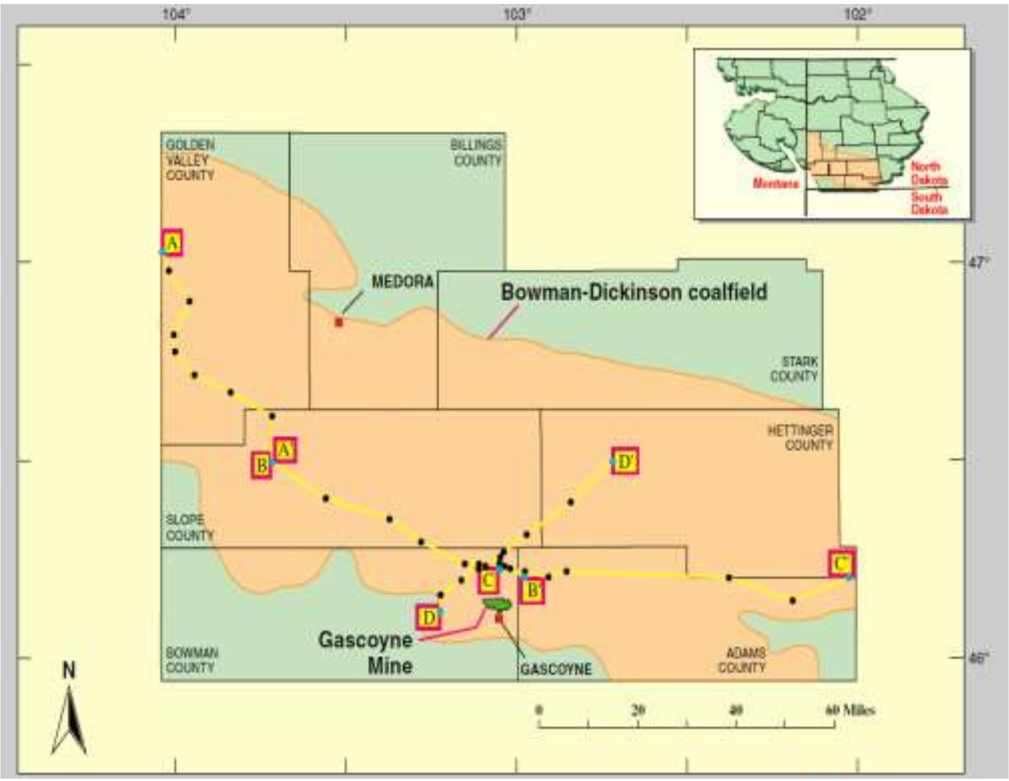


Figure 3. Map of the Harmon-Hansen Coal Zone - samples collected from Slope County [1]

The following sections provide additional details on the sampling activities at each of the above locations.

3.1.1 Sampling at Coal Creek Station

Three sampling series were performed at the Coal Creek Station (April 25 to May 6 2016, July 7 2016, July 27 to August 11 2016). Figure 4 displays a schematic of the Coal Creek Station and identifies the locations of the sampling.

Based on initial analysis performed prior to this study, and with the initial notion that the REEs would be concentrated in the mineral-rich sediments in the very fine mineral grains, it was anticipated that the air jig outlet and dryer fines streams would have the highest REE abundance. Sampling the other streams making up the DryFining™ process allowed understanding of the fate of the REEs in the DryFining™ process.

In the first sampling series at the Coal Creek Station, samples were collected from: dryer rejects to air jig (segregated coal), air jig cleaned coal, coal to the pulverizer, raw coal, fines from the fabric filter (FF) of coal dryer, and air jig rejects. The samples were collected according to the procedure laid out by ASTM standard method D2234, for collection of a gross sample of coal. Samples were collected at periodic intervals and over standard durations to ensure that a representative sample was acquired. Within each day of sampling, the multiple samples collected at each location were combined to form one-day composite samples of about 2 kg each.

The second sampling series was performed to collect bottom ash, fly ash, pulverizer rejects and FGD scrubber solids. Approximately 2 kg of sample were collected from each of these points.

The third sampling series was performed with multiple composite samples collected over a 16-day period to provide a larger quantity of fly ash and more samples allowing a better understanding of the variability of the REE content entering the plant.

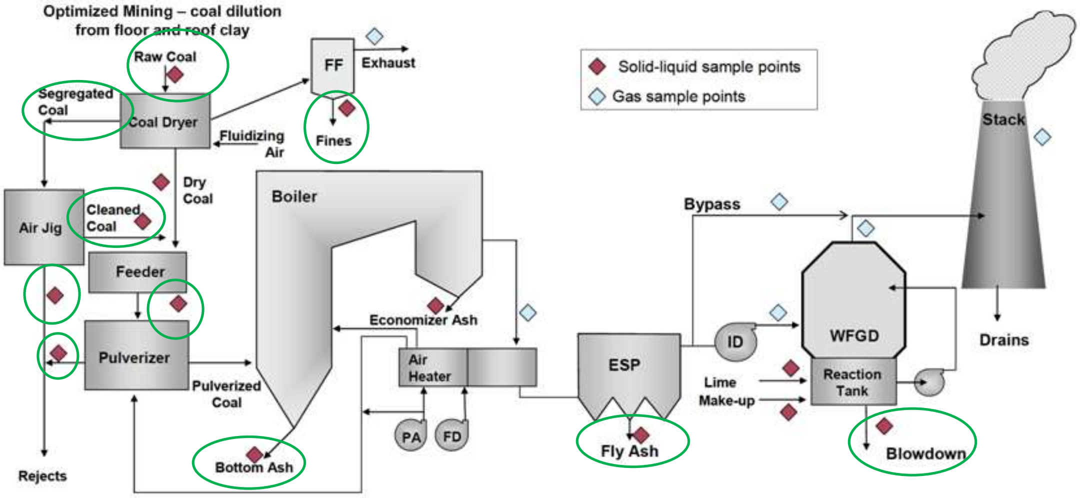


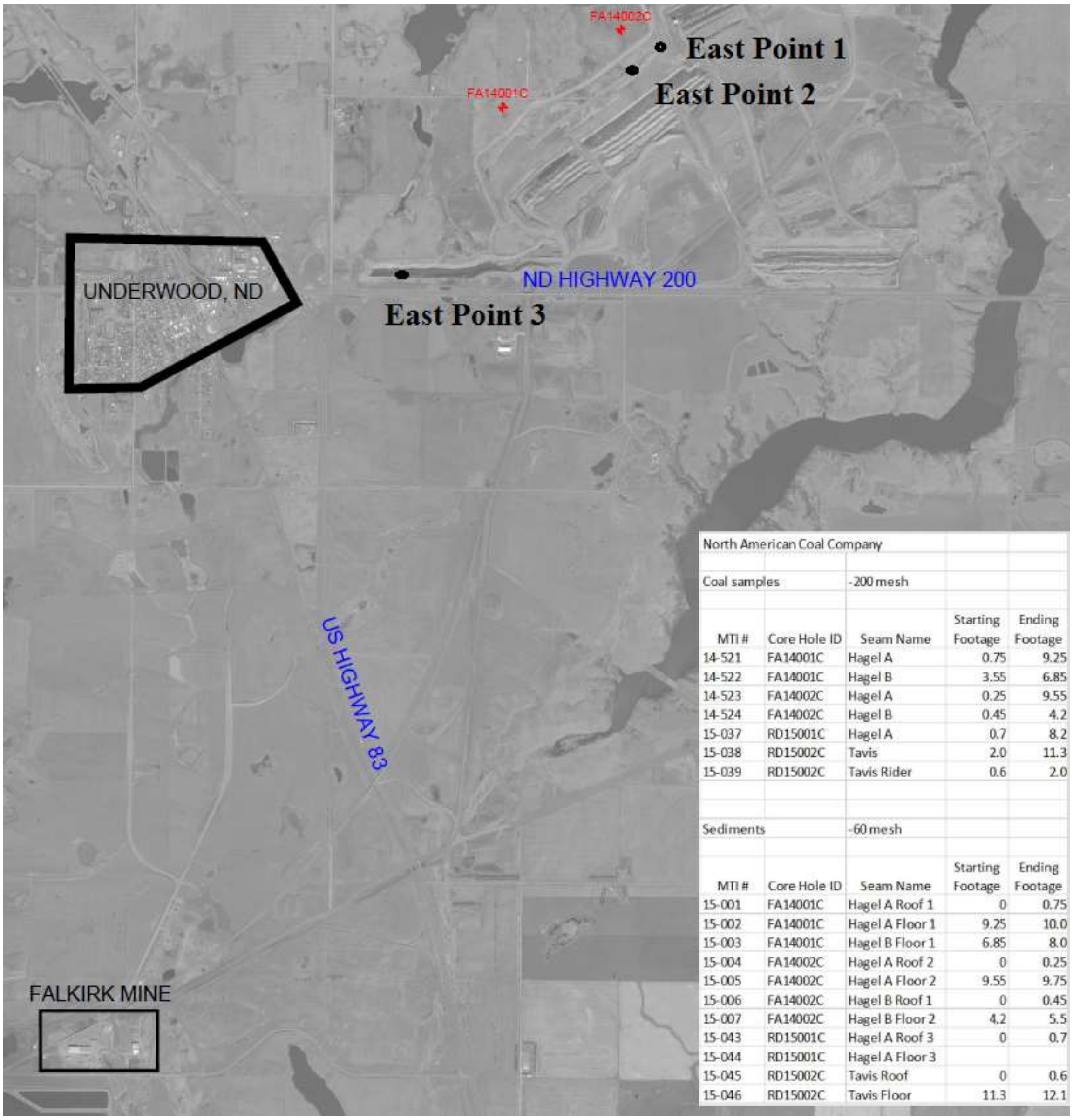
Figure 4. Schematic of the Coal Creek Station DryFining™ system and power system, with sampling points identified by green circles

3.1.2 Sampling at Falkirk Mine

Two sampling trips to the Falkirk Mine were completed. The first on April 7, 2016 was to obtain samples from several locations with potentially high REEs concentration. Based on the analysis results of samples from the first sampling trip, the second sampling trip was scheduled on September 6, 2016. During the second sampling trip, several larger samples of about 100 pounds of coal were collected from each of two locations (East Point 2 and East Point 3) identified by previous tests that were meant to provide an indication of the consistency of REE distribution over a wider sampling area, as well as to provide sufficient quantity of sample for subsequent laboratory extraction/concentration tests, which are described in Chapter 3 of this report. Sampling at the mine followed ASTM Standards D2234 and D4596.

In the first field trip, samples were collected from drilling cuttings and faces from the mine. Samples were collected from four locations named as South Point, East Point 1, East Point 2, and East Point 3 in this project. The sampling locations were determined based on previous results obtained by Microbeam Technologies Incorporated of Grand Forks, North Dakota, who was previously contracted by North American Coal Corporation (NA Coal) to do some analysis work on core samples from the mine. At South Point, the Hagel A coal and floor were collected as drilling cuttings, and the roof was collected from the face. At East Point 1, the Hagel A coal and floor were collected as drilling cuttings, and the roof was collected from the face. At East Point 2, the Hagel B coal and floor were collected as drilling cuttings, and the roof was collected from the face. At East Point 3, the B Rider coal and floor were collected from the stockpile, and the roof was collected from the face. Also at East Point 3, the Hagel B coal and floor were collected from the stockpile, and the roof was collected from the face. Figure 5 and Figure 6 show the map of sampling locations at the Falkirk mine. Figure 7 shows the generalized stratigraphic column and seam codes. The sampling focused on the Hagel bed shown.

To achieve project objectives, and specifically, based on the Falkirk Mine mining schedule, samples were collected from the drill cores and faces following the conceptual layout described in Table 1.



North American Coal Company				
Coal samples		-200 mesh		
MTI #	Core Hole ID	Seam Name	Starting Footage	Ending Footage
14-521	FA14001C	Hagel A	0.75	9.25
14-522	FA14001C	Hagel B	3.55	6.85
14-523	FA14002C	Hagel A	0.25	9.55
14-524	FA14002C	Hagel B	0.45	4.2
15-037	RD15001C	Hagel A	0.7	8.2
15-038	RD15002C	Tavis	2.0	11.3
15-039	RD15002C	Tavis Rider	0.6	2.0
Sediments		-60 mesh		
MTI #	Core Hole ID	Seam Name	Starting Footage	Ending Footage
15-001	FA14001C	Hagel A Roof 1	0	0.75
15-002	FA14001C	Hagel A Floor 1	9.25	10.0
15-003	FA14001C	Hagel B Floor 1	6.85	8.0
15-004	FA14002C	Hagel A Roof 2	0	0.25
15-005	FA14002C	Hagel A Floor 2	9.55	9.75
15-006	FA14002C	Hagel B Roof 1	0	0.45
15-007	FA14002C	Hagel B Floor 2	4.2	5.5
15-043	RD15001C	Hagel A Roof 3	0	0.7
15-044	RD15001C	Hagel A Floor 3		
15-045	RD15002C	Tavis Roof	0	0.6
15-046	RD15002C	Tavis Floor	11.3	12.1

Figure 5. Map of sampling locations East Point 1, 2 & 3 at the Falkirk mine.

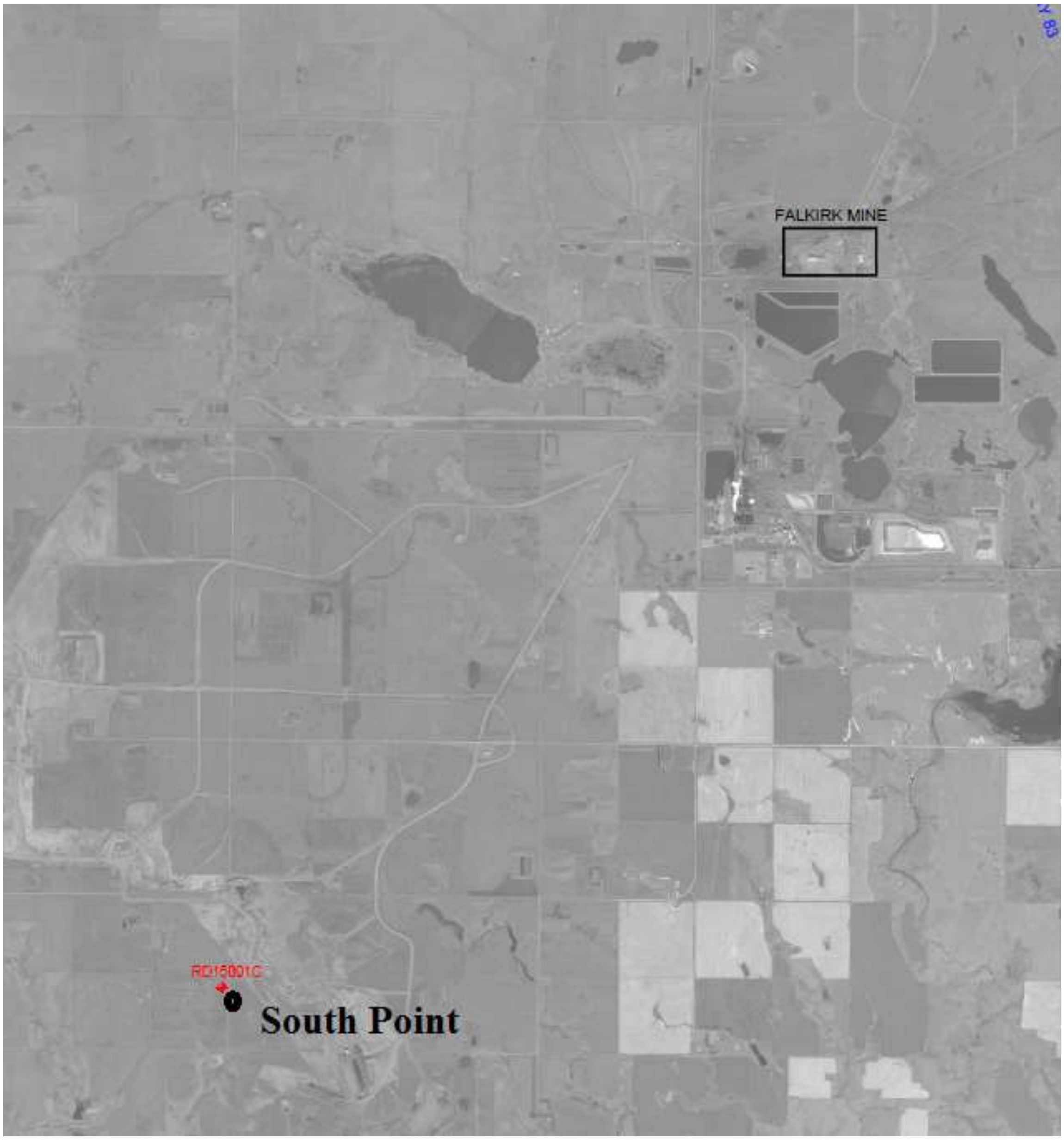
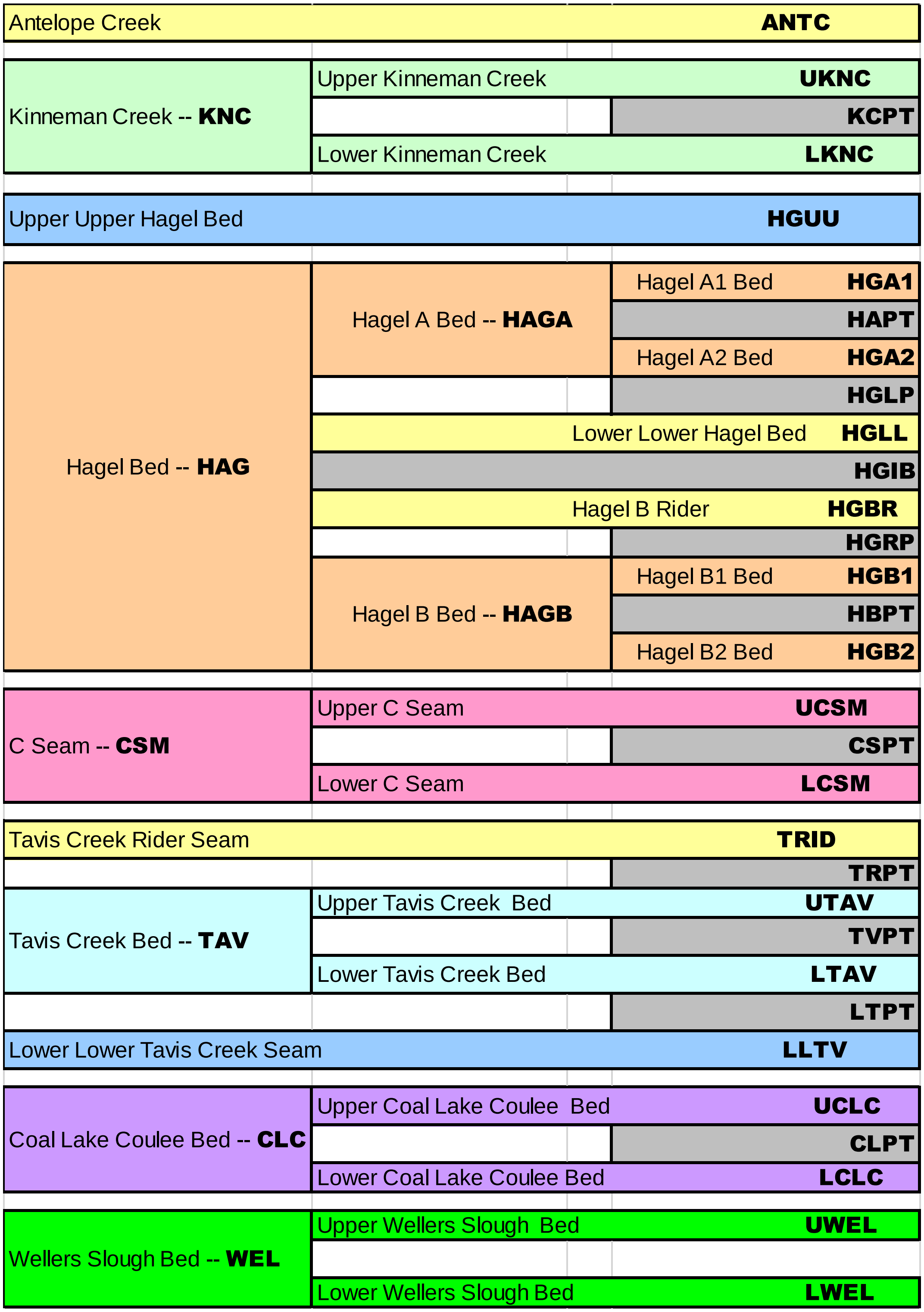


Figure 6. Map of sampling location South Point at the Falkirk mine.



Antelope Creek			**ANTC**
Kinneman Creek -- **KNC**	Upper Kinneman Creek		**UKNC**
			KCPT
	Lower Kinneman Creek		**LKNC**
Upper Upper Hagel Bed			**HGUU**
Hagel Bed -- **HAG**	Hagel A Bed -- **HAGA**	Hagel A1 Bed	**HGA1**
			HAPT
		Hagel A2 Bed	**HGA2**
			HGLP
	Lower Lower Hagel Bed		**HGLL**
			HGIB
	Hagel B Rider		**HGBR**
			HGRP
	Hagel B Bed -- **HAGB**	Hagel B1 Bed	**HGB1**
			HBPT
		Hagel B2 Bed	**HGB2**
C Seam -- **CSM**	Upper C Seam		**UCSM**
			CSPT
	Lower C Seam		**LCSM**
Tavis Creek Rider Seam			**TRID**
			TRPT
Tavis Creek Bed -- **TAV**	Upper Tavis Creek Bed		**UTAV**
			TVPT
	Lower Tavis Creek Bed		**LTAV**
			LTPT
Lower Lower Tavis Creek Seam			**LLTV**
Coal Lake Coulee Bed -- **CLC**	Upper Coal Lake Coulee Bed		**UCLC**
			CLPT
	Lower Coal Lake Coulee Bed		**LCLC**
Wellers Slough Bed -- **WEL**	Upper Wellers Slough Bed		**UWEL**
	Lower Wellers Slough Bed		**LWEL**

Figure 7. Generalized stratigraphic column and seam codes at Falkirk mine.

Table 1. Sampling locations in the Falkirk Mine during the April 7, 2016 sampling trip.

Sampling Point	Coal Seam	Layer	Location	Mining Status (Yes/No)	Collected from	Note
South Point (Close to RD15001C) - See Figure 6 South Point: N 1'218'17; E 18'231'94	Hagel A	Roof	1 ft.	Yes	Face	
		lignite	0~1 ft.	Yes	Drilling debris	
			1~2 ft.	Yes	Drilling debris	
			2~3 ft.	Yes	Drilling debris	
			3~4 ft.	Yes	Drilling debris	
			4~5 ft.	Yes	Drilling debris	
			5~6 ft.	Yes	Drilling debris	
			6~7 ft.	Yes	Drilling debris	Mixture of 2” coal and 10” floor
		Floor	0~1 ft.	Yes	Drilling debris	
			1~2 ft.	Yes	Drilling debris	
East Point 1 (Close to FA 14002C) - See Figure 5 East Point 1: N 1'740'01; E 18'562'13	Hagel A	Roof	2 ft.	Yes	Face	
			1 ft.	Yes	Face	
		lignite	0~1 ft.	Yes	Drilling debris	
			1~2 ft	Yes	Drilling debris	
			2~3 ft	Yes	Drilling debris	
			3~4 ft	Yes	Drilling debris	
			4~5 ft	Yes	Drilling debris	
			5~6 ft	Yes	Drilling debris	Mixture of 10” coal and 2” floor
		floor	0~1 ft	Yes	Drilling debris	
			1~2 ft	Yes	Drilling debris	
East Point 2 (Close to FA 14002C) - See Figure 5 East Point 2: N 1'756'43; E 18'562'82	Hagel B	roof	3 ft	Yes	face	
			2 ft	Yes	face	
			1 ft	Yes	face	
		lignite	0~1 ft	Yes	Drilling debris	
			1~2 ft	Yes	Drilling debris	
			2~3 ft	Yes	Drilling debris	
			3~4 ft	Yes	Drilling debris	
		floor	0~1 ft	Yes	Drilling debris	
			1~2 ft	Yes	Drilling debris	
			2~3 ft	Yes	Drilling debris	

Table 1 Continued

Sampling Point	Coal Seam	Layer	Location	Mining Status (Yes/No)	Collected from	Note
East Point 3 - See Figure 5	B rider	Roof	1	No	face	
		Lignite	Collected from pile	No	pile	
		floor	Collected from pile	No	pile	
	Hagel B	Roof	1	Yes	face	
		Lignite	Collected from pile	Yes	pile	
		floor	Collected from pile	Yes	pile	

3.1.3 Other Sampling

In addition to samples collected from Falkirk Mine and Coal Creek Station, other samples were supplied to UND for analysis in this project. These are as follows:

- North American Coal Corporation Freedom Mine (Operated by Coteau Properties Company)
    - Roof, Coal and Floor samples
- North American Coal Corporation Coyote Creek Mine (Operated by Coyote Creek Mining Company)
    - Roof, Floor, Ubeu Coal, Blackjack Coal samples
- Basin Electric Power Cooperative’s Antelope Valley Station
    - Fly ash and Bottom Ash samples
- Minnkota Power Cooperative’s Milton R. Young Station
    - Cyclone slag samples
- Harmon-Hanson Coal Zone (Samples provided by North Dakota Geological Survey)
    - Coal and Roof samples from exposed outcropping near Amidon, Slope County North Dakota
    - Additional samples of both lignite coals and clay-rich sediments from several locations in Western and Southwestern North Dakota.

3.2 Analytical Methods

The samples collected were analyzed in a variety of ways to determine bulk chemical composition and modes of REE occurrence. The primary analytical methods used are summarized in Table 2, with additional details in the following sections.

Table 2. Analysis methods

Category	Equipment	Function
Bulk chemical composition	ASTM standard analysis	Proximate analysis; Ultimate analysis; Ash composition
	X-ray Fluorescence	Bulk chemistry; major, minor and trace element
	Inductive Coupled Plasma-Mass Spectrometry	Abundance of trace elements including REE
REE modes of occurrence	Scanning Electron Microscopy	Morphological analysis – imaging and chemical composition of minerals
		CCSEM – chemical composition, size and associations (included or excluded relative to coal particles)
	Sequential Extractions	Quantitatively determine the modes of occurrence of the inorganic elements

The workhorse analytical method used in this project was inductively coupled plasma mass spectrometry (ICP-MS), which was used primarily to measure the abundance of REEs in the samples. A large amount of work was also done using scanning electron microscopy methods to determine REE modes of occurrence. Modes of occurrence were also determined using a sequential solvent extraction method. The following sections briefly describe each of the analytical methods used, along with equipment specifications.

3.2.1 Sample Preparation

Prior to analysis, to ensure complete homogenization of collected samples, the sample preparation methodology described below was adopted and maintained throughout the project. Complete homogenization of the samples was accomplished through grinding and/or mixing. During the homogenization of the samples, the materials were ground to -60 mesh to be ready for further sample preparation or analysis. ASTM standard methods (D2234/D2013) were followed. The collected samples were treated through the following steps.

1. Recording in inventory: each sample was assigned a unique identifier, and its sampling date and locations were recorded in the inventory sheet;
2. Drying: the portion of samples to be used for analysis was dried in a convection oven for 12 hours at 70°C;
3. Crushing and homogenization: the dried samples were crushed to -60 mesh size and mechanically mixed;
4. Grinding: the crushed samples were further ground to -200 or -325 mesh to meet the requirement of the analysis method;

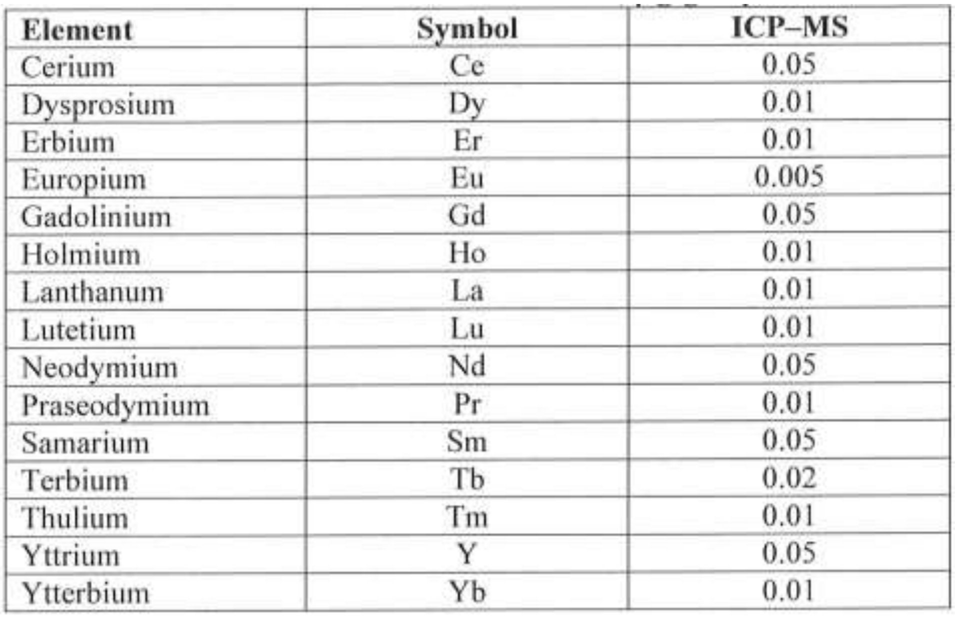
5. <u>Further Preparation</u>: additional preparation was performed based on the requirement of the analysis method.

3.2.2 Inductively Coupled Plasma Mass Spectrometry

Inductively coupled plasma mass spectrometry (ICP-MS) is currently the most widely utilized method to determine the concentration of trace elements in solid samples. The method has been described in detail by Bank and others (2016) [2], and has become the standard method for determination of the abundance of REEs in coal and coal-related samples. ICP-MS requires digestion of the solid samples prior to analysis in order to extract all of the REEs into a liquid solution. The digestion procedure is the critical piece for ensuring accurate measurement by ICP-MS. Testing in this project utilized two ICP-MS instruments, which are described below along with the UND-developed digestion procedure. The UND digestion and ICP-MS has proven to be highly accurate and repeatable based on analysis of Standard Reference Materials.

UND has two ICP-MS systems available. Both are the Thermo Electron iCAP SQ Quadrupole models from Fisher Scientific. The ICP-MS measures trace and major element analysis at the sub-part per trillion levels. Samples are prepared by a digestion method. To ensure total digestion and recovery of the trace elements, the digestion procedure recommended by the U.S. DOE NETL was used throughout the project. The sample is first ashed to remove carbon and then mixed with a borate fluxing agent (lithium metaborate and lithium tetraborate) and heated to 1000 – 1100°C to form a glass bead. The bead is then dissolved in dilute acid and brought to a known volume with reagent water. The solution is analyzed by ICP-MS and results are reported on a µg/g (ppmw) on a dry whole sample basis and ash basis. Detection limits using the above digestion procedure and instruments are provided in Table 3. Prior to beginning analysis under this project, and regularly during the project, the accuracy of the ICP-MS measurements was confirmed via analysis of Standard Reference Materials [3] and comparison of the measured versus certified values. At no point in the project did the analysis fall outside of an acceptable accuracy range.

Table 3. Detection limits in ppm using the UND digestion procedure and ICP-MS instruments



Element	Symbol	ICP–MS
Cerium	Ce	0.05
Dysprosium	Dy	0.01
Erbium	Er	0.01
Europium	Eu	0.005
Gadolinium	Gd	0.05
Holmium	Ho	0.01
Lanthanum	La	0.01
Lutetium	Lu	0.01
Neodymium	Nd	0.05
Praseodymium	Pr	0.01
Samarium	Sm	0.05
Terbium	Tb	0.02
Thulium	Tm	0.01
Yttrium	Y	0.05
Ytterbium	Yb	0.01

3.2.3 Scanning Electron Microscopy

Scanning electron microscopy with energy dispersive X-ray microanalysis (SEM-EDS) was used extensively throughout the project, in two modes of operation: i) manual mode for morphological analysis that includes imagining and point-by-point chemical analysis, and ii) computer controlled (CCSEM) mode to analyze thousands of mineral grains/particles in an automated mode. The manual SEM-EDS system was primarily focused on identifying REE-bearing minerals in the samples, as well as obtaining highly magnified images. The CCSEM method was focused on understanding elemental and mineral associations of REE-bearing mineral grains, as well as to determine size of the REE-bearing mineral grains. Prior to analysis, the coal and sediment samples were prepared by grinding if necessary. These ground samples were dried, mixed with molten carnauba wax, placed in a mold and allowed to harden. The samples were topped off with epoxy, cross-sectioned, and polished to a fine finish (1 µm) and coated with carbon for improved conductivity in the SEM. UND has two SEM systems that were used in the project, and are described below. Although both of these systems include chemical analysis, it is only considered a qualitative measurement.

FEI Quanta 650 FEG SEM: This is a field emission SEM capable of obtaining high-resolution data from almost any sample material. This system was purchased in 2014. The instrument is operable in both high and low vacuum modes. The x-ray microanalysis system consists of an energy dispersive Bruker QUANTAX 200 x-ray detector. The system is equipped with backscattered and secondary electron imaging. The backscattered imaging allows for discerning materials based on atomic number. The presence of higher atomic number materials increases the brightness and allows for easy identification and subsequent analysis. The instrument is able to achieve 1-3 nm resolution. The imaging software package allows for performing analysis of mineral association with coal and other minerals.

Hitachi Scanning Electron Microscope with an Energy Dispersive System (SEM/EDS). The SEM is equipped with backscattered and secondary electron detectors for imaging and is automated with energy dispersive x-ray detectors for chemical composition analysis. The system can perform computer controlled scanning electron microscopy (CCSEM) of particles to determine the size, composition (major, minor, trace elements), and mineral typing. The system is also equipped to perform included/ excluded analysis that provides information on association of minerals with coal particles or gangue materials. This instrument allows samples to be viewed at a high magnification and to acquire information about the coating thickness, porosity, adhesion, microstructure analysis, and elemental composition. To measure REE using this system, a modified operation is needed to increase spectra acquisition times in order to detect and measure REE peaks.

3.2.4 X-ray Fluorescence

Although not used extensively in this project, X-ray fluorescence (XRF) is a method to provide quantitative measurement and qualitative survey scans of the chemical composition of solid samples. UND has two XRF systems that were used in this project, as described below.

Rigaku Supermini 200 XRF: This XRF is a wavelength dispersive bench-top XRF able to provide low ppm detection limits for major, minor, and trace elements. The instrument is equipped with a 12 sample autosampler and can analyze either solids or liquids. The software allows rapid analysis of known and unknown samples. The system provides the ability to perform quantitative analysis and qualitative survey scans to identify the presence of elements.

Bruker Tracer IV Geo handheld XRF: The Tracer IV Geo is equipped with a large area silicon drift detector as well as a vacuum system for the analysis of lighter elements. This portable instrument can be taken to field sites. The flexibility of the system also allows for analysis of bulk samples (e.g., coal core samples, clays and other sediments for major elements) in the field without any sample preparation.

3.2.5 ASTM Analysis Methods

In addition to the above analytical methods, for some of the samples, standard ASTM measurements were made for proximate (ASTM D3172) and ultimate (ASTM D3176) analysis and ash composition (ASTM

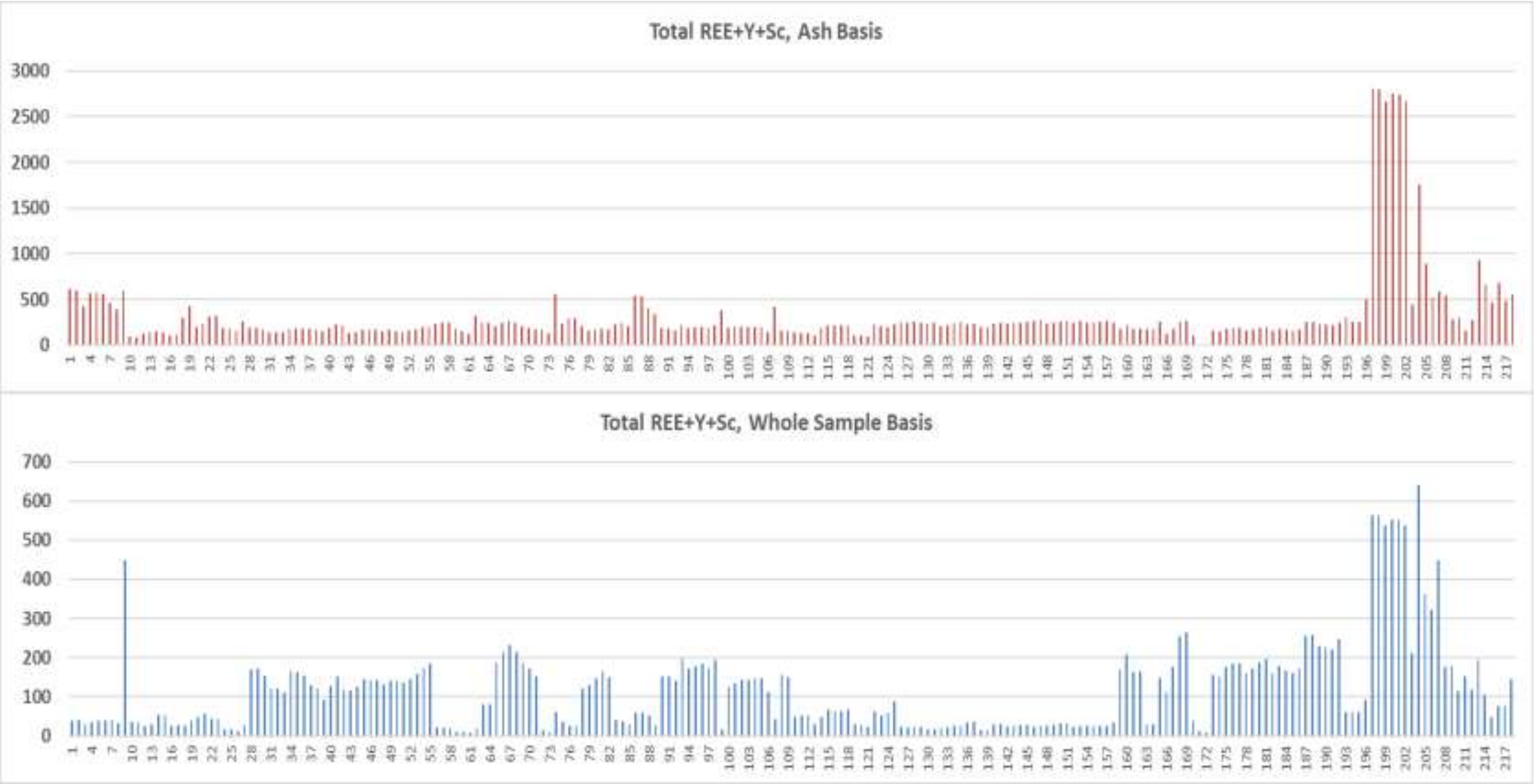
D4326-13). However, these were used for a very limited number of samples and were primarily to generate mass balances for laboratory extraction testing described in Chapter 3 of this report. Float-sink analyses was also conducted on one sample (ND15RE-6A-1) to identify the mass of sample and the distribution of the elements within the specific gravity fractions.

3.3 Characterization Results

The characterization results are presented in the following sections.

3.3.1 Overall ICP-MS Results and REE Classification of Samples

Appendix B contains the complete data for all of the ICP-MS analysis done in this project. Overall, 222 raw samples (including several repeats to establish instrument precision) were analyzed to determine REE abundance by ICP-MS, and the results are shown in Figure 8 on both an ash basis and whole sample basis (dry). The figures have random sample numbers and are only meant to provide an indication of the ranges of total REE content in the samples. Additional discussion is provided for specific sample sets in later sections of this Chapter.


Total REE+Y+Sc, Ash Basis

Total REE+Y+Sc, Whole Sample Basis

Figure 8. Results of ICP-MS for total REE content (includes duplicates)

A series of figures has been prepared that relate the ash content of the samples and a number of parameters that describe the distribution of the individual REEs within the total sample. This is an important data reduction technique because it provides information on the modes of occurrence of the individual REEs (i.e. affinity or enrichment of particular or groups of REE in organic-rich or mineral-rich samples). Figure 9 shows all of the data from Figure 8, with the ratio of LREE/HREE plotted against ash content of the sample. The data clearly shows that the ratio decreases in the low ash samples (i.e. the coal samples). This is consistent with information in the literature that suggests the HREE have higher affinity to organic matter than the LREE.

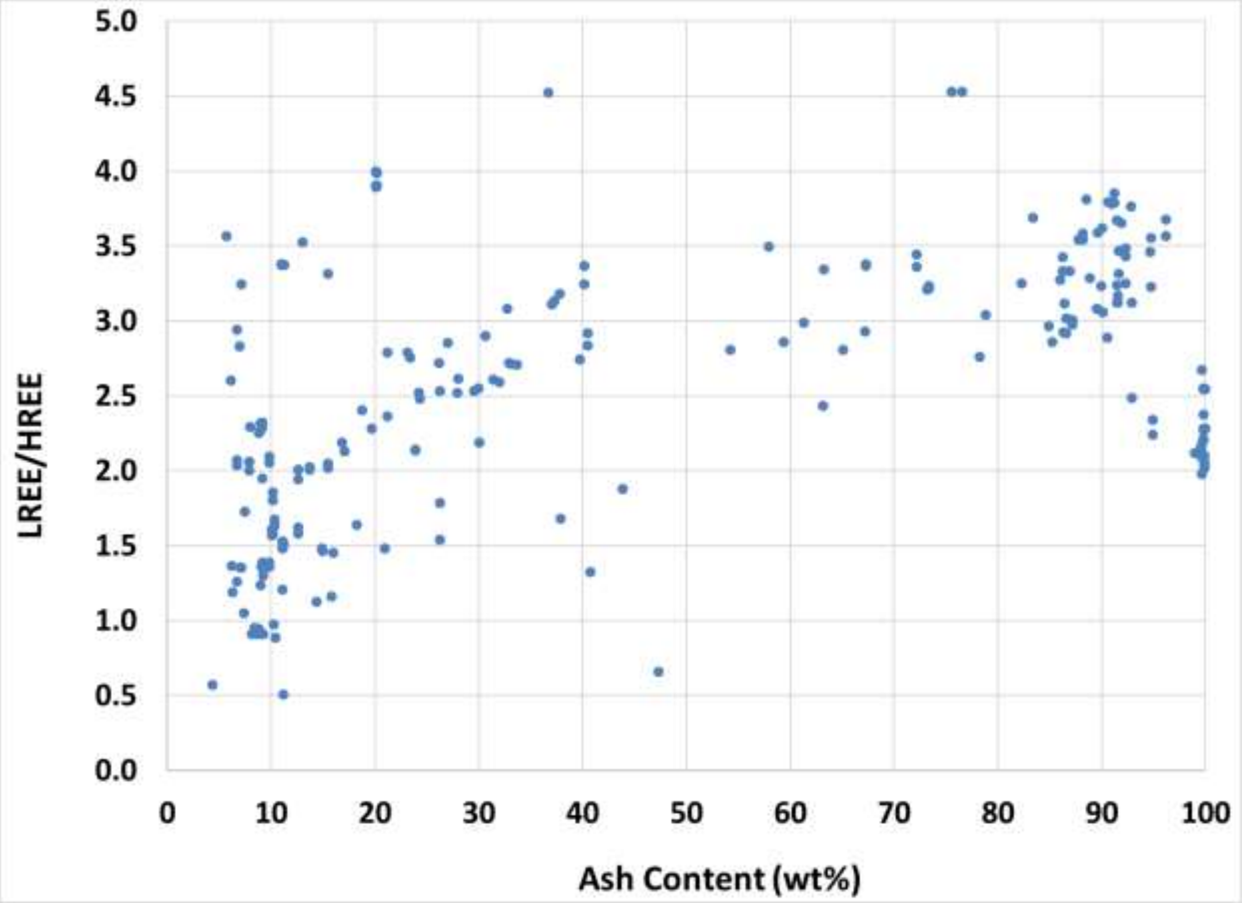


Figure 9. Ash content versus LREE/HREE for all samples analyzed in the project

Using a similar approach, the individual REEs have been broken out in light (La, Ce, Pr, Nd, Sm), medium (Eu, Gd, Tb, Dy, Y) and heavy (Ho, Er, Tm, Yb, Lu) molecular weights and the total REE (ash basis) in each molecular weight grouping have been normalized to the earth's upper continental crust (UCC) averages [5] and have been plotted against ash content of the sample, as shown in Figure 10. Here, the data clearly shows that the medium and heavy REEs have higher enrichment in low ash materials, as compared to the lights, whereas in the high-ash samples, the data shows a similar distribution to earth's crust (i.e Y-axis value of about 1.0). This also provides evidence of the heavier REEs having a higher affinity to organic matter. On the right hand side of the plot for the samples with ~100% ash, there is an increase in the enrichments. However, these are all samples of combustion ash, and accordingly would have the same (or similar) distribution as the raw coal samples.

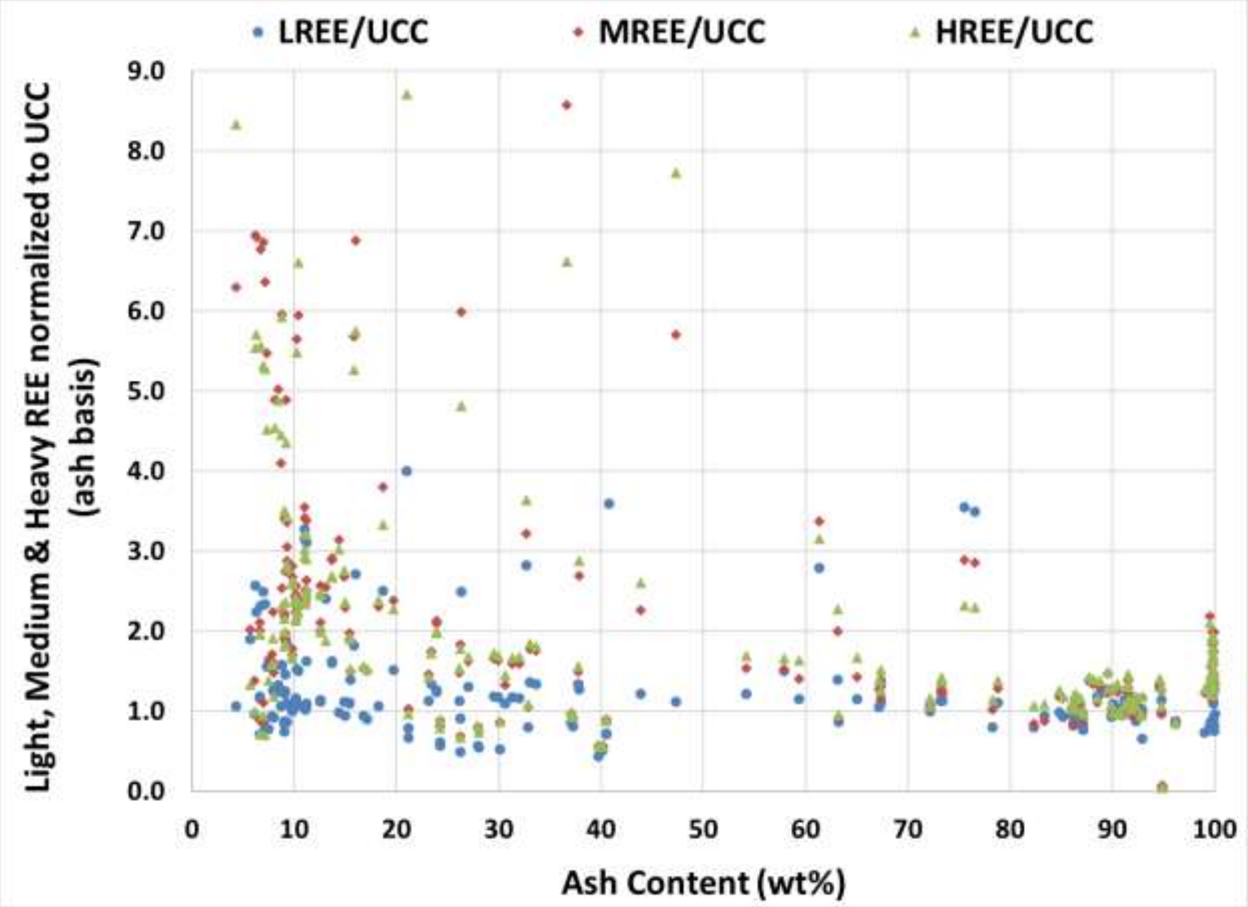


Figure 10. Total light, medium and heavy REEs normalized to crustal averages plotted against ash content for all samples analyzed

Figure 11 shows yet another similar set of data, but this time with a plot of total REE content (ash basis) versus the ash content in the sample. This data shows that the highest concentrations of REEs are actually found in the lower ash content samples. Note that this data excludes the samples provided by NDGS, several of which have significantly higher total REE content.

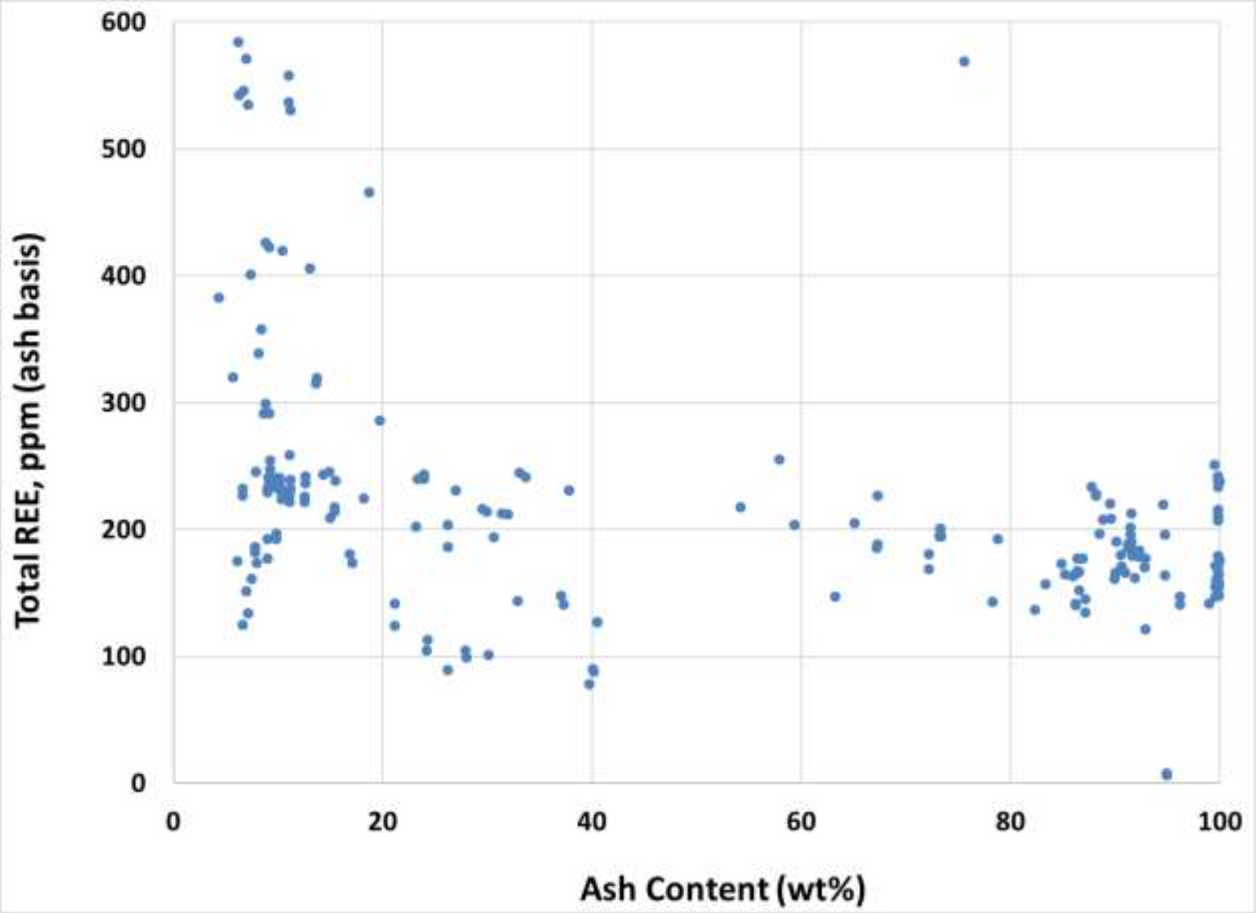


Figure 11. Total REE (ash basis) versus ash content of the sample for all samples analyzed (does not include NDGS samples)

Seredin and Dai (2012) [6] have previously developed a method to determine the suitability/favorability of a particular resource for REE recovery based on the content of critical REEs within the materials. Their method involved plotting the ratio of critical to excessive REEs on the x-axis and the percentage of critical REEs in the total REE on the y-axis. Their method grouped the materials into three clusters, with unpromising materials in the lower left portion of the plot, promising materials in the middle, and highly promising materials in the upper right hand portion. Using their methods, the entire ICP-MS dataset obtained in this project was plotted and compared against the clusters established by Seredin and Dai (2012), as shown in Figure 12. With the exception of one sample that was in Cluster III (B Rider Coal), all of the samples fit into Cluster II (promising). However, it is important to note that the Seredin and Dai (2012) method also included a total REE content threshold that was needed to qualify. Therefore, the analysis presented in Figure 12 is only meant as an indicator of the relative distribution of the critical REEs within each sample, and does not consider the total REE content. Using this same method, the outlook coefficient was plotted against ash content of the samples in Figure 13. Again, there is a clear trend that has the low ash samples being enriched in the critical REEs.

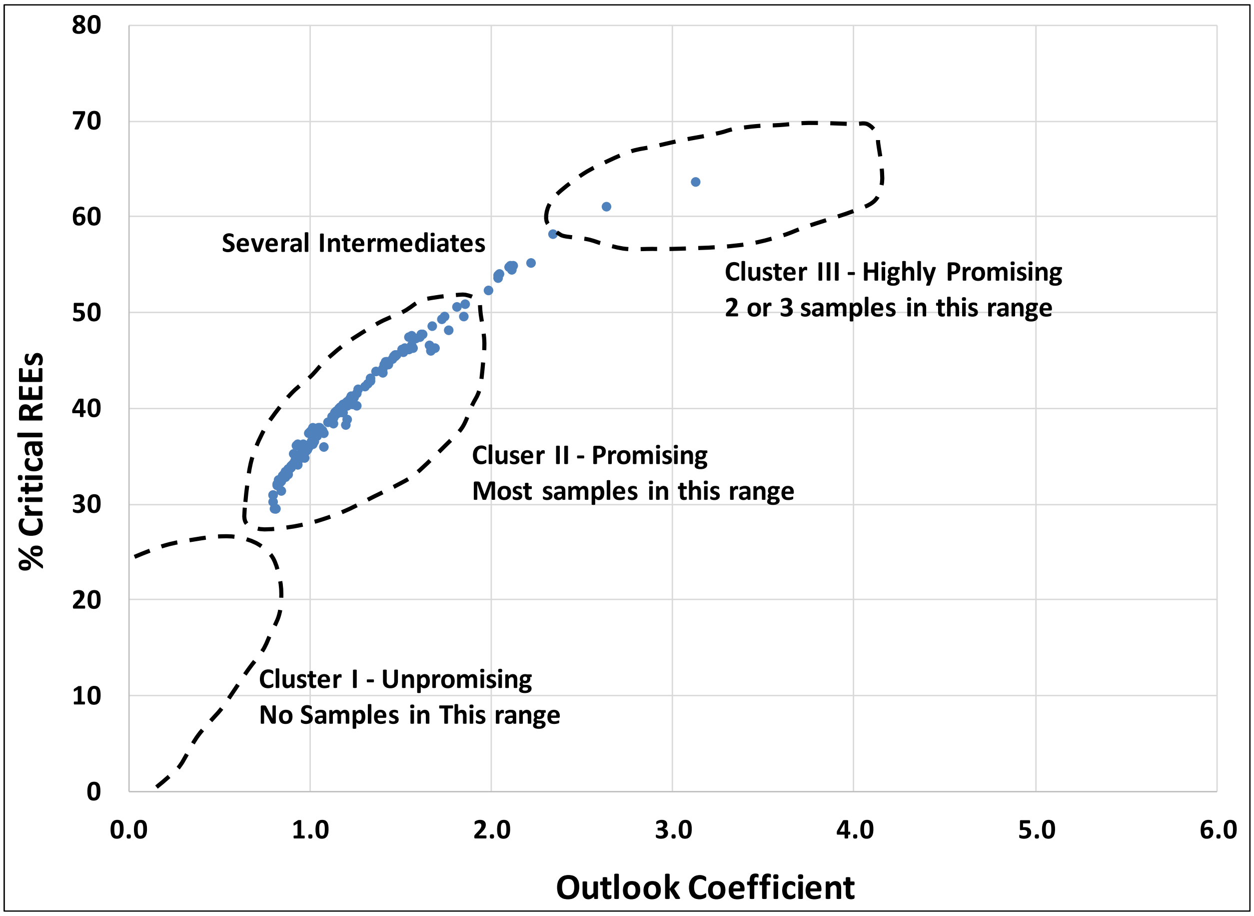


Figure 12. Method of evaluating the relative content of critical REEs within the material - Seredin and Dai method (2012) [6]; x-axis represents ratio of critical to excessive REE; y-axis represents percentage of critical REE within total REE

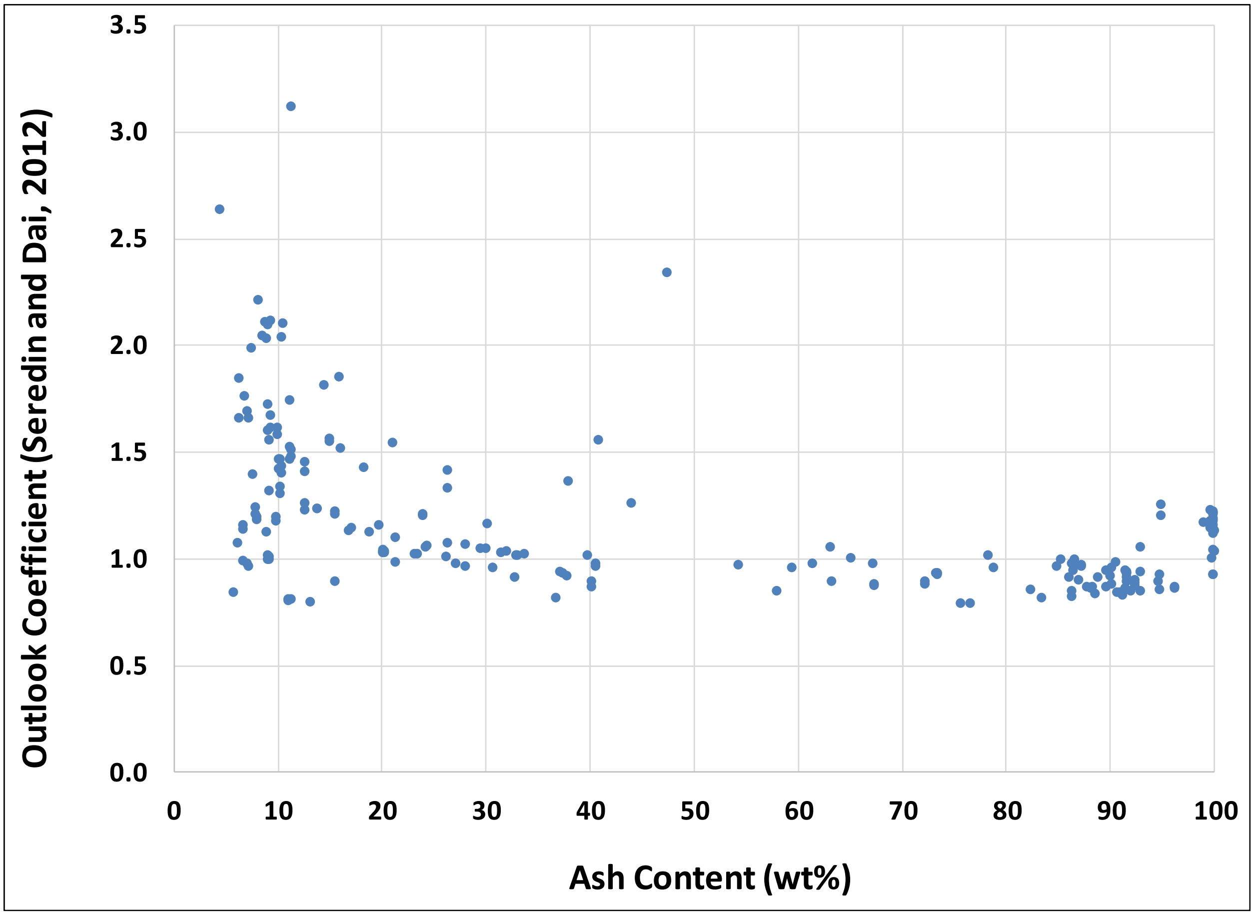


Figure 13. Seredin and Dai (2012) [6] outlook coefficient vs. ash content of the sample

Also following the method developed by Seredin and Dai (2012) several of the samples have been normalized to the concentration of REEs in earth's upper continental crust (UCC) and plotted against molecular weight to see the shape of the REE distribution. Seredin and Dai (2012) previously described L-type, M-type and H-type distributions (i.e. light, medium, heavy molecular weight) using this approach. Figure 14 shows the UCC-normalized REE distribution plots for several samples of coal, and one roof sediment sample from the Harmon-Hansen outcropping in Slope County, ND. The B Rider coal exhibits a strong H-type distribution. The Hagel B coal exhibits a moderate H-type distribution. The other samples show M-type distributions. Under the M-type, the samples exhibit the swell-like subgroup centered on Eu that was described by Seredin and Dai (2012). The other anomalies are for Y, as both minima and maxima. Both of the Harmon-Hansen samples exhibit pronounced Y-minima, while the Hagel B shows a pronounced Y-maxima.

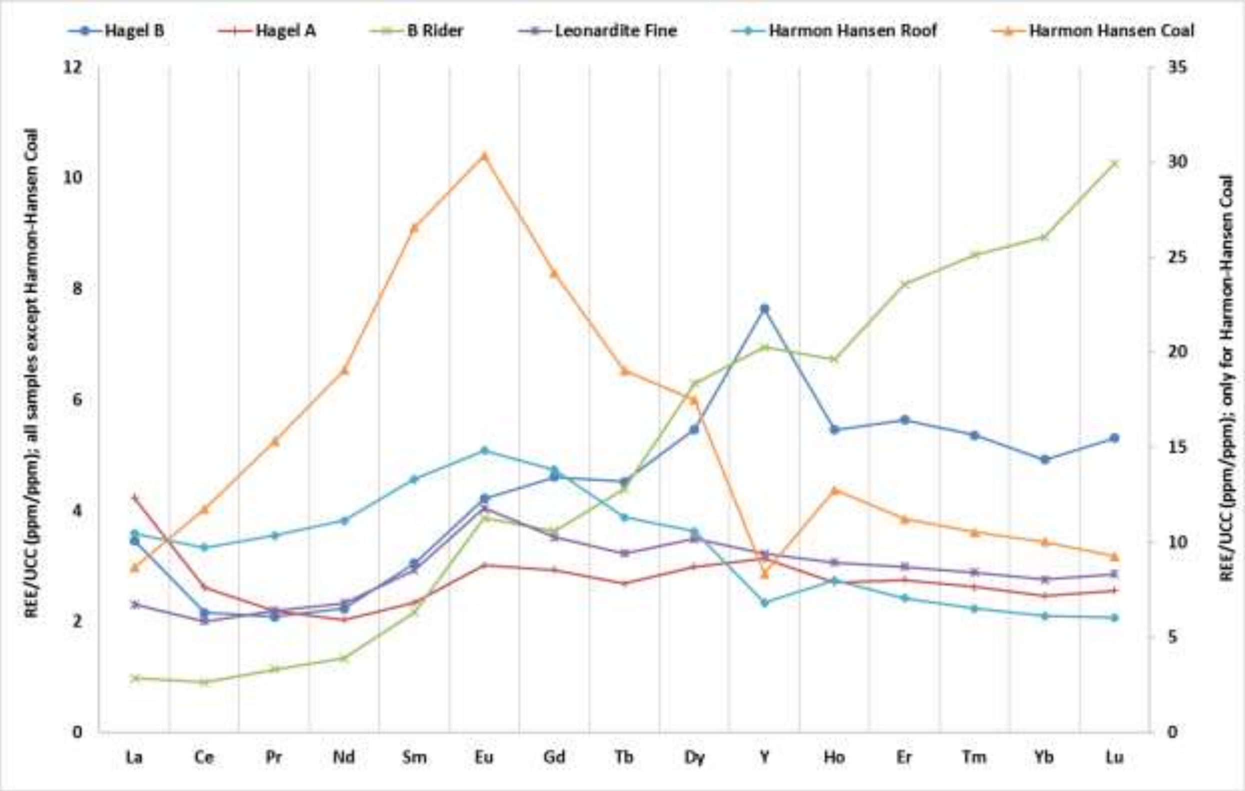


Figure 14. UCC-normalized REE distribution for selected samples

This same type of analysis method has been plotted in Figure 15 for some of the selected roof/floor samples from Falkirk Mine that had highest REE content. Samples were selected from roof and floor sediments for each of the major stratigraphic sections sampled in the mine. Overall, the data shows an M-type distribution, with the swell-like Eu peak. However, interestingly, in each case, the roof sediments for the stratigraphic sections are depleted in the HREEs compared to the floor sediments. Additionally, with the exception of the B Rider sediments (very close distributions), the LREEs are enriched in the roof materials compared to the floor materials. Combined, this data suggests the mode of accumulation in the coals was by preferential leaching of the HREEs from the clays and subsequent adsorption into the coal/organic matter, an assertion that is substantiated by the enrichment in the coal for these particular elements. Further, the B Rider sediments show the overall highest enrichment in the HREE, which is consistent with the observation of enrichment in these elements in the B Rider coal seam (Figure 14). The explanation for the specific enrichment in the HREE for the B Rider coal is likely due to the chemistry of the REE source materials (tuffaceous) and the surface water chemistry present during infiltrational accumulation of the REEs.

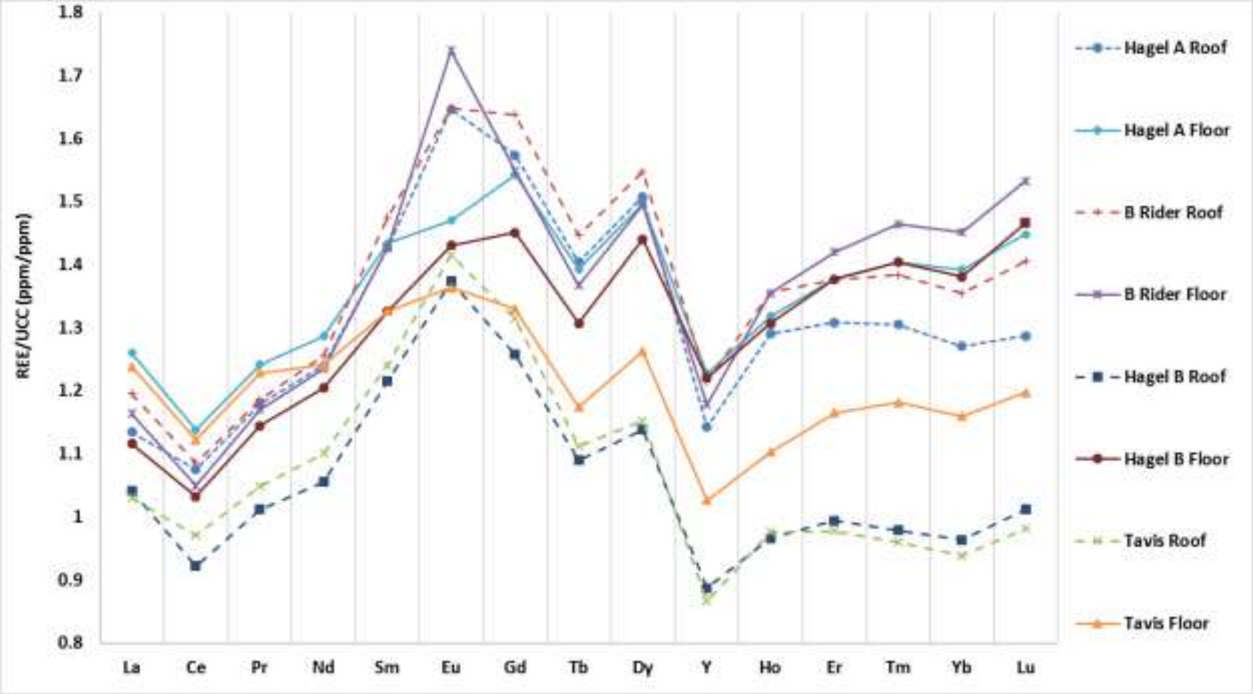


Figure 15. UCC-normalized REE distribution for selected roof/floor samples from Falkirk Mine

3.3.2 Rare Earth Elements Content at Falkirk Mine

The total REE content in samples collected from the Falkirk Mine is presented as the stratigraphic column on both a whole sample and ash basis in Figure 16 and Figure 17, respectively. Based on some prior work by Karner and others (1984, 1986) [7, 8] looking at REEs in North Dakota lignite and associated sediments, it was expected that the REEs would be concentrated in the margins of the seams in the roof/floor clays and in the coal partings. Based on these results, while the previous work has been verified on a whole sample basis, an alternative finding is that on an ash basis, in each case shown in Figure 17, the ash basis REE content is higher in certain locations in the coal seams sampled than in the roof or floor sediments. This was an unexpected finding, and ended up being a primary motivator for the REE recovery methods developed in this work (details in Chapter 3).

Overall, Hagel B showed the best combination of high REE content (ash basis), and uniform distribution. Although one Hagel A sample had high REE content, it was not repeatable with the other samples, and thus it was inferred that the distribution was not as uniform as Hagel B. This was the primary motivator for the choice of sampling locations for the several hundred pound samples of Hagel B that were collected on the second sampling trip to Falkirk Mine. The content in these larger samples was determined after taking seven approximately 100 pound samples over a distributed area at each location. Each sample was ground and homogenized separately prior to analysis, with results shown in Table 4. For East Point 2, a range of approximately 420 to 600 ppm was measured, which was slightly higher than the range of about 390 to 460 ppm for the East Point 3 location. For East Point 2 there is reasonably good distribution of REE-rich Hagel B coal.

Table 4. REE content in large samples of Hagel B collected from Falkirk Mine

Sample Location/Seam	Sample #	Whole Basis, ppm	Ash Basis, ppm
East Point 2 Hagel B	1	40	605
East Point 2 Hagel B	2	31	421
East Point 2 Hagel B	3	36	570
East Point 2 Hagel B	4	38	572
East Point 2 Hagel B	5	40	558
East Point 3 Hagel B	1	40	460
East Point 3 Hagel B	2	33	387

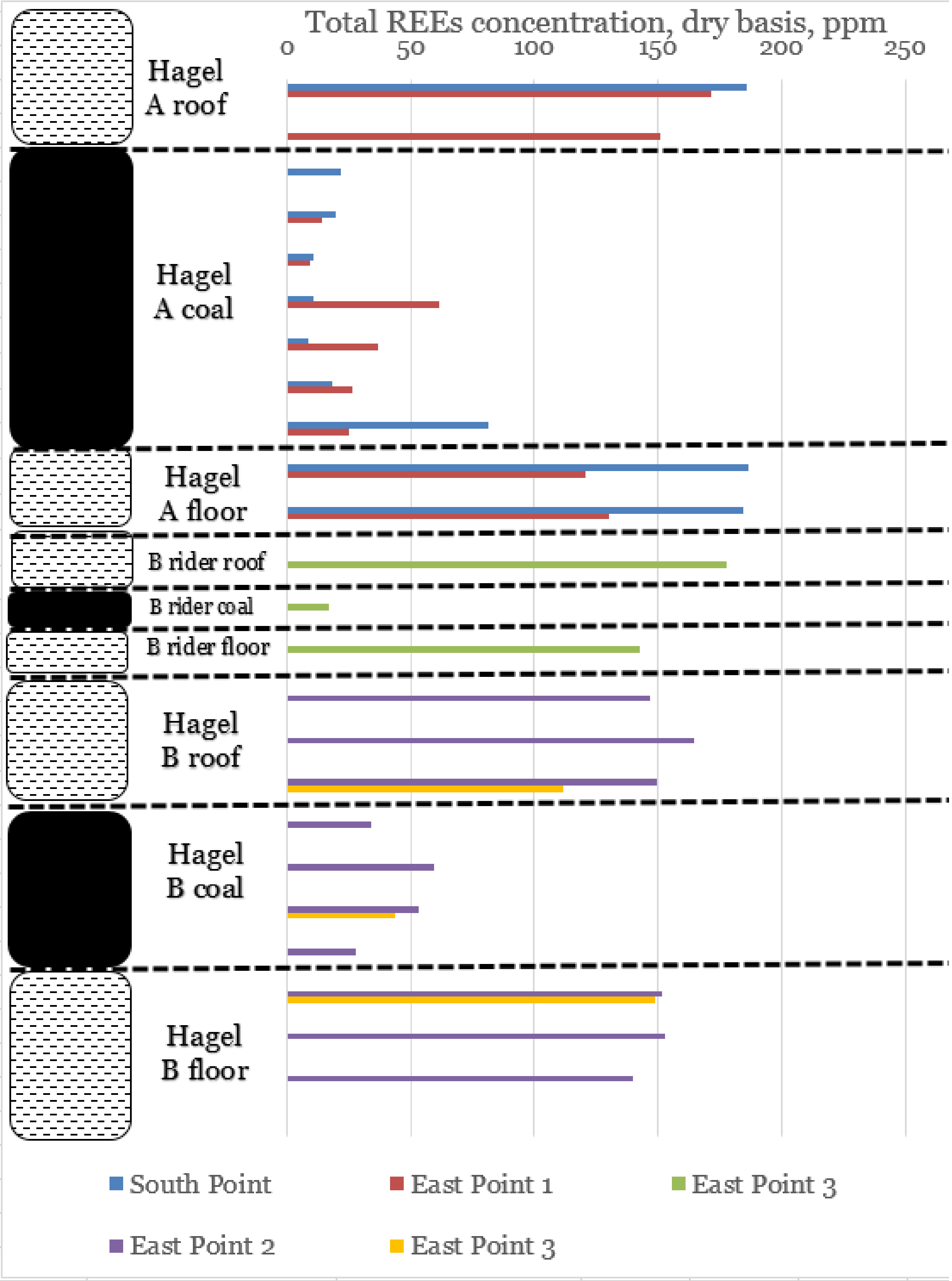


Figure 16. Total REE content in Falkirk Mine stratigraphic column as sampled (whole sample basis)

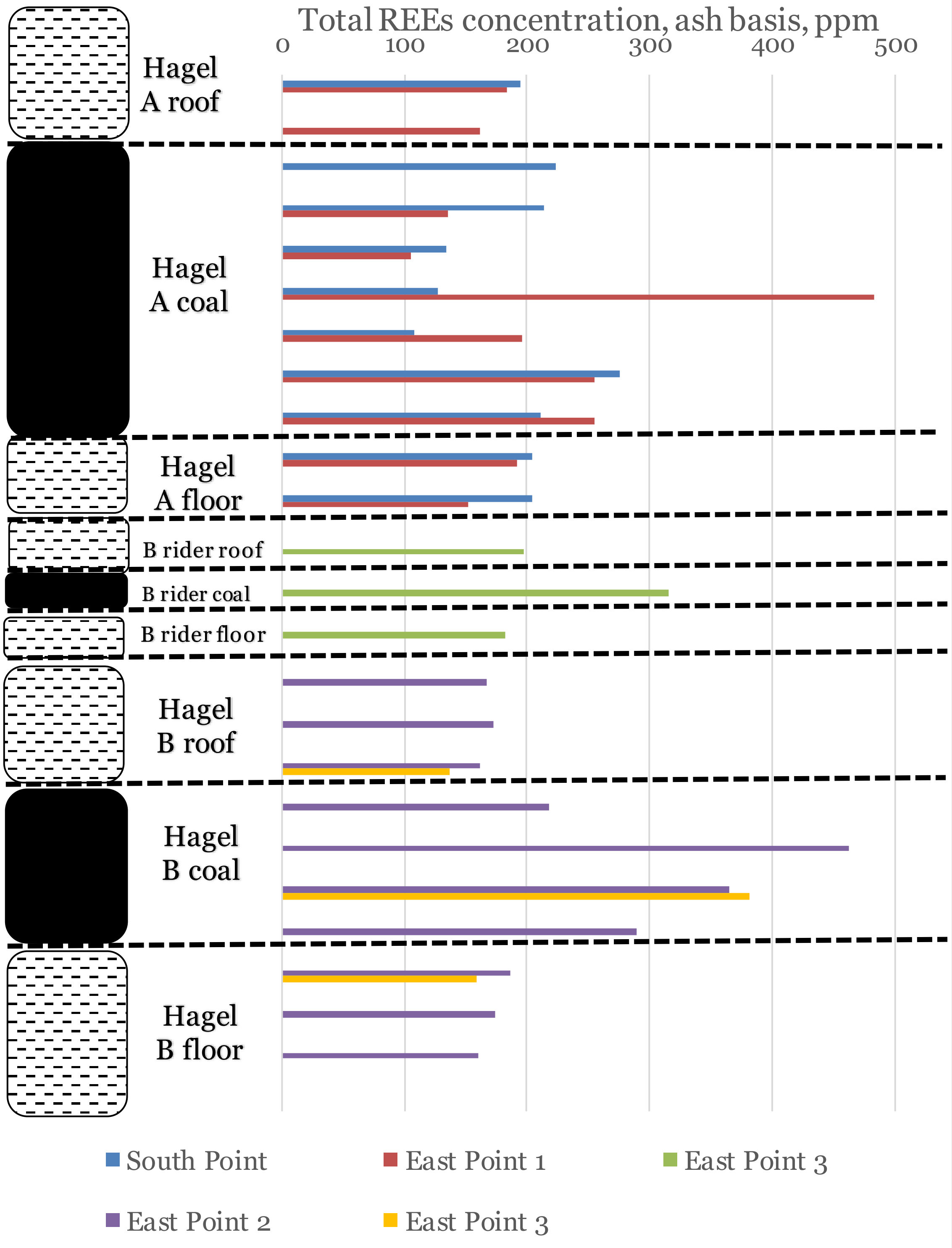


Figure 17. Total REE content in the Falkirk Mine stratigraphic column as sampled (ash basis)

3.3.3 Rare Earth Element Content in Coal Creek Station Samples

As described previously, multiple streams associated with the GRE DryFining™ process at Coal Creek Station were sampled along with the combustion bottom ash and fly ash and the FGD scrubber solids to determine the partitioning of the REEs within the plant. The average REE content for the samples analyzed are provided in Table 5. Although samples from the pulverizer feed, the raw coal, and the dryer segregated coal were collected, they were not analyzed in this project. The FGD scrubber solids had very low REEs, and is not discussed hereafter.

Table 5. REE content in samples from Coal Creek Station

Sample Location	REE Content (whole sample, ppm)	REE Content (ash, ppm)
Air Jig Rejects[1]	39	122
Coal Dryer Fines[1]	66	214
Air Jig Clean Coal[2]	25	243
Fly ash[3]	242	242
Bottom ash[4]	266	267
Pulverizer Rejects[4]	40	100
FGD Solids[5]	10	10

1. Average of 8 analyses 2. Average of 32 analyses 3. Average of 7 analyses

4. Analysis of 1 sample 5. Average of 2 analyses

Based on the initial expectations for this project, the findings in Table 5 were unexpected, particularly as it relates to the samples making up the DryFining™ process. On an ash basis, the air jig reject stream has about half the REE content of the air jig clean coal stream. This is exactly opposite of what was expected. Further, it was found that the dryer fines (another high ash material) also has lower REE content than the clean coal samples. According to discussion with GRE, the air jig primarily focuses on rejection of the heavy mineral content (i.e. pyrite) that contains a large fraction of the sulfur and mercury found in the raw coal. Therefore, based on these results, it would appear that the REEs are not associated with the pyrites or other high density minerals.

In regards to the other samples shown in Table 5, several samples were taken for the clean coal and the fly ash in order to establish a better concept of the variability of the fuel at Coal Creek Station. It was observed that the REE content in the coal (ash basis) and fly ash match up very nicely, as would be expected given the refractory nature of the REEs. Somewhat interesting, although difficult to draw a conclusion due to only one sample being analyzed, is that the bottom ash exhibited the highest content of REE in any of the samples analyzed at Coal Creek Station. Because the bottom ash is likely to contain the low melting point phases, this may point towards possible modes of occurrence of the REE in the coal.

3.3.4 Rare Earth Element Content in Samples from Other Locations

As mentioned previously, although the focus of this project was on the Falkirk Mine and the Coal Creek Station, several additional samples were provided by others for analysis in the project. Table 6 shows the content of REEs in samples from the Freedom Mine, the Coyote Creek Mine as well as the Antelope Valley Station and the Milton R. Young Station. These values are quite similar to the Falkirk Mine and the Coal Creek Station.

Table 6. REE content in samples from other mines and power plants in North Dakota

Sample ID	Sample Location/Description		Whole Basis, ppm	Ash Basis, ppm
IES 16138	Freedom Mine coal	Freedom Mine	35	244
IES 16139	Freedom Mine roof	Freedom Mine	169	183
IES 16140	Freedom Mine floor	Freedom Mine	208	220
IES 16141	Coyote Creek roof	Coyote Creek Mine	163	180
IES 16142	Coyote Creek floor	Coyote Creek Mine	165	178
IES 16143	Coyote Creek Ubeu Coal	Coyote Creek Mine	30	177
IES 16144	Coyote Creek Blackjack Coal	Coyote Creek Mine	148	255
IES 16145	Fly Ash	Antelope Valley St.	113	121
IES 16146	Bottom Ash	Antelope Valley St.	176	176
IES 16151-62	Cyclone slag	Milton R. Young St.	173	174

Samples of Leonardite, which is an oxidized lignite coal, were acquired from Leonardite Products LLC, which operates a Leonardite mine near Williston, North Dakota. Three samples of their bulk packaged products were obtained that included, Leonardite coarse (+11 mesh), Leonardite 11 (-11 mesh), and Leonardite Fine (62% -270 mesh). The Leonardite was considered a target in this project because literature has suggested that its surface properties make it particularly adsorptive due to presence of oxygen and other chemical functional groups, and thus may be enriched in REEs [9]. Table 7 provides the results, and shows that the fine product has the highest REE content, and on a whole sample basis is actually higher than any coal sampled at Falkirk, Freedom or Coyote Creek Mines. Because these samples were bulk materials prepared at Leonardite Product LLC’s plant, it is likely that higher REE content exists in the mine. This makes it an interesting target for continued and future work.

Table 7. Content of REE in Leonardite materials (Leonardite Products LLC)

Sample Description	Whole Basis, ppm	Ash Basis, ppm
Leonardite Coarse	62	257
Leonardite 11	60	306
Leonardite Fine	93	497

As part of a separate effort, the North Dakota Geological Survey (NDGS) [10, 11], has been sampling lignite coal and related materials primarily in western and southwestern North Dakota and analyzing for REE content. In total, 17 unique samples have been provided to UND for testing/analysis in this project. The REE data and associated metrics is provided in Table 8. Several of these samples have exceptionally high REE content, both on a whole coal and ash basis, as indicated in the table, and values that are well above anything found in other locations in the State. More specifics and a general discussion of selected samples are provided in the following sections.

Samples 6A, 6A-1 and 6A-2 were all taken from an exposed outcropping in Slope County. They were sampled from a coal seam of about 12-18 inch thickness. The 6A sample (lowest ash) is representative of the entire coal seam. The 6A-1 represents the roof material, and the 6A-2 is an intermediate material taken at the margin of the coal/roof. On a whole coal/sample basis, each of these is approximately an order of magnitude higher in total REE than the samples from Falkirk Mine. The roof sample has the lowest REE content, with the margin sample being highest and the coal in the middle. The coal sample has the most favorable LREE/HREE ratio, as well as the most valuable REE content ($/MT).

Sample 6AA is also very interesting. While it has a relatively high ash content (47%), it has a peculiar distribution of the REE, being very enriched in the HREE, with an LREE/HREE ratio of 0.5. Further, even though the total REE is about one-third of the 6A sample, the $/MT value is nearly the same. A somewhat similar behavior exists with sample 3A, although the HREE enrichment is not as exceptional as 6AA. However, the 3A sample has a higher total REE content at over 300 ppm on a dry coal basis. It also has the highest content of Y, Dy, Ho, Er, Tm, Yb, and Lu of any sample analyzed in Phase 1.

Of the very low ash samples, 7E is perhaps the most interesting. Although it has a relatively modest total REE of about 76 ppm (dry whole coal), it is also highly enriched in the HREE and particularly the critical REEs (as identified by Seredin and Dai, 2012). This sample has the highest outlook coefficient (3.1) of any sample analyzed in Phase 1, with 63% of the REE content classified as critical REE. It has an ash basis REE content of 680 ppm, as well, which means that based on the minimum threshold established by Seredin and Dai (2012) of 800 ppm (oxide basis) content, that it would classify as a Cluster III – highly promising – coal ash for REE recovery.

The 6A, 6A-1 and 6A-2 samples were received from NDGS early on in the project, and thus these samples were available for laboratory extraction/concentration testing in Phase 1. The other samples were not received until May 2017, and thus no extraction/concentration testing has yet been performed.

Table 8. REE content and metrics for 17 NDGS samples analyzed in Phase 1

Sample ID	Ash (wt%)	Sc	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	TREE (dry whole, ppm)	LREE/ HREE	TCREE (dry whole, ppm)	$/MT	TREE (ash, ppm)
6A	25.2	38.4	45.6	63.4	180.2	26.1	119.3	29.0	6.4	22.0	2.9	14.7	2.5	6.3	0.8	5.3	0.7	563.7	2.9	188.9	598.5	2234.6
6AA	47.3	38.0	67.0	16.5	29.5	3.8	15.7	3.9	1.4	5.3	1.1	8.5	2.2	7.9	1.3	8.8	1.6	212.4	0.5	93.6	579.5	448.8
6A-2	36.7	27.6	54.1	104.4	231.5	28.7	114.3	24.4	5.3	20.5	2.8	14.1	2.4	6.0	0.8	4.6	0.6	642.2	3.6	190.6	436.9	1752.0
3A	40.7	25.6	87.0	39.9	87.6	10.7	43.8	10.2	2.7	12.8	2.3	14.9	3.3	10.0	1.4	9.3	1.5	363.2	1.1	150.7	400.5	891.6
3C	61.3	21.9	42.1	49.3	103.1	12.3	49.5	10.3	2.5	9.7	1.4	8.0	1.6	4.6	0.6	4.1	0.6	321.7	2.3	103.5	340.6	524.8
6A-1	76.5	19.5	38.9	81.3	161.4	19.0	75.1	15.5	3.4	13.6	1.9	9.6	1.7	4.2	0.6	3.5	0.5	449.5	3.6	128.8	307.2	587.3
15G	32.7	15.7	22.4	26.2	57.7	6.9	25.9	4.9	1.0	4.2	0.7	4.1	0.9	2.7	0.4	2.7	0.4	176.8	2.2	54.0	241.9	540.7
1Q	63.1	15.1	28.1	27.2	53.0	6.4	24.0	4.7	1.0	4.4	0.7	4.7	1.0	3.2	0.5	3.3	0.5	177.9	1.8	58.5	233.4	281.8
17B	37.9	12.6	22.3	13.7	28.7	3.6	14.4	3.2	0.8	3.8	0.6	3.9	0.8	2.5	0.4	2.4	0.4	114.0	1.3	42.0	193.7	301.0
BE	92.3	12.6	18.9	26.0	49.8	5.7	21.2	3.9	0.7	3.4	0.5	3.4	0.7	2.2	0.3	2.2	0.4	151.8	2.4	44.7	193.3	164.5
10G	43.9	11.3	22.3	16.0	31.6	4.0	15.5	3.3	0.8	3.4	0.5	3.6	0.8	2.5	0.4	2.6	0.4	119.0	1.4	42.8	173.6	271.1
7F	21.0	9.2	45.9	20.0	50.3	6.7	27.1	6.1	1.4	7.3	1.2	7.6	1.6	4.4	0.6	3.7	0.6	193.7	1.3	83.2	146.7	924.3
5F	16.0	8.8	25.8	14.5	25.8	2.9	11.4	2.5	0.7	3.3	0.5	3.5	0.7	2.2	0.3	1.9	0.3	105.2	1.2	42.0	136.8	659.1
5E	10.3	5.6	13.5	4.3	9.0	1.2	4.9	1.3	0.4	1.7	0.3	2.0	0.4	1.3	0.2	1.2	0.2	47.5	0.8	21.1	85.8	462.1
7E	11.2	5.4	31.7	5.7	9.9	1.2	5.4	1.6	0.5	2.7	0.5	4.0	1.0	2.9	0.4	2.7	0.4	76.2	0.5	42.1	85.4	680.5
9H	15.8	5.3	20.3	7.7	16.4	2.2	9.2	2.4	0.6	3.0	0.5	3.3	0.7	2.0	0.3	1.7	0.3	75.9	1.0	33.9	83.3	479.6
10	26.3	3.3	37.7	21.3	40.7	4.5	16.7	3.2	0.8	4.5	0.7	4.7	1.1	3.1	0.4	2.5	0.4	145.7	1.5	60.7	55.4	554.5

NOTE: $/MT is value of REEs per metric ton of sample using data available in Appendix C (Phase 2 Renewal Package Instruction document) – uses metal prices with the exception of Eu (oxide); no pricing available for Ho, Tm, Yb or Lu.

3.3.5 Modes of Rare Earth Element Occurrence in Roof/Floor Sediments

From literature, it appears to be a consensus that REEs can be present in host and basement rocks associated with coal seams either in various mineral forms or as adsorbed ions. The following section provides results of work done, primarily using SEM methods to elucidate the modes of REE occurrence in the roof and floor sediments associated with the Hagel bed at Falkirk Mine in North Dakota and other selected locations.

3.3.5.1 Manual SEM-EDS

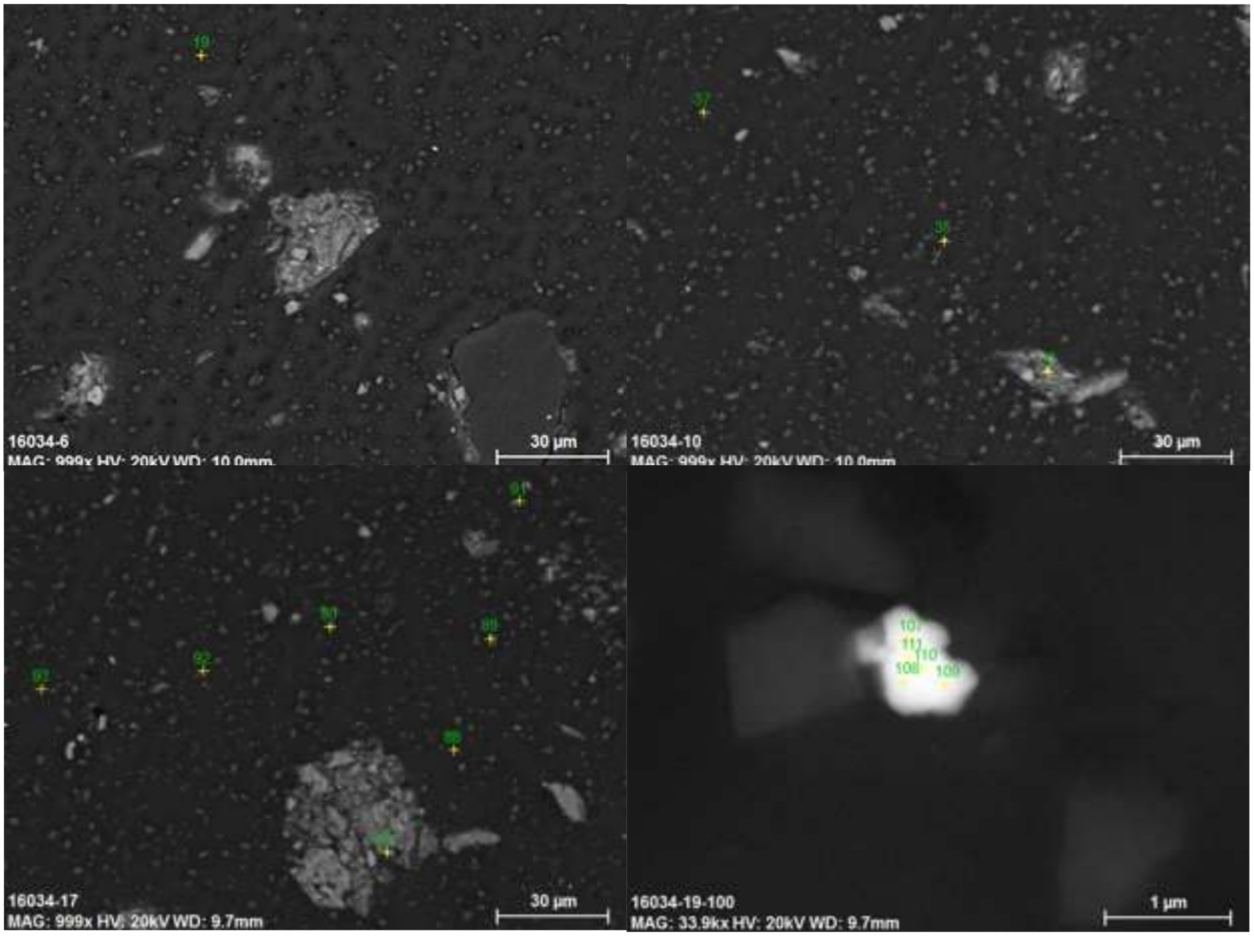
Overall, three sediment samples were analyzed by SEM-EDS in manual mode to find and type various REE-bearing mineral grains in the samples. The samples tested included:

- IES16034 – Hagel A Floor
- IES16140 – Freedom Mine Floor
- IES16141 – Freedom Mine Roof

Despite extensive searching, REE-bearing minerals were only detected in the Hagel A floor sample. The series of figures and associated tables presented in the following section show the results. Figure 18 shows the SEM images and accompanying point analyses for multiple particles with Y (points 19, 35, 88, 90, 91-93) and Ce (points 107-111). For the particles with Y, the major association is with zirconium and oxygen, with lower amounts of chlorine. For the particles with Ce, the major associations are again zirconium, oxygen and chlorine, but also iron. The content of silicon is fairly low in these analysis points, so it is difficult to ascertain the exact mineral form. However, from literature, eudialyte ($Na_4(Ca,Ce)_2(Fe^{2+},Mn^{2+},Y)ZrSi_8O_{22}(OH,Cl)_2$) and zircon ($(Zr,REE)SiO_4$) are two zirconium mineral forms that are known to contain REEs. REE association with zirconium and niobium (also contained in several particles) is an indicator of tuffaceous origin.

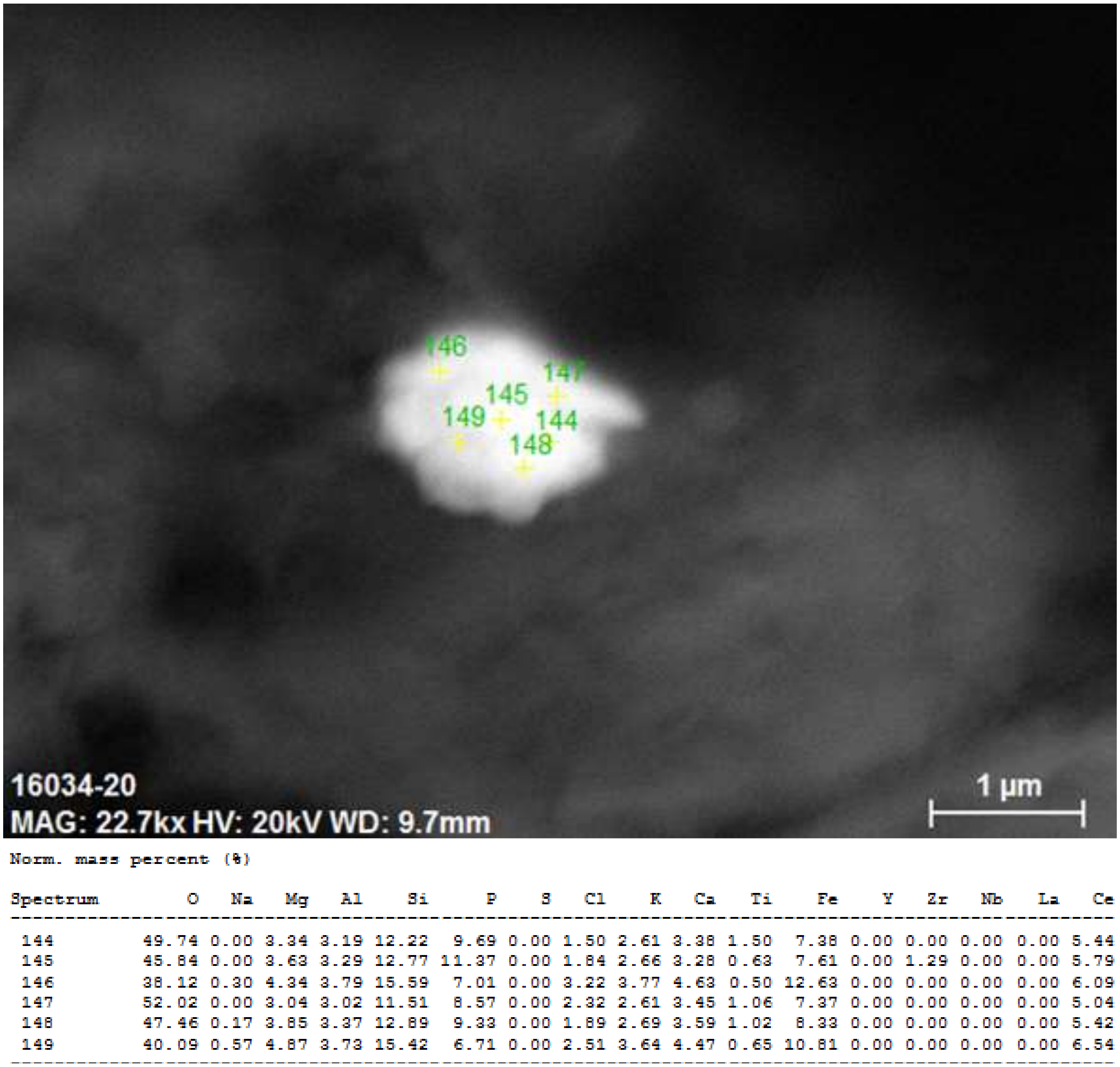
Figure 19 shows the analysis of a single mineral grain containing Ce that appears to be associated with Si, P, Fe, Mg, Al, Ca, K, Cl, Ti and oxygen. This is a much more complicated mineral form than the ones identified in Figure 18. However based on information in literature, this is potentially steenstrupine mineral ($Na_{14}Ce_6Mn_2Fe_2(Zr,Th)(Si_6O_{18})_2(PO_4)_7*3H_2O$) or other form of aluminosilicate clay.

The exact mineral form in either case is not clear given these results, but it would appear that the two major forms of REEs in this particular sample (and likely the other roof/floor sediments as well) are zirconium minerals and clays.



Spectrum	O	Na	Mg	Al	Si	P	S	Cl	K	Ca	Ti	Fe	Y	Zr	Nb	La	Ce
19	39.94	0.07	0.03	0.07	0.00	0.00	0.00	3.41	0.11	0.19	0.00	0.14	9.82	45.17	0.54	0.00	0.00
35	29.27	0.00	0.00	0.07	0.09	0.00	0.00	2.49	0.17	0.19	0.11	0.16	13.88	52.90	0.40	0.28	0.00
88	32.16	0.00	0.13	0.13	0.00	0.00	0.00	3.77	0.21	1.13	0.00	0.18	10.65	51.63	0.00	0.00	0.00
90	48.44	0.10	0.14	0.06	0.06	0.00	0.00	2.44	0.00	0.07	0.00	0.26	8.15	39.79	0.40	0.00	0.11
91	47.12	0.08	0.00	0.01	1.21	0.00	0.00	1.91	0.15	0.64	0.00	0.12	10.45	38.12	0.19	0.00	0.00
92	36.17	0.00	0.00	0.23	0.00	0.00	0.00	4.71	0.00	0.27	0.09	0.00	13.46	44.77	0.08	0.07	0.15
93	35.24	0.00	0.04	0.22	0.00	0.00	0.00	5.49	0.02	0.29	0.00	0.00	9.10	49.59	0.00	0.00	0.00
107	42.40	0.00	0.03	0.11	0.06	0.00	0.00	3.71	0.07	0.30	0.00	1.30	0.00	49.78	0.77	0.00	1.48
108	35.70	0.00	0.00	0.13	0.33	0.00	0.00	3.75	0.07	0.31	0.08	1.04	0.00	55.81	1.25	0.00	1.53
109	42.62	0.00	0.01	0.11	0.18	0.00	0.00	3.75	0.09	0.23	0.00	1.32	0.00	49.85	0.54	0.00	1.30
110	40.04	0.00	0.05	0.15	0.16	0.00	0.00	3.32	0.02	0.26	0.00	1.12	0.00	52.65	0.80	0.00	1.44
111	36.49	0.00	0.01	0.00	0.05	0.00	0.00	4.10	0.00	0.21	0.00	1.45	0.00	54.93	1.05	0.00	1.70

Figure 18. SEM-EDS result showing REE-bearing zirconium minerals



```
Norm. mass percent (%)

Spectrum          O    Na    Mg    Al    Si     P     S    Cl     K    Ca    Ti    Fe     Y    Zr    Nb    La    Ce
----------------------------------------------------------------------------------------------------------------------

 144          49.74 0.00 3.34 3.19 12.22  9.69 0.00 1.50 2.61 3.38 1.50  7.38 0.00 0.00 0.00 0.00 5.44
 145          45.84 0.00 3.63 3.29 12.77 11.37 0.00 1.84 2.66 3.28 0.63  7.61 0.00 1.29 0.00 0.00 5.79
 146          38.12 0.30 4.34 3.79 15.59  7.01 0.00 3.22 3.77 4.63 0.50 12.63 0.00 0.00 0.00 0.00 6.09
 147          52.02 0.00 3.04 3.02 11.51  8.57 0.00 2.32 2.61 3.45 1.06  7.37 0.00 0.00 0.00 0.00 5.04
 148          47.46 0.17 3.85 3.37 12.89  9.33 0.00 1.89 2.69 3.59 1.02  8.33 0.00 0.00 0.00 0.00 5.42
 149          40.09 0.57 4.87 3.73 15.42  6.71 0.00 2.51 3.64 4.47 0.65 10.81 0.00 0.00 0.00 0.00 6.54
----------------------------------------------------------------------------------------------------------------------
```

Figure 19. SEM-EDS result of Ce-bearing mineral

3.3.5.2 CCSEM

In addition to the manual SEM-EDS analysis, several samples were analyzed via computer controlled SEM with the goals of identifying mineral/element associations in REE-bearing particles and also the size of REE-bearing particles. The method used involved an automated analysis of 1000 particles/grains in each sample for both size and chemical composition. The data was then ordered according to the total REE content and the particles with highest REE content were grouped and the elemental and mineral associations evaluated. Elemental analysis was completed on the following samples:

- IES16015 – Hagel A Roof
- IES16016 – Hagel A Floor
- IES16017 – Hagel B Floor
- IES16018 – Hagel A Roof

- IES16020 – Hagel B Roof
- IES16021 – Hagel B Floor
- IES16056 – B Rider Roof

The elemental associations for all of the Hagel A and Hagel B roof and floor samples were very similar, with the primary associations being similar to those observed in Figure 19 above. An example is provided for sample IES16018 in Figure 20. The B Rider roof sample was somewhat different, with the primary associations appearing to be aluminosilicate and aluminophosphate minerals, as shown in Figure 21.

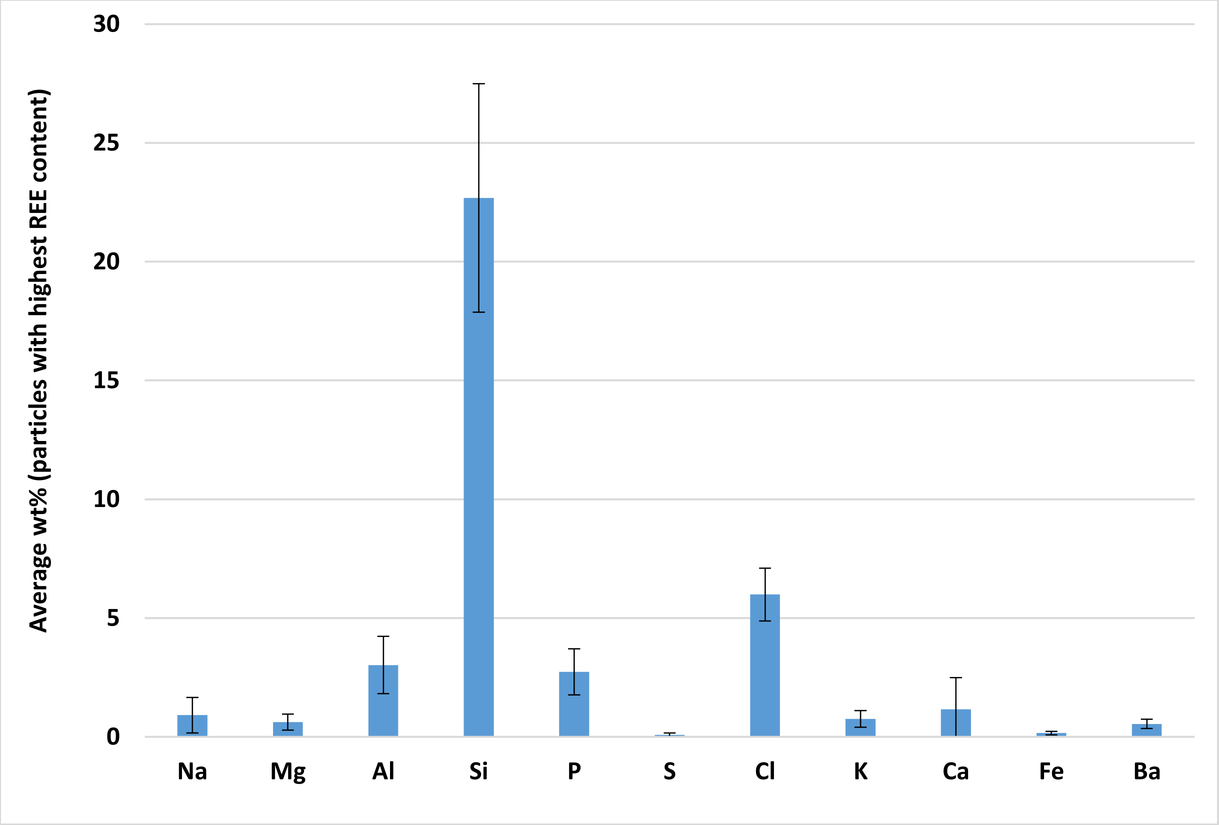


Figure 20. CCSEM analysis results for REE-bearing particles in Hagel B floor sample

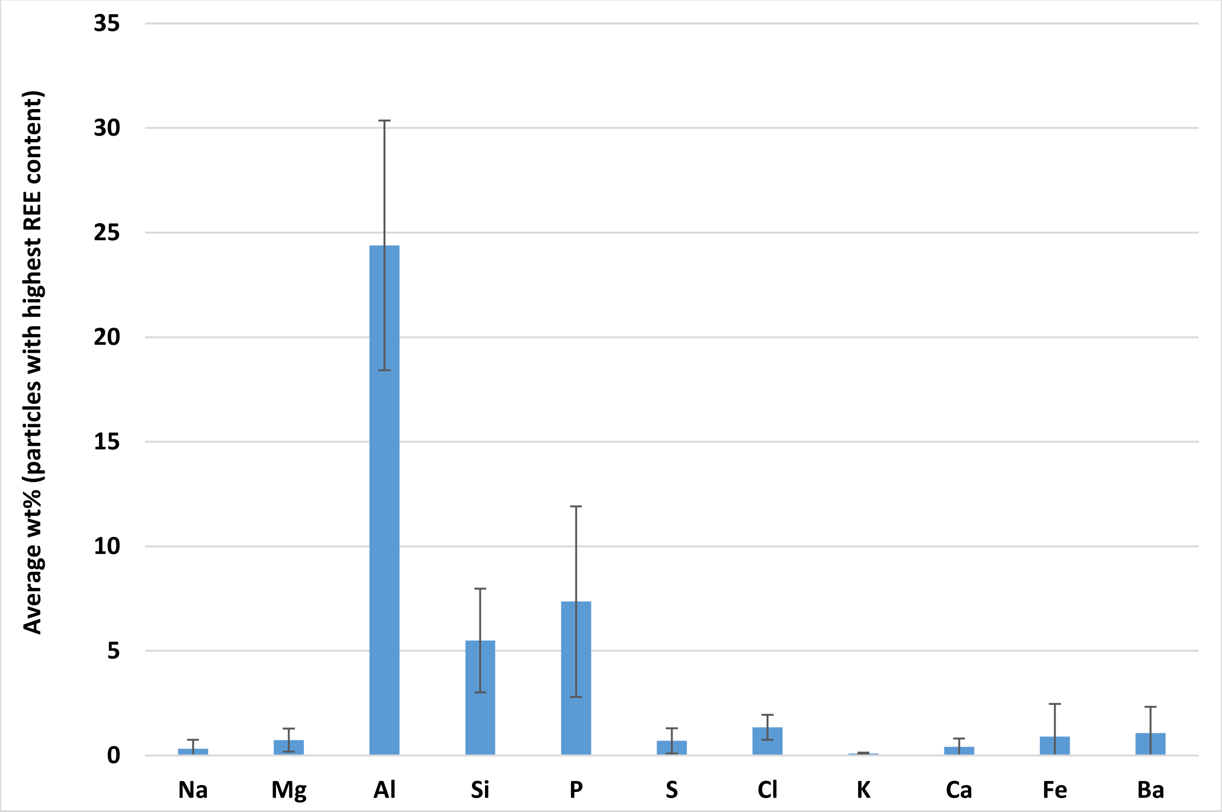


Figure 21. CCSEM analysis results for REE-bearing particles in B Rider roof sample

In addition to the elemental analysis, a proprietary mineral typing software program was available to the project via Microbeam Technologies Incorporated of Grand Forks, North Dakota. Using the CCSEM elemental association results, the Microbeam software was able to type the minerals, as shown in Figure 22 for Hagel A roof and floor samples (IES16015 and IES16016, respectively). The results show that the major REE-bearing mineral forms are clays and other silicates and aluminosilicates. Unclassified minerals do not fit in any of mineral types known by the Microbeam software.

Lastly, the CCSEM system was used to measure the size of REE-bearing mineral grains in the samples. The results show that the vast majority of the REE-bearing minerals are very fine, typically less than four microns in diameter. An example of the analysis results are shown in Figure 23 for a Hagel A roof sample. In this sample, approximately 90-95% of the REE-bearing mineral grains were smaller than four microns, with more than 60% being smaller than two microns.

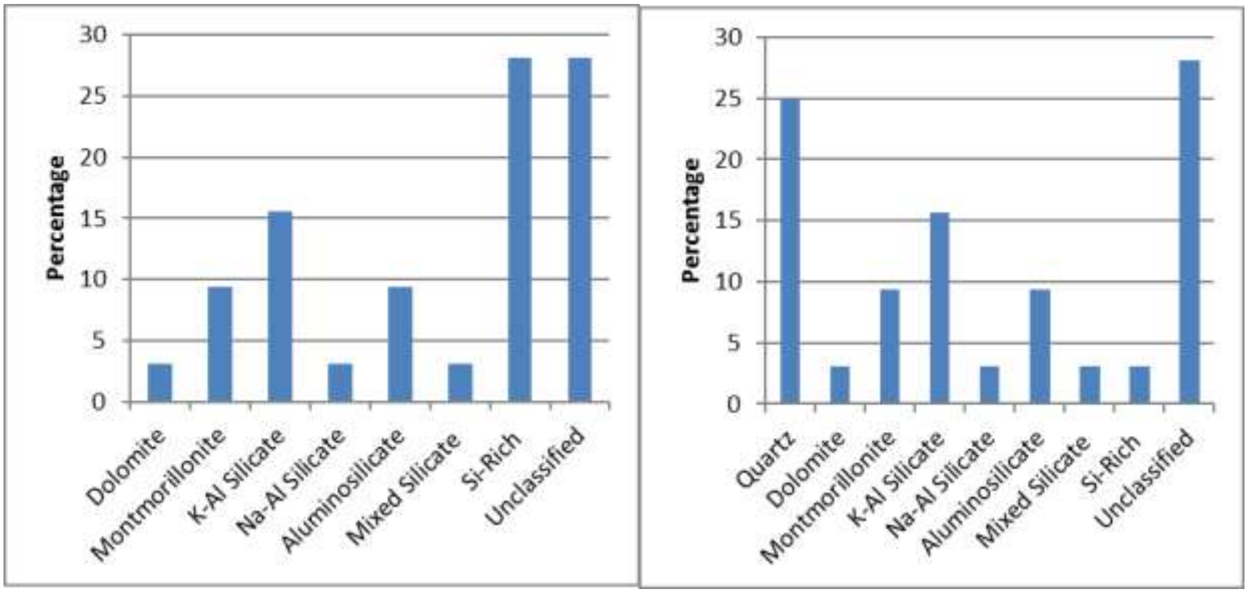


Figure 22. Mineral analysis for REE-bearing particles from CCSEM for Hagel A roof (left) and Hagel A floor (right)

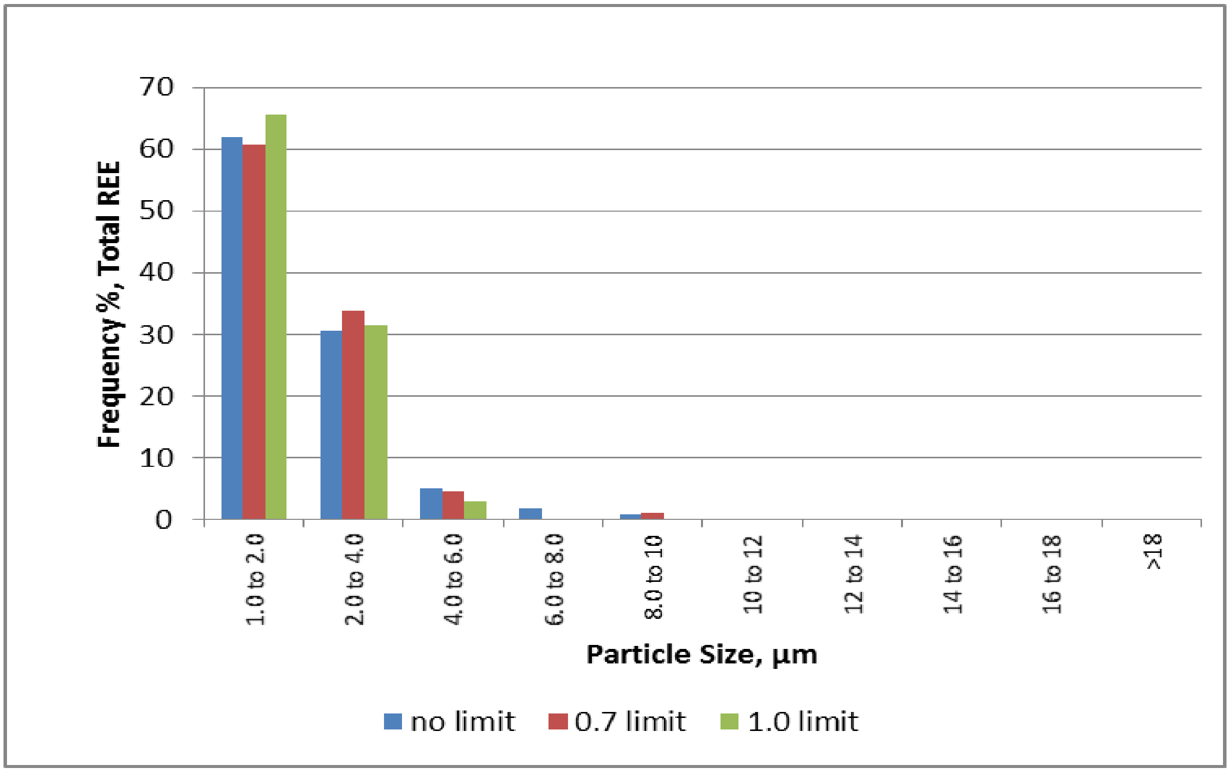


Figure 23. Size distribution of REE-bearing mineral grains based on CCSEM analysis for Hagel A roof sample - limits refer to analysis detection limits placed on the REE content of the REE-bearing mineral grains

3.3.6 Modes of Rare Earth Element Occurrence in Coal Samples

As noted above in the discussion of REE distribution classification in Section 3.3.1, the modes of occurrence of the REEs in the coal are likely to be significantly different than in the host and basement rocks for the seams. Two main methods were used in this project to identify REE modes of occurrence in the North Dakota lignites – SEM and sequential extractions. Each is discussed separately with results in the following sections.

3.3.6.1 Manual SEM-EDS and CCSEM

Manual SEM-EDS was performed on the following lignite coal samples:

- IES16040 – Hagel A coal
- IES16050 – Hagel B coal
- IES16051 – Hagel B coal
- IES16060 – Hagel B coal

However, no REEs were detected in any of these samples despite extensive efforts. CCSEM was performed on one coal sample (IES16033 – Hagel A coal). The results of elemental analysis are plotted in Figure 24, and show that the REEs are associated with many of the major species in the coal, most notably Si and Ba. In general, this type of analysis proved inconclusive for the raw lignites. The difficulty in detecting REEs in the raw coals by SEM methods, combined with literature, and the inferences described previously in Section 3.3.1, suggests that much, or a majority of the REEs in raw North Dakota lignite are associated with the organic matrix, essentially making them invisible to SEM methods.

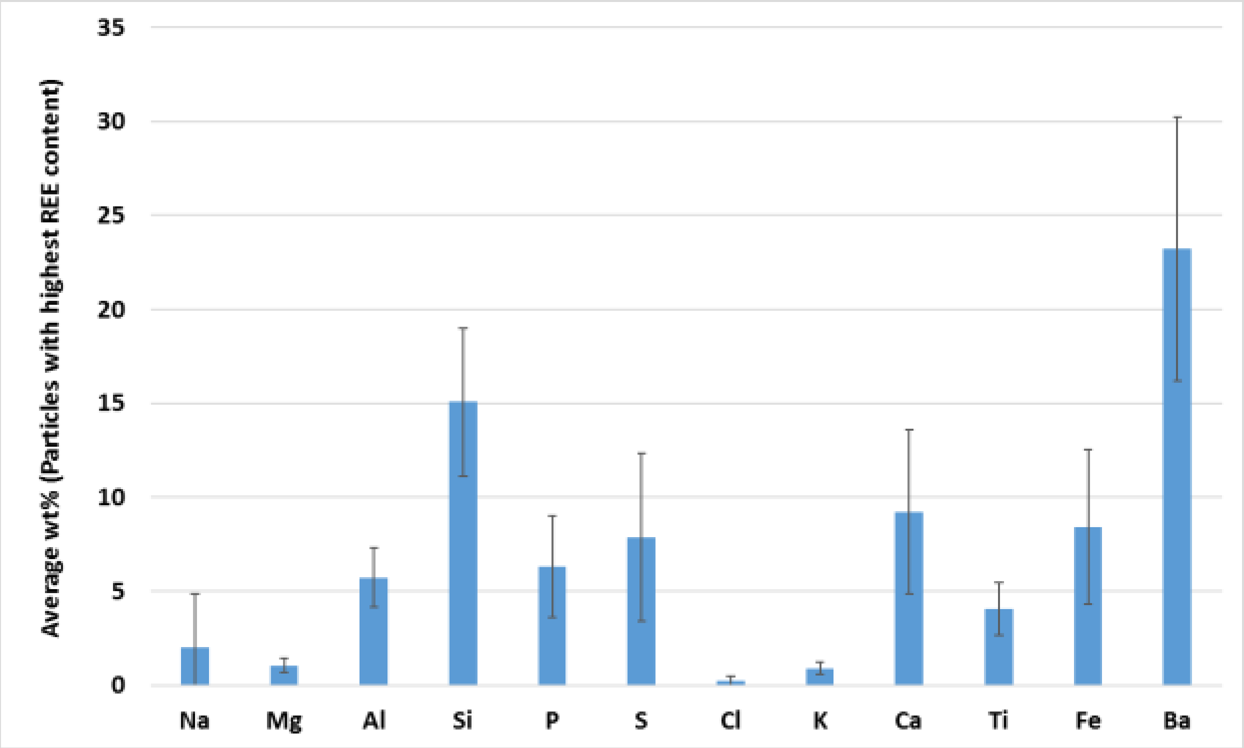


Figure 24. CCSEM analysis for REE-containing particles in Hagel A coal sample

3.3.6.2 Sequential Extractions

Due to the inability of SEM to detect REE minerals in the coals, a sequential extraction procedure developed at UND for low-rank coals was used as a quantitative method to determine REE modes of occurrence in the lignites. The method involves a series of sequential solvent extractions that target specific trace element associations in low-rank coals based on their solubility in water, ammonium acetate and hydrochloric acid. Overall four coals were evaluated as shown below:

- IES16050 – Hagel B
- IES16051 – Hagel B
- IES16060 – Hagel B
- ND15RE-6A – Harmon-Hansen

The results of the testing for each of the coals is shown in Table 9. The results are fairly consistent for each of the coals tested. The majority of the REEs were extracted by HCl, indicating their presence as organic complexes, or in acid soluble minerals such as carbonates, sulfates and some oxides. In each of the samples there was some small amount of either water soluble or ion-exchangeable REEs, with IES16051 having the highest fraction of these forms. Overall, these results show that about 80-95% of the REEs are extractable by HCl. The remaining REEs would be associated in non-soluble minerals, such as clays, silicates, sulfides or others.

Table 9. Results of chemical fractionation testing for four ND lignite coals

Element	16050				16051				16060				ND15RE-6A			
	% by H_2O	% by NH_4OAc	% by HCl	% Residual	% by H_2O	% by NH_4OAc	% by HCl	% Residual	% by H_2O	% by NH_4OAc	% by HCl	% Residual	% by H_2O	% by NH_4OAc	% by HCl	% Residual
Y	0.0	0.0	89.5	10.5	15.4	0.0	71.5	13.1	0.0	0.1	93.5	6.4	12.1	0.0	78.9	8.9
La	0.0	0.1	95.7	4.2	20.4	0.0	70.2	9.4	0.3	12.3	74.2	13.2	7.2	0.0	86.2	6.6
Ce	0.0	2.1	92.5	5.4	22.3	0.0	68.5	9.3	5.0	11.5	73.9	9.6	6.2	0.0	88.5	5.3
Pr	0.3	2.6	90.2	6.8	22.0	0.0	68.0	9.9	4.8	10.7	76.0	8.5	5.3	0.0	89.5	5.2
Nd	1.7	2.5	88.3	7.6	22.9	0.0	66.9	10.2	6.6	9.8	76.1	7.5	4.9	0.0	90.0	5.2
Sm	0.0	2.8	89.5	7.6	21.5	0.0	67.5	11.0	4.9	8.9	80.2	6.0	4.5	0.0	90.3	5.2
Eu	0.4	3.9	88.8	6.9	20.4	0.0	66.1	13.5	2.8	7.5	84.3	5.3	5.0	0.0	90.1	4.9
Gd	2.3	3.3	86.8	7.6	24.0	0.0	65.4	10.6	3.7	7.0	83.9	5.5	6.9	0.0	88.9	4.2
Tb	1.8	3.4	86.0	8.9	22.8	0.0	65.7	11.5	3.6	6.1	84.6	5.7	7.6	0.0	87.7	4.7
Dy	2.3	2.7	84.9	10.1	22.8	0.0	64.8	12.5	3.9	6.2	83.9	6.1	7.5	0.0	86.8	5.7
Ho	1.6	2.1	84.9	11.3	22.2	0.0	64.4	13.4	2.0	6.8	84.8	6.5	7.3	0.0	85.5	7.2
Er	1.8	3.1	82.1	13.0	23.4	0.0	62.1	14.6	2.4	6.8	83.8	7.1	7.6	0.0	83.5	8.9
Tm	2.1	2.6	80.2	15.0	22.8	0.0	60.6	16.6	3.3	6.4	82.4	7.8	7.5	0.0	82.1	10.4
Yb	1.9	3.6	77.3	17.2	23.1	0.0	58.2	18.7	3.2	7.0	81.1	8.7	7.4	0.0	81.2	11.4
Lu	1.3	1.9	77.8	19.0	21.6	0.0	58.0	20.4	0.8	6.6	83.2	9.4	7.1	0.0	79.8	13.1

3.3.6.1 Float-Sink Analysis

In addition to sequential extractions, another way to determine the association of the REEs is to separate the sample into multiple specific gravity fractions and analyze each separately for REE or elemental concentration. One sample was analyzed via this method. Approximately four kilograms of the 6A-1 (NDGS sample with ~80% ash content) was provided to Standard Laboratories (South Charleston, WV), and was separated into specific gravity fractions of: 1.4 FL, 1.5 FL, 1.6 FL, 1.7 FL, 1.9 FL, 2.1 FL, 2.3 FL, 2.3 SK. The mass of sample in each fraction, the ash content of each fraction and the elemental composition in each fraction were analyzed. The results are provided in Table 10 and Table 11 for the bulk ash species and the REE, respectively, and in Figure 25 for the REE. Overall, the results show that for the REEs, the highest concentrations are in the < 1.9 gravity fractions, with total REE above 500 ppm (dry coal basis). The concentration of REEs in these organic rich fractions is consistent with the 6A and 6A-2 samples which were taken from the same location, but in more coal-rich zones. The concentrations drop significantly in the higher gravity fractions. This data is consistent with the sequential extractions data that indicates a high proportion of the REEs are organically associated. However, because this sample is high ash, there is also a significant portion of the REEs (~55%) that are in the > 1.9 gravity fraction. These would presumably be in mineral/clay associations or in middling particles containing both organics and minerals (grind size results in less than full liberation of organic from minerals). There is, however, some modest enrichment of the HREE in the lighter gravity fractions, as evidenced by an average LREE/HREE of 3.1 for the < 1.7 gravity fraction, and an average of 3.6 for the > 1.7 gravity fraction. This is also consistent with previous data that showed a higher enrichment of the HREE in low ash samples.

For the bulk ash species, it appears that there is a significant portion of the iron and sodium that is organically associated. The calcium behaves significantly different than would be expected. Specifically, there should be a notable fraction of calcium that is organically associated, but this data suggests that some oxidation of the sample has occurred that resulted in gypsum formation, whereby almost all of the calcium is concentrated in the >2.1 gravity fraction. This would be expected given that the sample was taken from an outcropping. This may have also caused some of the pyrite species to become oxidized, but the evidence is not as clear given this data.

Overall, this data suggests that there is a distribution of the modes of REE occurrence in this particular sample. With a significant fraction likely found in both organic associations and mineral forms. A gravity concentration method could potentially be used to generate an organic rich and mineral rich fraction that would isolate the modes of REE occurrence and would dictate the processes used for each fraction to recover the contained REEs.

Table 10. Float-sink results for bulk ash species

	Cum% Through Fraction							
	1.4 FL	**1.5 FL**	**1.6 FL**	**1.7 FL**	**1.9 FL**	**2.1 FL**	**2.3 FL**	**2.3 SK**
Si	0.3	1.0	1.9	4.2	28.1	94.9	98.4	100.0
Al	0.6	1.4	2.4	5.2	31.7	96.1	98.9	100.0
Ti	0.8	2.0	3.1	5.4	28.8	95.8	98.6	100.0
Ca	0.4	0.7	1.0	1.5	4.9	15.1	93.6	100.0
K	0.4	1.1	2.1	4.4	25.7	92.8	97.1	100.0
Mg	1.4	2.8	4.2	7.2	31.8	95.0	98.7	100.0
Na	5.0	8.8	11.8	16.5	39.4	95.7	97.4	100.0
Fe	4.4	8.1	11.2	11.7	38.8	90.7	93.7	100.0
P	0.0	0.4	1.3	3.9	30.5	99.5	99.9	100.0
	Concentration in SG Fraction (wt%, dry coal basis)							
Si	6.1	12.2	19.8	30.9	43.5	55.8	49.6	51.6
Al	4.6	7.1	10.3	15.7	21.5	23.9	17.4	15.8
Ti	0.2	0.4	0.4	0.5	0.7	0.9	0.6	0.7
Ca	0.2	0.2	0.2	0.3	0.2	0.3	39.9	7.4
K	0.4	0.6	1.0	1.5	1.8	2.7	2.9	4.4
Mg	0.6	0.6	0.7	0.8	1.0	1.2	1.1	0.9
Na	1.2	1.0	0.9	0.8	0.6	0.6	0.3	1.1
Fe	7.6	6.8	6.3	0.6	4.6	4.0	3.9	18.9
P	0.0	0.0	0.1	0.2	0.2	0.3	0.0	0.0

Table 11. Float-sink results for REE

	Cum% Through Fraction							
	1.4 FL	**1.5 FL**	**1.6 FL**	**1.7 FL**	**1.9 FL**	**2.1 FL**	**2.3 FL**	**2.3 SK**
Sc	4.6	9.0	13.1	18.8	49.2	97.8	99.1	100.0
Y	3.3	6.4	9.3	13.8	44.7	97.7	99.1	100.0
La	2.7	5.2	7.6	11.5	43.8	97.6	99.0	100.0
Ce	3.2	6.2	8.9	13.2	45.5	97.9	99.2	100.0
Pr	3.4	6.5	9.3	13.7	46.0	97.9	99.2	100.0
Nd	3.5	6.6	9.5	14.0	46.6	98.0	99.3	100.0
Sm	3.6	6.9	9.9	14.4	47.5	98.1	99.3	100.0
Eu	3.5	6.7	9.7	14.2	47.9	97.9	99.1	100.0
Gd	3.3	6.3	9.1	13.5	47.2	98.1	99.3	100.0
Tb	3.4	6.4	9.3	13.8	47.3	98.1	99.3	100.0
Dy	3.4	6.6	9.5	14.2	47.0	98.0	99.2	100.0
Ho	3.6	6.9	9.9	14.6	46.3	97.8	99.1	100.0
Er	3.6	6.9	10.0	14.7	45.4	97.6	99.0	100.0
Tm	3.7	7.1	10.2	14.9	44.5	97.6	99.0	100.0
Yb	3.6	7.0	10.0	14.7	43.7	97.3	98.9	100.0
Lu	3.7	7.0	10.1	14.7	43.1	97.3	98.8	100.0
TREE	3.3	6.3	9.1	13.5	45.7	97.8	99.2	100.0
LREE	3.2	6.1	8.8	13.0	45.5	97.8	99.2	100.0
HREE	3.6	7.0	10.2	14.9	46.4	97.8	99.1	100.0
	Concentration in SG Fraction (ppm, dry coal basis)							
TREE	511	485	515	476	492	365	159	225
LREE	386	367	388	361	387	286	124	173
HREE	124	119	127	114	105	79	35	51

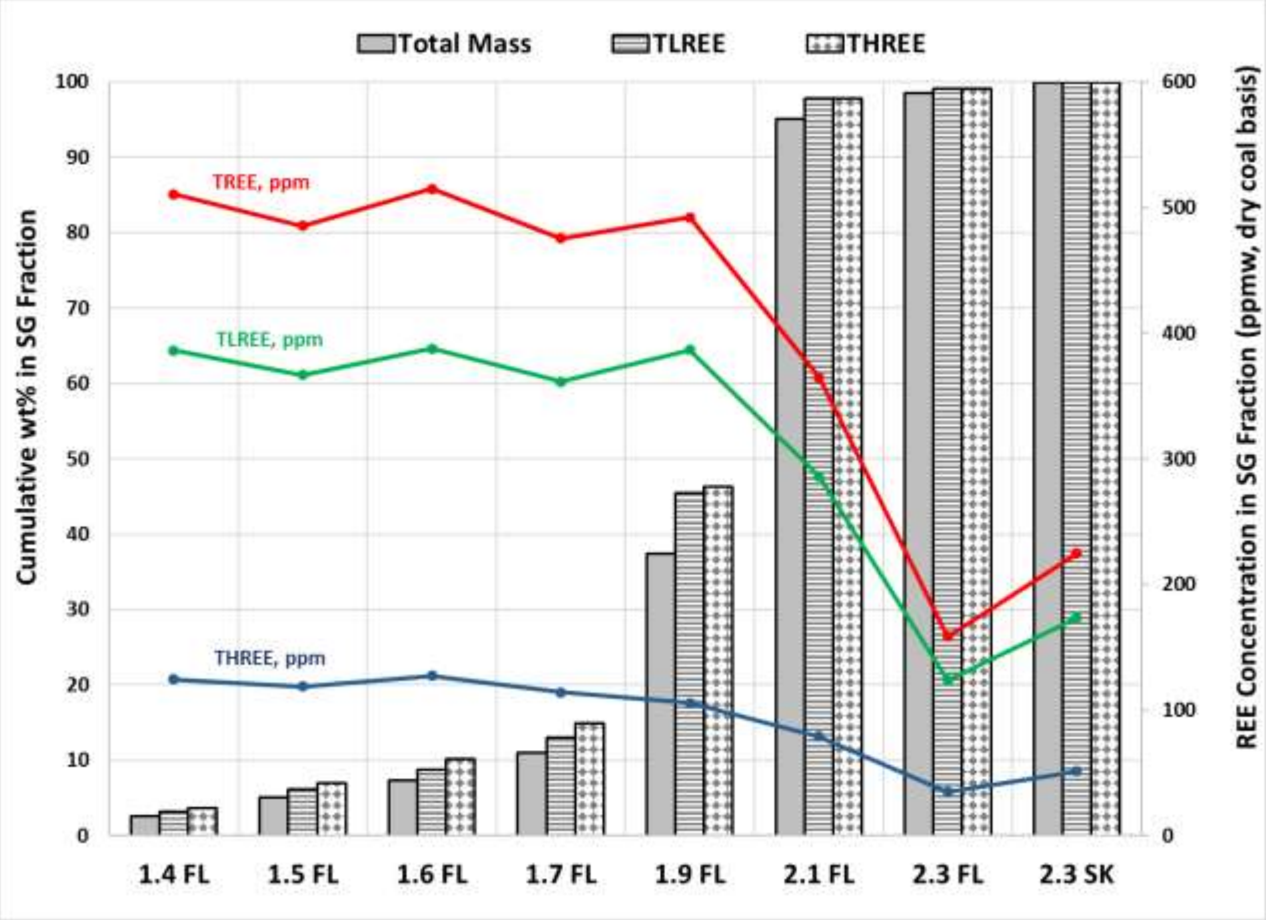


Figure 25. Float-sink results for REE

3.4 Summary and Conclusions

In summary, sampling was conducted on a range of North Dakota lignite and lignite-related materials. Characterization identified the content of REEs, the distribution of the specific REEs and the modes of occurrence of the REEs in the various samples. The primary conclusions are summarized below:

- In the Falkirk Mine, the associated sediments had the highest REE content on a whole sample basis, and typically ranged from about 100-200 ppm. However, on an ash basis, for each of the coal seams evaluated (Hagel A, B Rider, Hagel B), specific locations within the coal seams showed significantly higher REE content, ranging from about 300-600 ppm, with the Hagel B exhibiting the highest content and most uniform distribution over the sampling area.
- The content of REE was found to be inconsistent along the stratigraphic column at Falkirk Mine. However, REE content appears to be more uniform on horizontal planes. For REE recovery to be feasible, "selective" mining practices to target specific areas to mine coals with highest REE content are likely needed.

- In the Coal Creek Station, overall REE content was significantly lower than expected. This is caused by the blending practices at the mine, which results in dilution of high REE content coal with coals of lower REE content. The DryFining™ process shows lowest overall REE content in the air jig reject stream, indicating REE depletion in the heavy mineral/pyrite fraction of the coal. The bottom and fly ash in the plant showed highest overall REE concentration, ranging from about 240 to 260 ppm on an ash basis. These values correlated well to the cleaned coal from the DryFining™ process, which showed approximately equal ash basis REE content.
- Samples collected from the Harmon-Hansen coal zone in southwestern North Dakota showed by far the highest REE concentration, with concentrations as high as 640 ppm on a dry whole coal basis, and about 2200 ppm on an ash basis. This is compared to the Hagel B coal from Falkirk which had about 42 ppm on a whole sample basis, or about 580 ppm on an ash basis. Several other samples from the West and Southwest portions of the state also showed very high REE concentrations, with a total of five samples exceeding the 300 ppm total REE content target on a dry whole sample basis. On an ash basis, there were 10 samples that exceeded 500 ppm total REE.
- Overall, the distribution of REEs in the North Dakota lignites shows significant enrichment of the middle and heavy weight REEs, compared to earth’s crustal averages. In the Falkirk Mine, at the same time, the roof sediments appear to be depleted in these same elements compared both to the coal seams and floor sediments below. This would point to preferential leaching of the heavier REEs from the roof materials and subsequent adsorption by the organic matter in the coals. For most of the coals at Falkirk, a medium-type distribution is present, but for the B Rider and some portions of the Hagel B, a heavy-type distribution exists. In general, the data regarding distribution of the REEs in the various samples provides strong inferred evidence of organically associated REEs in the coals. For the NDGS samples collected from the Harmon-Hansen coal zone and other locations in the West and Southwest portions of the state, there are several samples that have very pronounced H-type distributions. Float-sink analysis of one of the high-ash NDGS samples, indicated a distribution of the REEs in both organic and mineral forms, with the highest concentration of REEs being in the low gravity fractions, with a slight enrichment of the HREE in these fractions.
- Experimental evidence of organic associations was gathered via sequential extractions tests, which showed that REEs can be present in North Dakota lignites as both organically and mineral bound. The data, combined with inferred evidence and literature indicates that the REEs in North Dakota lignite appear to be primarily associated with the organic matrix, at an estimated 80-95%, depending on the sample and the specific element.

- The results, combined with data available in the USGS CoalQual database indicate the strong possibility of commercially feasible REE-rich coal resources in the State.
- Several feedstocks were identified for extraction/concentration testing in the Phase 1 project.

4 LABORATORY-SCALE RARE EARTH ELEMENT EXTRACTION AND CONCENTRATION TEST RESUTLS

This chapter details the results of REE extraction methodology development, results and conclusions.

4.1 Experimental Methods

The initial expectation going into this project was that the REEs would be concentrated in the margins of the coal seams in the roof and floor clays/sediments. Thus, some of the first extraction/concentration testing was performed with these clay materials using two physical beneficiation methods: fine grinding followed by i) wet-screening, and ii) dry elutriation. Once coming to the realization that on an ash basis the REEs were more concentrated in the coal than in the sediments, the focus was shifted to development of methods to concentrate REEs directly from the coal. A limited amount of work was done looking at the partitioning of the REEs by size in the combustion fly ash. Finally, with the data gathered from sequential extractions testing, it was discovered that the REEs are primarily organically bound in the raw coal and could be removed by a solvent process. Thus, the remainder of the project focused on development of a novel leaching process to extract the REEs directly from the raw coal. The following sections outline the experimental methods used for each of the above.

4.1.1 Physical Beneficiation of Roof/Floor Sediments and Fly Ash

The first method of physical beneficiation was tested on both the roof/floor sediments and combustion flyash and involved simple wet screening of the materials to understand the partitioning of the REEs as a function of size during the grinding process in the case of the roof/floor sediments, and during the combustion process in the case of the fly ash. Samples were ground to -270 mesh (roof/clays only) and screened into -10 micron, 10 to 25 micron, and +25 micron size fractions. The sized fractions were then subjected to ICP-MS analysis to determine the REE content in each size fraction.

The second method of physical beneficiation was based on a dry elutriation process being developed by Envergex LLC of Sturbridge, Massachusetts and UND, for separation of unburned carbon and fly ash from oxygen carrier material in Chemical Looping Combustion systems [13]. The technology combines a dry fluidized bed with several novel enhancement methods to improve separation performance of very fine particles based on density/size differences. A small laboratory-scale system was available to this project (Figure 26), and the method was adapted for the REE separation application. The ultimate goal of the testing was to determine the feasibility of separating the ultra-fine REE-bearing minerals from the gangue materials in the sample. A 2-inch diameter fluidized bed was employed in a batch testing mode, with elutriated particles being collected in a filter and the non-elutriated fraction remaining in the bed. After completion of testing, the two fractions were analyzed for particle size distribution (PSD) and REE content by ICP-MS.

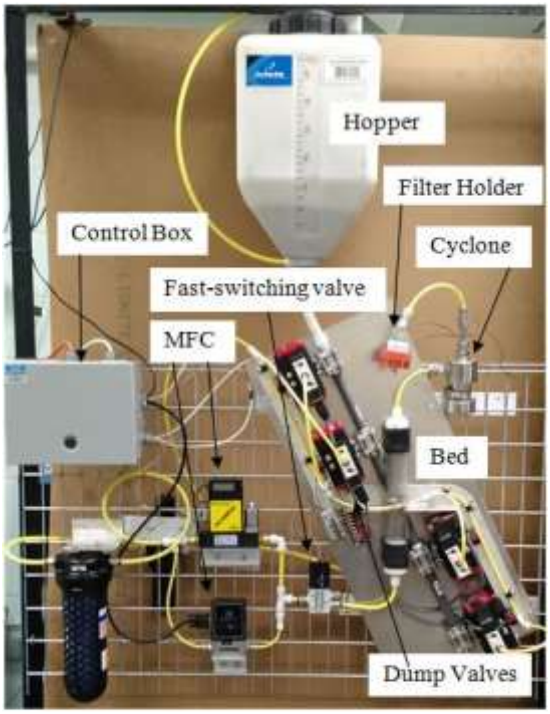


Figure 26. Dry elutriation test system.

4.1.2 Leaching Tests

All chemicals used were high purity reagent grade and extreme care was taken during cleaning of glassware to ensure cross contamination did not occur. The procedures are summarized below:

- All glassware and beakers were cleaned extensively with a combination of dilute nitric acid and DI water prior to use
- Mass of starting coal/feedstock was 60 grams dry
- Volume of leaching solution was 125 mL
- Flasks were 250 mL polycarbonate
- Solutions were stirred with a stir bar and hot plate set to achieve the desired solution temperature
- After finishing desired leaching duration, the slurry was filtered using a vacuum-assisted Buchner funnel
- Once extraction was complete, the separated residual material was rinsed extensively with DI water, collected and dried in a convection oven to dryness.

- The extraction of each of the elements in the starting coal was determined by difference of the unleached and leached coal solids by ICP-MS and by XRF.

For some of the tests, in addition to determination of the REE extraction efficiency, other high-value elements or impurities were also measured both to determine REE concentration in solution and to determine the extraction of the other elements. In these cases, the trace element components were measured by ICP-MS and the bulk species by ASTM standard XRF ash composition.

4.2 Results

The sections below provide results for the physical beneficiation testing for the roof/floor sediments and one sample of combustion fly ash, as well as the leaching testing for the raw lignite samples, Leonardite and the Harmon-Hansen roof sediments.

4.2.1 Physical Beneficiation

Dry elutriation and classification methods were investigated for roof/floor clays and combustion fly ash. Results are presented in the following sections.

4.2.1.1 Dry Elutriation

Testing was completed on 11 samples of associated roof/floor sediments from Falkirk Mine using the dry elutriation method previously described in Section 4.1.1. Samples tested were those that had the highest REE concentration measured up to that time, and are listed below:

- IES16024 – Tavis Roof
- IES16025 – Tavis Floor
- IES16026 – Hagel A Roof
- IES16035 – Hagel A Floor
- IES16036 – Hagel A Roof
- IES16037 – Hagel A Roof
- IES16047 – Hagel B Roof
- IES16048 – Hagel B Roof
- IES16053 – Hagel B Floor
- IES16054 – Hagel B Floor
- IES16056 – B Rider Roof

Prior to testing, each of the samples was ground to -270 mesh to identify if natural partitioning of the ultra-fine REE-bearing mineral grains would occur during the grinding process. The ICP-MS results shown in Table 12, however, do not show any detectable enrichment in either material fraction generated. However, as indicated in the PSD data in Figure 27 for the elutriate and non-elutriate fractions, there was a measurable enrichment of the -5 micron particles in the elutriate. Therefore, one would have expected to see a corresponding enrichment in REE content in the elutriate if partitioning of the REEs by size had indeed occurred during grinding. Based on these results, grinding alone does not appear to be a feasible approach to generate any measurable concentration of the REEs by size.

Table 12. Results of dry elutriation-based physical beneficiation testing for roof/floor sediments

Sample ID		Dry ash basis		
		Original Total REE (ppmw)	Elutriate Total REE (ppmw)	Non-Elutriate Total REE (ppmw)
IES	16024	158	178 & 172	170
IES	16025	174	194	201
IES	16026	186	213	210
IES	16035	185	202	204
IES	16036	172	186 & 172	182
IES	16037	151	171	169
IES	16047	164	175	179
IES	16048	150	179	179
IES	16053	152	150	146
IES	16054	153	178	168
IES	16056	178	185	182

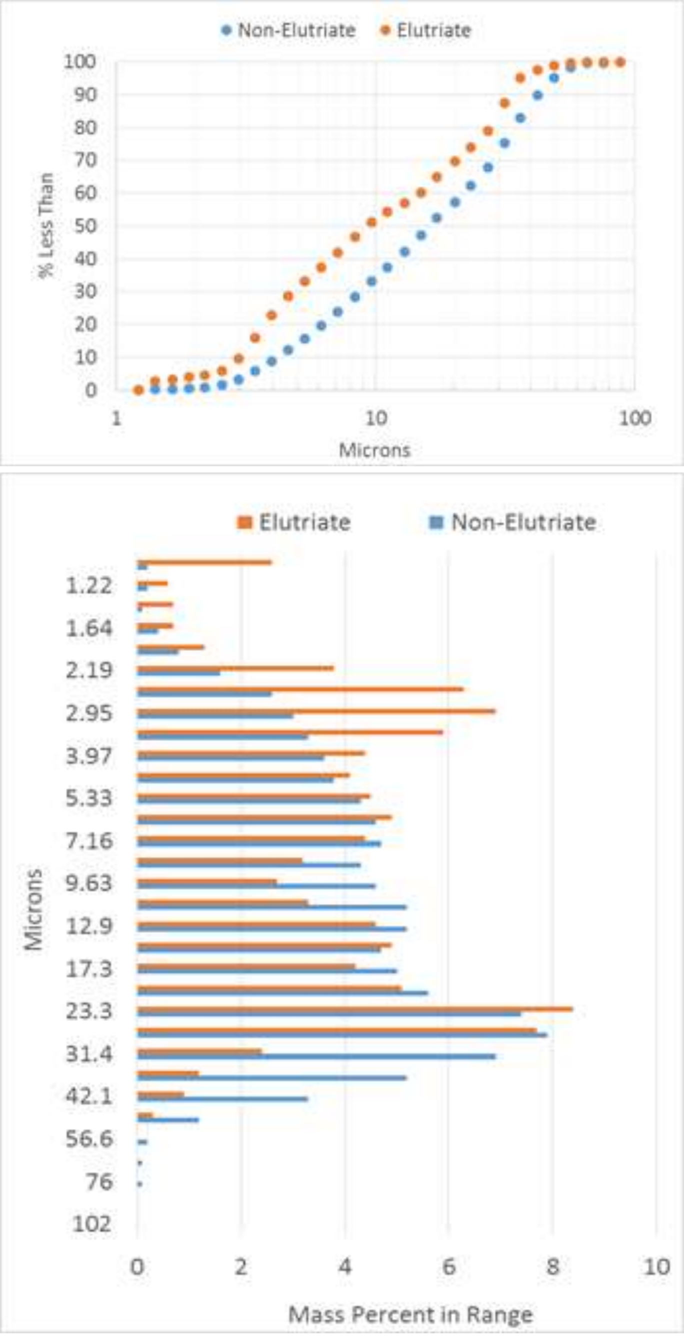


Figure 27. Particle size distributions of the elutriate and non-elutriate fractions generated from dry elutriation-based physical benefication testing for Falkikrk Mine roof/floor sediments

4.2.1.2 Wet Screening

Although results of the dry elutriation testing with roof/floor sediments showed no measureable increase in REE content in the finer elutriate fraction, the particle size separation was not as clear as was initially hoped for. Thus, a sharp separation by wet screening was warranted to confirm whether or not a grinding and classification operation could achieve any degree of REE concentration. Further, to determine any partitioning of REEs as a function of size during the combustion process, a fly ash sample was also tested. The following samples were evaluated using this approach:

- IES16141 – Coyote Creek Roof
- IES16147 – Coal Creek Station Fly Ash

The results of REE content and overall mass of sample in each size fraction is shown in Table 13. The results here do show some potential enrichment in both sample types. For the roof sample, approximately 80% of the REEs in the starting material reported to the minus 10 micron fraction that also observed a modest enrichment in the REE concentration (186 ppm versus 177 ppm for starting sample). For the fly ash sample, there does appear to be some enrichment in the coarse size range. However, only about 28% of the starting REEs reported to that size range.

Table 13. Results of wet-screening size separation (Hazen Labs) and REE content

Sample ID	Size Fraction (microns)	Size Distribution (wt%)	Total REE (ppmw) Dry ash basis
IES16141	+ 25	8.4	169
	25 x 10	15.8	139
	-10	75.9	186
IES16147	+25	25.0	274
	25 x 10	40.2	244
	-10	34.8	243

Overall, although there does appear to be some measurable enrichment in REE content by particle size for both the roof/floor sediments and the combustion fly ash, the overall concentration factor was not sufficient enough to warrant continued evaluation. Ultimately, the results of these initial tests, combined with the fairly low REE content in the materials tested and a literature review resulted in the conclusion that physical beneficiation processes would not be feasible for the roof/floor sediments from Falkirk Mine or the combustion fly ash from Coal Creek Station. Therefore, the focus was shifted to evaluation of alternate strategies.

4.2.2 Leaching Tests

Four series of leaching tests were accomplished: i) initial screening of solvent types and concentrations, ii) additional testing with down-selected solvent type and concentration, iii) leaching kinetics testing, and iv) additional parametric testing. Each is described separately in the following sections.

4.2.2.1 Screening Tests – Hagel B and Harmon-Hansen Roof

Table 14 and Table 15 display leaching test results for two feedstocks, respectively: i) raw Hagel B coal, and ii) Harmon-Hansen roof sediments. Three solvent types were tested in two concentrations each. Tests were conducted using a purposefully long contact time of about 48 hours. The long contact time was used to ensure equilibrium extraction was achieved (or nearly achieved).

Table 14. Solvent leaching screening test results for Hagel B coal (Three solvent types – A, B, C – each with low and high concentration tested)

	wt% Extracted					
	Type A - Low	Type A - High	Type B - Low	Type B - High	Type C - Low	Type C - High
Sc	11.8	26.7	4.0	53.2	12.4	69.9
Y	10.6	92.6	5.3	84.0	8.7	74.1
La	10.8	90.4	4.5	64.5	7.5	61.1
Ce	11.2	88.2	4.8	63.1	7.2	58.0
Pr	11.0	87.0	3.8	63.3	7.2	57.5
Nd	11.4	86.4	3.9	64.7	6.7	57.7
Sm	11.7	86.4	3.7	68.4	6.9	64.0
Eu	10.9	85.0	0.6	66.1	7.7	59.5
Gd	11.4	89.4	2.6	75.6	7.5	67.7
Tb	12.1	90.0	2.4	77.3	7.9	67.2
Dy	11.8	90.1	2.9	79.1	7.2	66.4
Ho	11.4	90.3	3.5	80.8	7.6	65.1
Er	11.4	90.0	3.8	81.7	7.7	62.8
Tm	11.6	89.1	4.1	82.2	8.5	61.5
Yb	10.9	87.7	3.1	82.0	7.6	61.4
Lu	11.3	87.4	3.4	82.0	7.7	62.0
Total wt% extracted	11.0	86.8	4.5	70.9	7.9	64.6
LREE wt% extracted	11.2	83.9	4.3	63.8	7.6	60.4
HREE wt% extracted	10.8	91.8	4.8	83.1	8.4	71.7
CREE wt% extracted	10.9	90.8	4.7	79.0	8.1	69.2
n-CREE wt% extracted	11.1	83.7	4.4	64.6	7.7	60.9

NOTE: CREE denotes critical REE; n-CREE denotes non-critical REE

Table 15. Solvent leaching screening test results for high-ash Harmon-Hansen roof sediments (NDGS sample 6A-1) (Three solvent types – A, B, C – each with low and high concentration tested)

	wt% Extracted					
	Type A - Low	Type A - High	Type B - Low	Type B - High	Type C - Low	Type C - High
Sc	19.8	36.0	30.6	47.2	15.4	53.4
Y	25.9	57.3	31.8	51.8	11.8	25.9
La	19.9	62.0	22.3	53.8	5.2	14.9
Ce	20.1	63.1	23.7	56.1	5.9	16.4
Pr	19.5	63.2	23.1	56.1	5.8	15.6
Nd	19.3	63.9	22.8	56.3	6.6	16.8
Sm	19.7	66.4	24.0	57.7	7.3	19.5
Eu	20.4	68.7	25.1	59.6	7.8	20.6
Gd	20.8	68.4	24.7	57.6	8.1	19.3
Tb	21.5	67.9	25.9	57.6	8.7	19.9
Dy	22.2	64.9	29.1	56.3	8.7	22.3
Ho	24.0	60.0	30.9	53.0	9.9	23.6
Er	24.1	53.9	30.2	48.8	9.3	22.8
Tm	23.2	48.5	29.8	44.6	9.9	22.4
Yb	22.7	44.8	28.7	41.9	9.8	23.1
Lu	23.8	41.1	29.0	39.8	11.6	23.3
Total wt% extracted	20.5	61.5	24.6	54.9	7.1	19.1
LREE wt% extracted	19.9	62.1	23.6	55.4	6.5	18.2
HREE wt% extracted	24.8	57.7	30.9	51.8	10.9	24.7
CREE wt% extracted	21.7	61.9	26.3	54.9	8.4	20.2
n-CREE wt% extracted	20.1	61.3	23.9	54.9	6.5	18.7

NOTE: CREE denotes critical REE; n-CREE denotes non-critical REE

The REEs in Harmon-Hansen roof sediments (Table 15) were still extractable with reasonable efficiency. Based on the Float-Sink analysis of this material presented previously, it appears that a significant fraction of the REEs present are organically associated, despite the high ash content. Thus, the REEs that were extracted in this testing were those that were organically associated. Later testing will show that the REE extraction efficiency is, in general, a function of the fraction of the REEs that are organically versus mineral associated.

The results shown for the Hagel B coal in Table 14 indicate that overall, Type A solvent had the highest recovery of REEs. In each case the low concentration solvents did a poor job of REE extraction. The data is shown in graph form in Figure 28 for the three higher concentration tests. The behavior of scandium was significantly different among the solvent types, with Type C producing the best extraction. With the exception of Type B, the extraction was fairly uniform across the LREE and HREE. Type B, however, showed a strong selectivity towards the HREE, which, in fact is an opposite trend observed for Type A, which showed a slightly decreasing extraction in the heaviest REE with the exception of Y. However, for all three solvent types, extraction of the HREE was higher than the LREE, again providing more evidence of differing modes of occurrence or bond strengths as a function of the REE molecular weight.

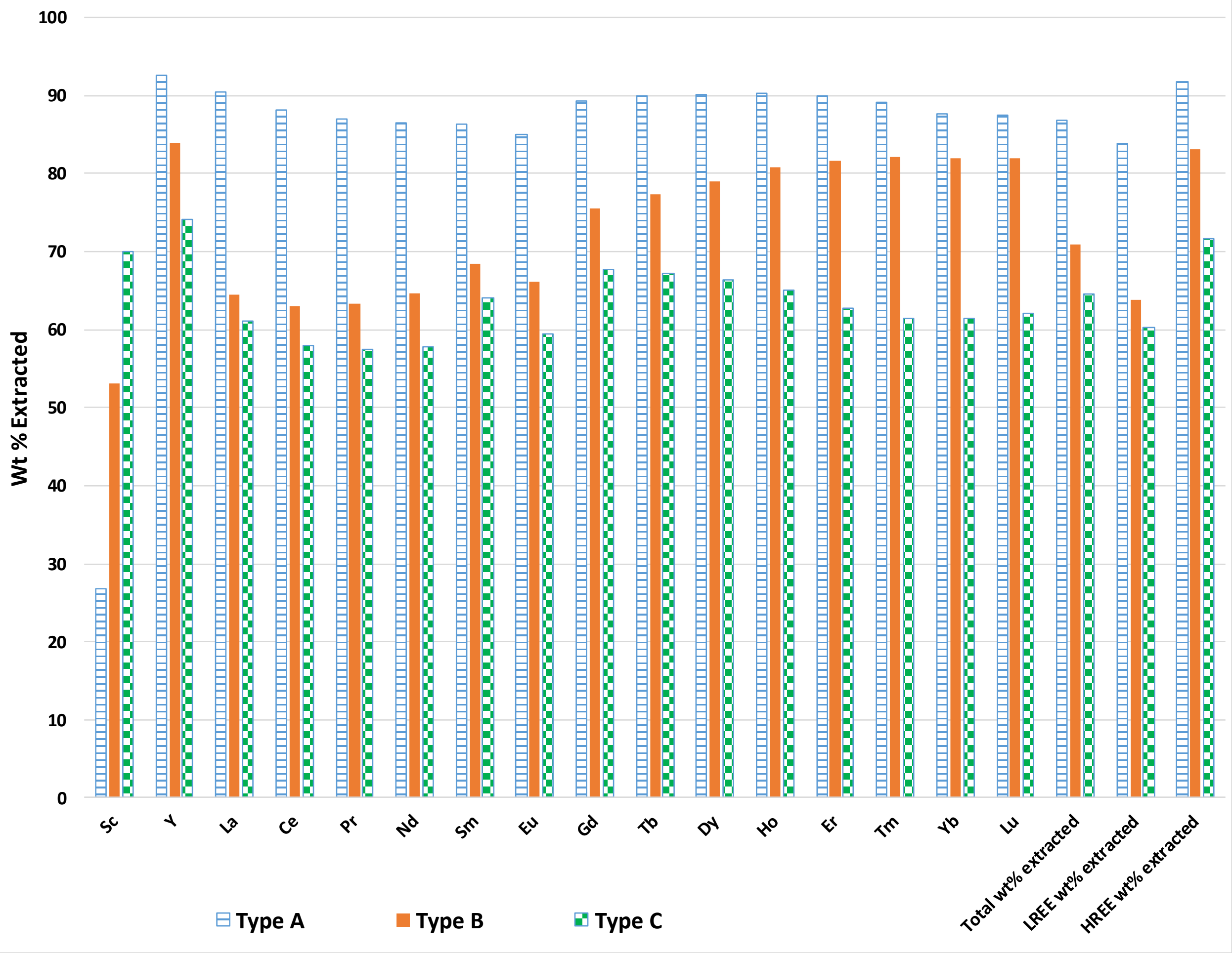


Figure 28. REE extraction results for three solvent types using Hagel B coal

Another way to look at performance of the extraction is to look at the total extraction of inorganic components into solution along with the REEs in order to determine the concentration of REEs in solution, as shown in Table 16. Here, it is clear that although the Type A solvent had the highest REE extraction, it also extracted a large quantity of other inorganic components into solution with the REEs (i.e. reduction in ash content of 76% compared to unleached coal). The REE concentration in solution ranged from 0.03 wt% to 0.74 wt% on a dry basis (mass of solution not included). Because of the extremely low reduction in ash content of the coal, the low concentration Type C solvent actually produced the highest REE concentration in solution even though only about 8% of the REEs were extracted from the coal. The test that exhibited the best combination of high REE extraction and REE concentration in solution was the high concentration

Type B solvent that extracted 71% of the REEs with only about 16% reduction in ash content, resulting in an REE concentration in solution of about 0.25 wt%.

Table 16. Mass balances for REE extraction for Hagel B screening tests

Sample	Ash Content (wt%)	% Ash Reduction	Total % REE Extracted	Wt% REE in Solution
Unleached Coal	7.2	-	-	-
Type A - Low	5.9	18.1	11	0.03
Type B - Low	6.9	4.3	4.5	0.06
Type C - Low	7.2	0.6	7.9	0.74
Type A - High	1.7	76.1	86.8	0.07
Type B - High	6.1	15.6	70.9	0.25
Type C - High	3.1	56.4	65.6	0.06

Although Type A solvent was the most effective in extraction of REEs, the Type B solvent was chosen for additional investigation in the project for the reason discussed above regarding selectivity as well as environmental and economic considerations.

4.2.2.2 Down-selected Leaching Tests

As described above, based on the results of screening tests, Type B solvent (higher concentration) was chosen for continued evaluation in the project. The next set of tests conducted had the following goals:

- Determine REE extraction from Harmon-Hansen coal (NDGS sample 6A) compared to Hagel B
- Determine extraction of other inorganic components with REEs – both high value elements and low/negative value impurities

Using the same methods as for the screening tests, both the Harmon-Hansen coal and the Hagel B coal underwent leaching with Type B solvent. The staring and residual coals were analyzed for a range of elements shown below to determine extraction for each.

- Elements measured by ICP-MS: REE, Co, Cu, Ga, Ge, In, Li, Ni, Se, Ag, Te, V, Zn, Cd, Pb, Hg, Th, U
- Elements measured by XRF: Si, Al, Fe, Ti, P, Ca, Mg, Na, K, Sr, Ba, Mn

It is important to note that the above elements are not inclusive of the entire chemistry of the coals, but were rather chosen based on a combination of measurability given existing analytical capabilities as well as perceived value either as monetizable elements or as impurities that may increase costs of purification. The platinum group elements, in particular, would have been interesting elements to measure, but the existing analytical capabilities did not allow for this with reasonable cost. Regardless, it is also important to note that while not inclusive of the entire chemistry, the above elements do represent essentially the entire mass of the inorganic portion of the coal, with other elements not measured being present in only trace amounts.

The results of extraction for both the Harmon-Hansen and the Hagel B coals are shown in Table 17. Of note is the vastly different inorganic composition of the coals. The Harmon-Hansen is a higher ash coal (~25% versus ~7% for Hagel B), so in general the concentration of most of the inorganic species is accordingly higher in the Harmon-Hansen on a whole coal basis. However, there are some striking differences that are worth pointing out. For instance, in many cases, the concentration of some of the trace inorganic species is more than an order of magnitude higher in the Harmon-Hansen, including Co, Cu, Ga, Ge, Ni, V, Th and U. Vanadium is actually two orders of magnitude higher in Harmon-Hansen. There are also some very large differences in the bulk inorganic species (i.e. those measured by XRF in the lists above). For example, the content of Si, Fe and Ti are all more than an order of magnitude higher in Harmon-Hansen. Also interesting is that the content of some species is actually higher in the Hagel B, including Ca, Mg, Na, Sr, and Mn. Clearly, the geochemistry of these two coal samples are very different.

Table 17. Extractions for Type B solvent leaching of Harmon-Hansen and Hagel B coals

Harmon-Hansen Coal				Hagel B Coal			
	Dry Coal Basis Concentration		% Extracted to Solution		Dry Coal Basis Concentration		% Extracted to Solution
	Initial Coal (ppm)	Leached Coal (ppm)			Initial Coal (ppm)	Leached Coal (ppm)	
Sc	36.33	7.16	82.5	Sc	1.97	0.94	53.2
Y	45.59	6.15	88.0	Y	11.77	1.93	84.0
La	63.30	9.56	86.6	La	7.27	2.63	64.5
Ce	176.44	21.63	89.1	Ce	9.66	3.64	63.1
Pr	26.59	3.20	89.3	Pr	1.04	0.39	63.3
Nd	121.88	14.85	89.2	Nd	4.06	1.46	64.7
Sm	29.32	3.59	89.1	Sm	0.96	0.31	68.4
Eu	6.55	0.78	89.3	Eu	0.26	0.09	66.1
Gd	22.28	2.59	89.7	Gd	1.23	0.31	75.6
Tb	2.98	0.34	90.0	Tb	0.20	0.05	77.3
Dy	14.94	1.69	89.9	Dy	1.34	0.29	79.1
Ho	2.51	0.29	89.6	Ho	0.31	0.06	80.8
Er	6.38	0.79	89.1	Er	0.91	0.17	81.7
Tm	0.85	0.11	88.7	Tm	0.12	0.02	82.2
Yb	5.38	0.72	88.2	Yb	0.76	0.14	82.0
Lu	0.74	0.10	87.7	Lu	0.12	0.02	82.0

Table 17. Extractions for Type B solvent leaching of Harmon-Hansen and Hagel B coals

Harmon-Hansen Coal				Hagel B Coal			
	Dry Coal Basis Concentration		% Extracted to Solution		Dry Coal Basis Concentration		% Extracted to Solution
	Initial Coal (ppm)	Leached Coal (ppm)			Initial Coal (ppm)	Leached Coal (ppm)	
Co	865	20.60	97.9	Co	39.30	2.60	93.5
Cu	172	126.00	34.9	Cu	11.10	5.20	54.1
Ga	23.8	6.30	76.5	Ga	2.10	1.10	48.6
Ge	28	9.10	71.1	Ge	0.90	0.50	45.5
In	nd	nd	n/a	In	nd	nd	n/a
Li	25	23.10	17.9	Li	3.70	2.70	28.4
Ni	75.4	6.00	92.9	Ni	6.90	4.10	41.7
Se	2.7	1.40	53.9	Se	0.55	0.14	75.0
Ag	0.58	0.59	9.6	Ag	nd	nd	n/a
Te	nd	nd	n/a	Te	nd	nd	n/a
V	616	122.00	82.4	V	3.80	1.70	56.1
Zn	26.8	4.60	84.7	Zn	3.30	0.50	85.1
Cd	0.55	0.04	93.5	Cd	0.05	nd	100.0
Pb	14.7	10.90	34.1	Pb	1.60	1.00	38.7
Hg	0.16	0.17	5.6	Hg	0.02	0.03	0.0
Th	29.9	6.90	79.5	Th	1.00	0.80	21.5
U	16.3	4.60	74.9	U	1.10	0.90	19.8
Si	82129	94138	0.0	Si	7325	10746	0.0
Al	48341	55253	0.0	Al	6749	4521	34.3
Fe	76425	35689	58.5	Fe	3966	1143	71.7
Ti	3369	3109	18.0	Ti	159	215	0.0
P	646	303	58.4	P	98	25	74.8
Ca	7847	1279	85.5	Ca	25773	22702	13.6
Mg	893	352	64.9	Mg	5289	28	99.5
Na	1131	217	83.0	Na	3686	17	99.5
K	2062	1850	20.3	K	385	135	65.7
Sr	241	320	0.0	Sr	484	452	8.4
Ba	1732	1980	0.0	Ba	627	599	6.3
Mn	51	23	60.3	Mn	115	25	78.9

NOTE: % extraction determined by difference between initial and leached coal combined with mass of initial and leached coal. Those elements with leached coal ppm higher than initial coal ppm may or may not have 0% extraction for that element, depending on the overall mass balance. Also note that significant figures have been exaggerated for the element concentrations.

As shown in Figure 29, the overall REE extraction for the Harmon-Hansen was higher, with a range of about 86 to 89%, with the exception of Sc which was slightly lower. The very high Sc extraction compared to Hagel B is an important result, as Sc has the highest sale price of the REEs. These results would suggest that the bonding of the REEs in the Harmon-Hansen is weaker.

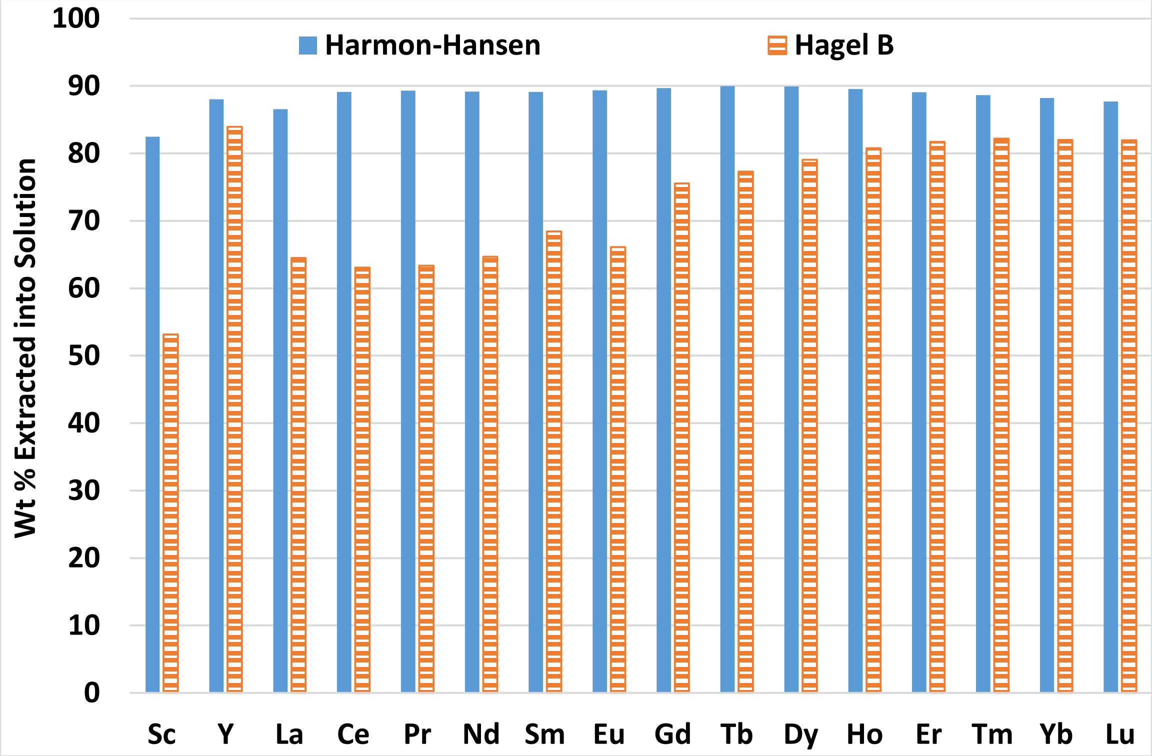


Figure 29. Comparison of REEs extraction by Type B solvent for Harmon-Hansen and Hagel B coals

For the major ash-forming elements shown in Figure 30, there were some considerable differences between the two coal types. For example, no Al was extracted for Harmon-Hansen, but about 35% was extracted from Hagel B, indicating differing modes of occurrence in the coals. Titanium, strontium and barium are also examples where extraction only occurred with one of the coals. Major differences also existed with extraction of the alkali and alkaline earth elements. For example, nearly all of the Ca was extracted for Harmon-Hansen, but only about 13% for Hagel B. Similarly, about 66% of K was extracted for Hagel B, but only about 20% for Harmon-Hansen. For Mg and Na, smaller differences existed, but nearly 100% of both Mg and Na were extracted from Hagel B, with 65% Mg and 82% Na for Harmon-Hansen. Manganese, Fe, and P were all extracted in fairly high quantities for both coals, with the Hagel B being slightly higher in all cases.

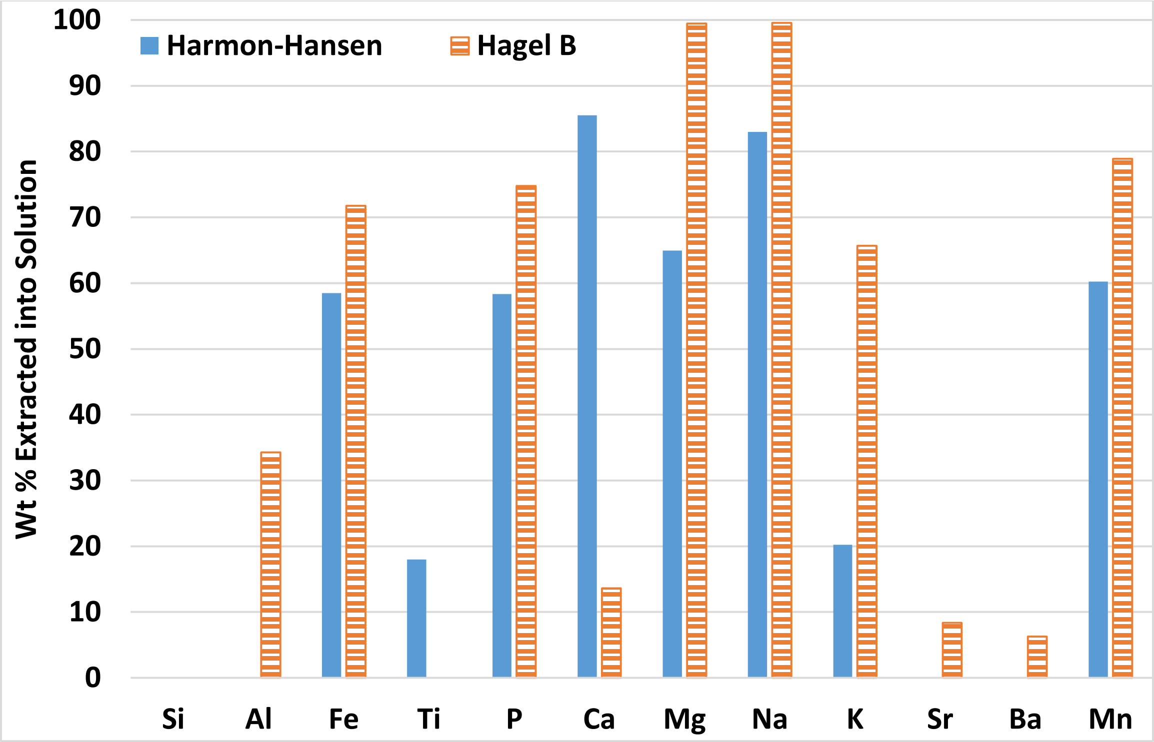


Figure 30. Comparison of the extraction of the bulk ash species by Type B solvent leaching for Harmon-Hansen and Hagel B coals

When looking at the remaining species shown in Figure 31, two elements were either not detected or not extracted into the solutions. These were In and Te. Very small amounts of Ag and Hg were extracted according to the data for Harmon-Hansen, but none for the Hagel B. Several of these elements represent potential targets for monetization in an actual commercial operation, namely Co, Cu, Ga, Ge, Li, Ni, Ag, V and Zn. Some others represent toxic species or radioactive species that could potentially represent environmental or health hazards for a commercial operation, including Se, Cd, Pb, Hg, Th and U. Thorium and uranium, in particular, being in the closely related actinide series, are often found with REEs and behave similarly in separation/extraction processes. Because they are considered radioactive source materials, they represent environmental challenges for any REE processing technology.

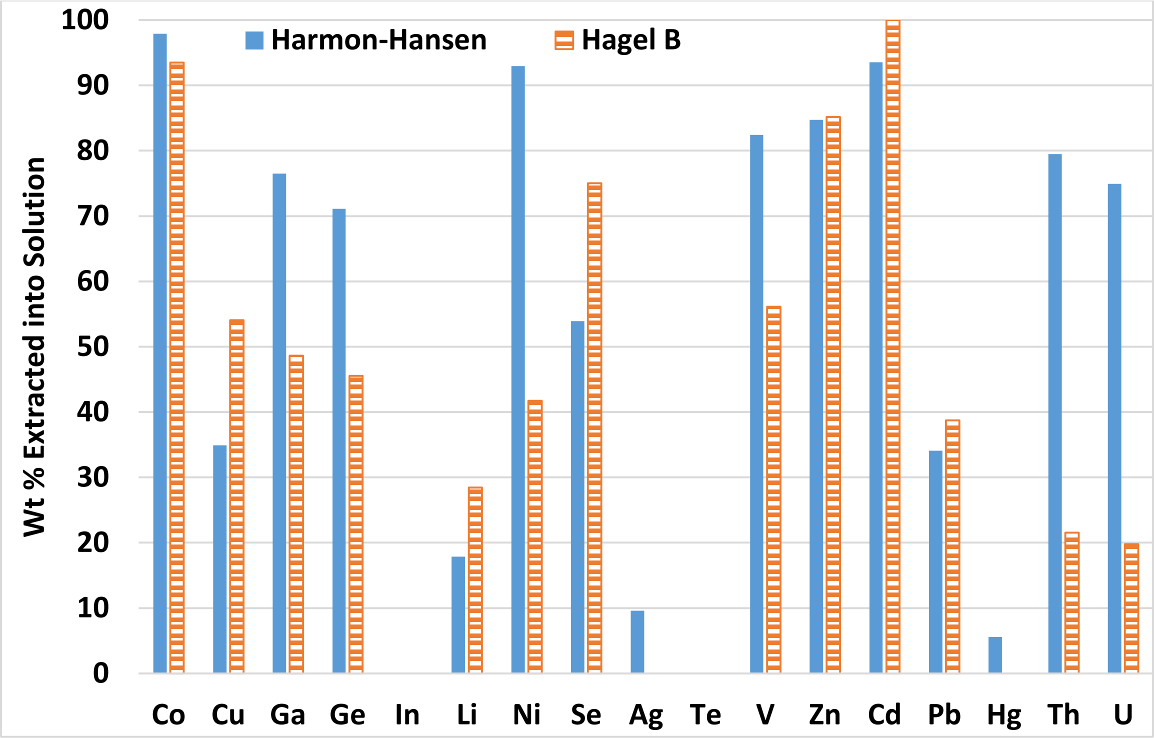


Figure 31. Comparison of the extraction of non-REE species by Type B solvent leaching for Harmon-Hansen and Hagel B coals

Based on the results shown above, the mass balances can be calculated as shown in Table 18. As would be expected given the higher initial content and higher extraction, the REE concentration in the extract solution is considerably higher for the Harmon-Hansen. A similar reduction in ash content of the starting coal was observed for both coals, however there are some significant differences regarding the composition of the extract solution as it relates to the impurities. For Hagel B, the dominant impurity forms are the alkali and alkaline earth elements, whereas for the Harmon-Hansen, by far the largest impurity is iron. However, for both coals, the iron and alkali/alkaline earth elements combined make up about 80 to 85% of the total mass in the extract solution, indicating that if methods can be effectively developed to target these species, that the content of REEs in the extract solution will be dramatically increased.

Table 18. Overall mass balances for Type B solvent leaching of Hagel B and Harmon-Hansen coals

Mass Balance Parameter	**Hagel B**	**Harmon-Hansen**
Starting Ash Content (wt%)	7.2	25.6
% Ash Reduction	15.6	19.3
% REE Removed	65.3	87.7
wt% REE in Solution	0.23	0.79
wt% Target Elements in Solution[1]	1.3	3.3
wt% Fe in Solution	16.0	68.8
wt% alkali/alkaline earth in Solution[2]	69.6	13.6

1. Includes: Sc, Y, REE, Co, Cu, Ga, Ge, Li, Ni, V, Zn, Mn
2. Includes: Ca, Na, K, Mg

Note: wt% in solution is on dry basis and does not include mass of solution

4.2.2.3 Leaching Kinetics Tests – Hagel B Coal

As mentioned previously, the leaching tests performed were all done using a purposefully long contact time of 48 hours. Therefore, to establish the kinetics of the leaching process, several tests were performed at varying contact times and the REE extraction evaluated. Tests were performed using Hagel B coal with Type B solvent as the leaching solution. Besides the contact time, methods described previously for the leaching tests were used. Table 19 and Figure 32 display the results for extraction as a function of leaching contact time for the individual REEs. Figure 33 displays the results for groupings into Total REE, LREE, HREE and critical REE (CREE).

Table 19. Leaching kinetics results for Hagel B coal with Type B solvent

	Mass % Extracted by Type B Solvent at Specified Contact Time						
	1 hr	2hr	4hr	8hr	14hr	24hr	48hr
Sc	10.3	11.2	11.5	5.1	29.9	15.7	52.9
Y	60.7	65.4	69.9	70.8	78.2	77.1	83.8
La	12.8	14.5	19.0	18.6	54.6	47.8	64.3
Ce	22.7	23.6	28.5	28.0	55.8	50.4	62.8
Pr	29.3	30.8	35.9	35.7	56.7	52.5	62.8
Nd	33.2	35.8	41.1	41.1	58.4	53.3	64.5
Sm	38.1	42.0	46.4	47.3	61.5	56.9	68.1
Eu	39.5	42.9	46.9	46.7	62.2	54.3	65.8
Gd	48.0	51.8	56.1	57.6	68.6	65.0	75.0
Tb	50.9	55.5	60.6	60.4	70.5	70.3	75.7
Dy	53.1	57.4	61.3	62.7	72.0	69.5	78.6
Ho	56.0	59.1	62.6	65.9	72.9	72.7	80.6
Er	56.9	61.1	64.5	65.5	74.6	72.2	81.5
Tm	59.1	58.8	67.1	67.0	75.4	75.2	84.1
Yb	53.5	58.6	61.4	63.9	73.4	70.6	81.7
Lu	55.3	55.0	64.1	64.0	73.2	73.0	83.4
Total	36.2	38.9	43.3	43.3	62.9	58.4	70.6

	Mass % Extracted by Type B Solvent at Specified Contact Time						
	1 hr	2hr	4hr	8hr	14hr	24hr	48hr
LREE	22.4	24.0	28.8	28.5	56.1	50.5	63.8
HREE	52.9	57.0	60.9	61.2	71.1	68.1	78.9
CREE	53.4	57.6	62.2	62.9	72.8	70.6	78.7

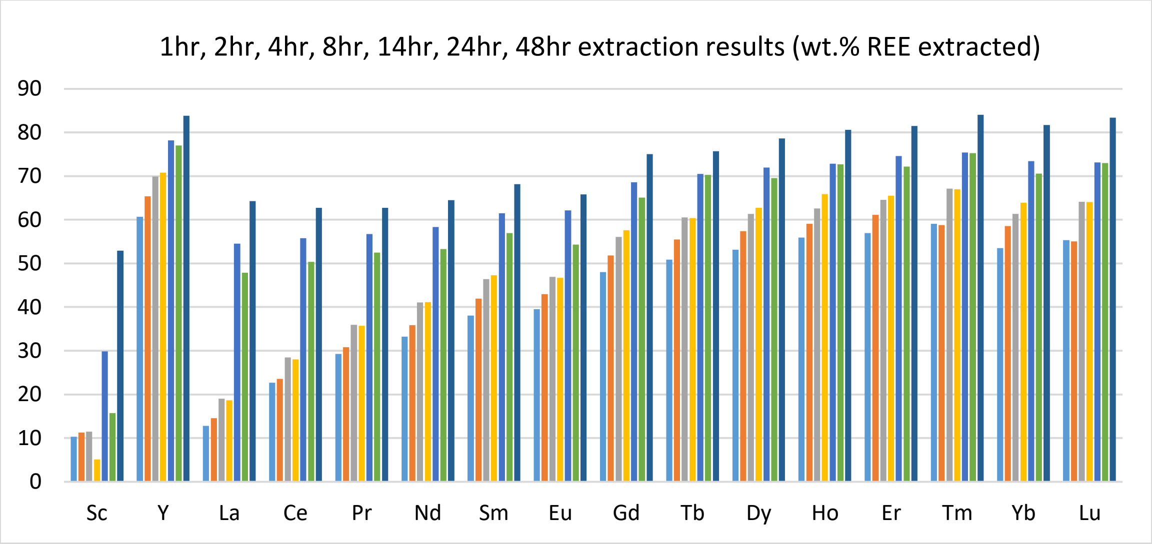


Figure 32. REE leaching kinetics for Hagel B coal with Type B solvent. Bars left to right represent increasing contact time

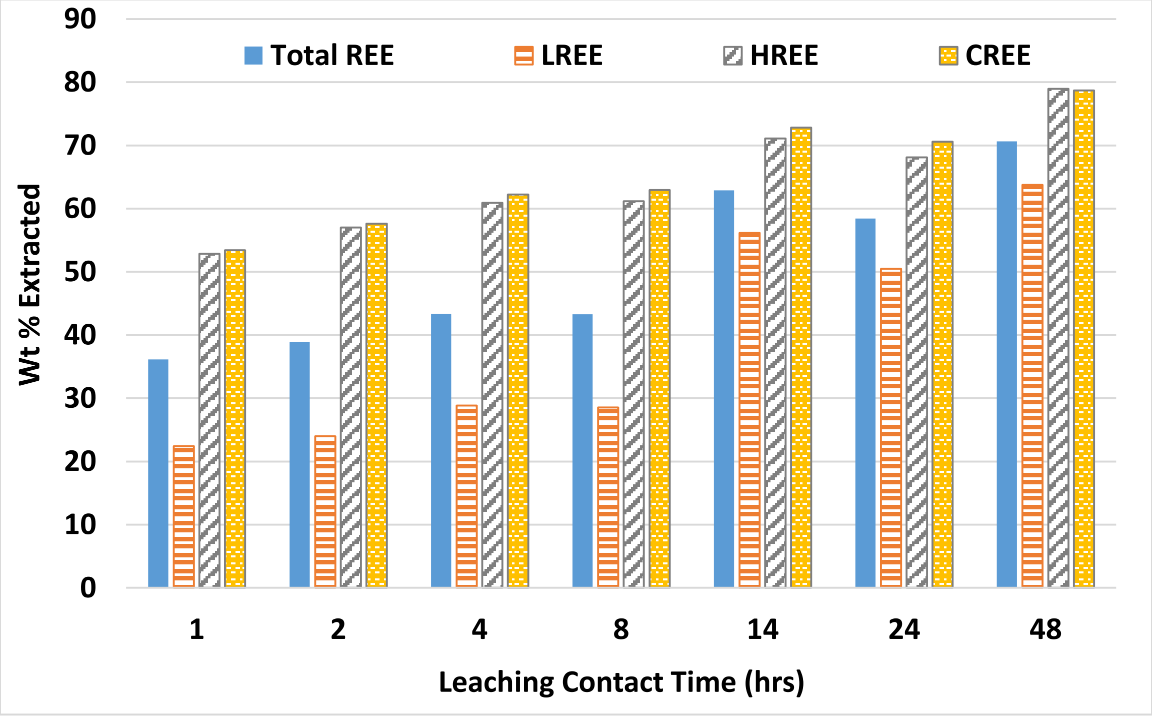


Figure 33. Leaching kinetics for groupings of REE for Hagel B coal with Type B solvent

The results do show a trend of increasing extraction with increased contact time up through about 14 hours, where a plateau exists. Scandium is the exception to this, where it appears that significantly longer contact times would be needed to achieve equilibrium extraction. Yttrium also behaves somewhat differently, as it has the highest extraction of any element at any of the time intervals. However, because the ionic radius of Y places it between Dy and Ho, this behavior is somewhat less exceptional. In general there is a strong trend of higher extraction of the HREE at each time interval, again pointing to differing modes of occurrence as a function of the molecular weight. Specifically looking at the more valuable HREE and CREE, within one hour of contact time more than 50% extraction is achieved, and through 14 hours more than 70% extraction is achieved, with minimal increase beyond that point. When looking at the LREEs, there is a very large increase in extraction between 8 and 14 hours. This would appear to indicate association in a mineral form that became solubilized in Type B solvent after eight hours.

Overall this data suggests that there will be a tradeoff between total REE extraction and contact time (i.e. analogous to equipment size or feed throughput). However, there is strong selectivity towards the heavy and critical REE, especially with shorter contact times. Because these are the more valuable elements that provide the most value relative to refining costs and combined with the possibility of smaller equipment sizes, it may be economically beneficial to limit contact time to less than 14 hours. In fact, the marginal gain in revenues associated with REE sales between 1 hr and 14 hr contact time may not be worth the added expense of a 14-fold increase in equipment size to handle the additional contacting time.

4.2.2.4 Leaching Kinetics Tests – Harmon-Hansen Coal

Besides the impact of kinetics on extraction of the REEs it is also important to determine the kinetics of leaching for the other components in the coal, as they will impact the concentration of the REEs in the extract solution and thus the level of purification that would be required. Therefore, two additional tests were completed with Harmon-Hansen coal (NDGS sample 6A) at contact times of 2 hours and 14 hours and are compared to the previous data for 48 hours. The time intervals for these additional tests were decided upon based on results for the Hagel B kinetics tests that showed an extraction plateau at about 14 hours. The overall extraction results for each of the elements measured are provided as Figure 34 for the REEs and Figure 35 for all other elements.

For the REEs shown in Figure 34, the results show faster kinetics than Hagel B, with about 70% total REE extraction in two hours of contact time. There was very minimal improvement in extraction through 14 hours, and then a fairly significant increase with the 48 hour contact time. Similar to the Hagel B, there does appear to be a trend of faster kinetics with the HREE, albeit less pronounced for Harmon-Hansen. Scandium behaved much differently than Hagel B, however, in that its kinetics were very close to the rest of the REEs for Harmon-Hansen. Whereas for Hagel B, the kinetics of scandium extraction were significantly slower.

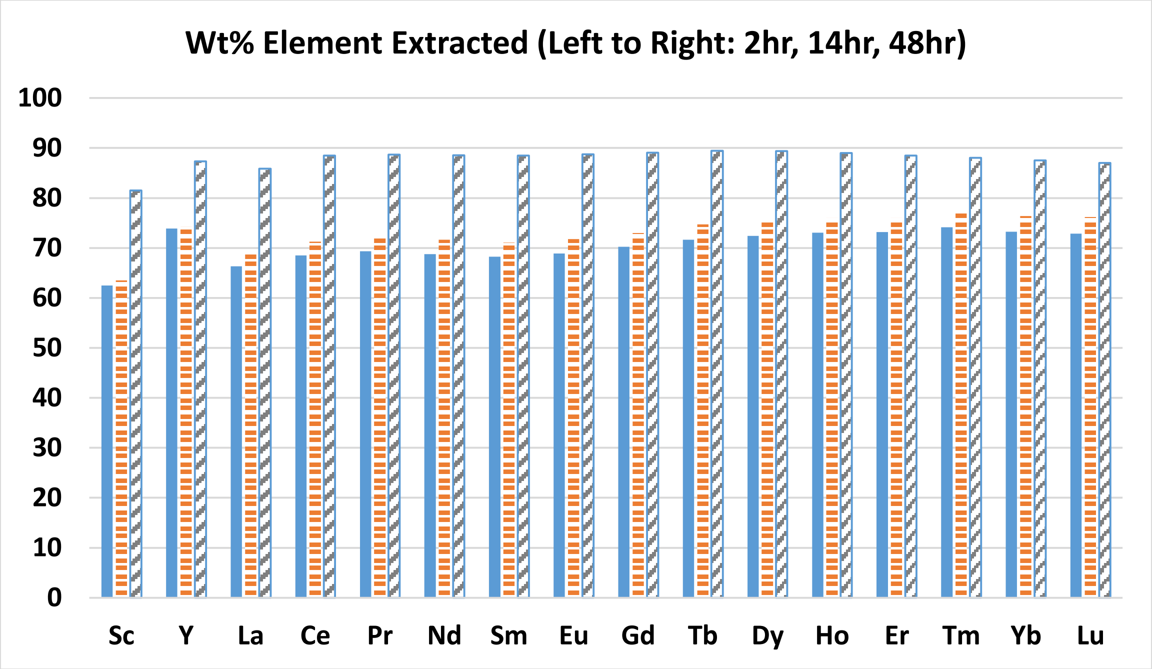


Figure 34. Results of REE extraction kinetics testing for Harmon-Hansen coal

For the other elements analyzed, consisting both of monetizable target elements and impurities, results are shown in Figure 35. Here, the kinetics of Ni, Co, V, Zn, Ga, Ge and Mn, all appear to be very fast, with minimal increase in extraction beyond the 2 hour contact time. Since these are all considered monetizable byproducts, this result would be a benefit to the economics of REE extraction. When looking at the impurities, primarily Fe, Ca, Mg, Na, K, Th and U, several of the elements show significant dependence of extraction on contact time. For example, the radioactive elements Th and U, show very large increase in extraction after the 14 hour contact time, albeit not much difference between 2 and 14 hours. This suggests that further tuning of the process may result in high REE extraction with minimal extraction of the hazardous radioactive elements. Additionally, Ca and K extraction show a strong dependence on contact time. Phosphorous also exhibited much higher extraction at the 48 hour contact time, while Pb was only extracted with the 48 hour contact time. Perhaps the most important finding from this testing is that with the shorter contact time, approximately half of the iron that was extracted into solution with the REEs at 48 hours was extracted at the shorter contact times.

Because iron is the dominant impurity form in the extract solution, this has a dramatic impact on the concentration of REEs in the extract solution, as shown in the mass balance calculations in Table 20. This result shows that with Type B solvent leaching of the raw coal, 1.36wt% REEs in solution is achieved at the two hour contact time, and 1.32wt% REEs at the 14 hour contact time, both of which are significant improvements over the 0.79wt% concentration for the 48 hour contact time. This result suggests that further improvement can be expected once the leaching chemistry and process conditions have been completely optimized, meaning there exists a real possibility to achieve the 2wt% target in a single processing step. For the two hour data, this represents concentration factors of 6.0 and 24 on an ash and whole coal basis, respectively.

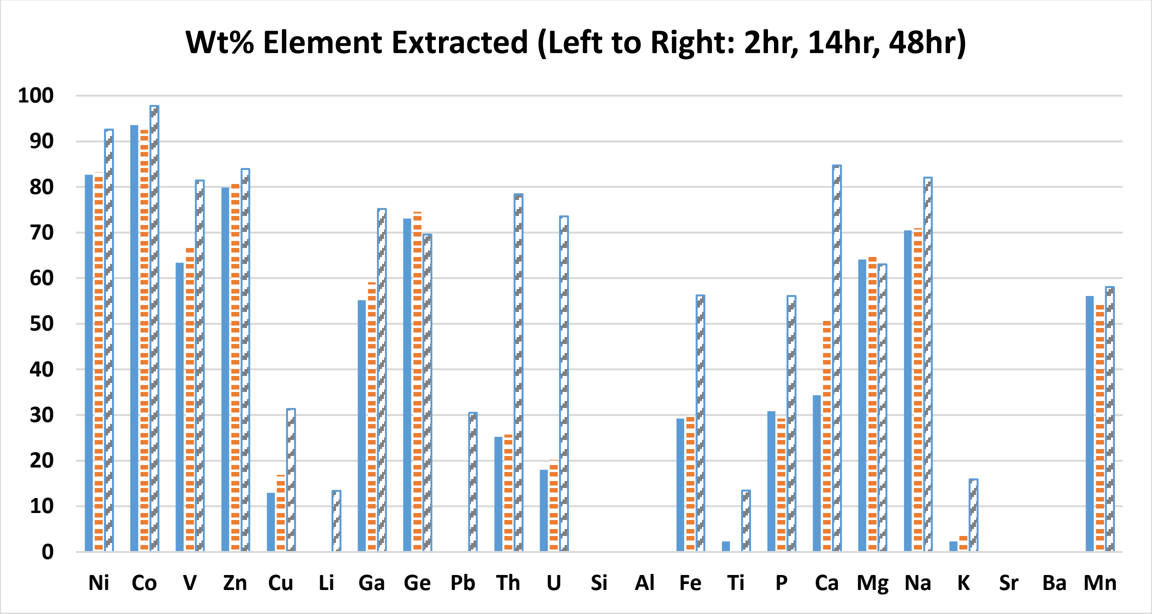


Figure 35. Results of extraction kinetics testing for other elements for Harmon-Hansen coal

Table 20. Mass balances for Harmon-Hansen extraction kinetics testing

Contact Time (hr)	Ash Content (wt%)	Ash Reduction (wt%)	Total Mass Extracted (g)	% Total REE Extracted	Wt% REEs in Solution (dry basis)
Unleached Coal	25.6	-	-	-	-
2	22.7	11.5	1.52	68.7	1.36
14	22.4	12.7	1.62	71.3	1.32
48	20.7	19.3	3.34	87.7	0.79

4.2.2.5 Additional Leaching Tests – Leonardite

As mentioned previously, literature suggests that the surface properties of Leonardite make it particularly adsorptive, and thus the modes of occurrence of REEs in Leonardite are likely to be different that with lignite coals. To investigate, three leaching tests were conducted that looked only at the extraction of REEs.

The starting material was the Leonardite Fine product provided by Leonardite Products LLC. Tests were completed using Type B solvent, Type D solvent and Type E solvent, each with 24 hours of contact time.

The results showed that no measurable extraction of the REEs occurred with either Type D or Type E solvent, but that there was some extraction with the Type B solvent, as shown in Figure 36. Overall, these results are significantly poorer extraction performance than the raw lignite coal samples (Hagel B, Harmon-Hansen). However, again there appears to be significant selectivity towards the HREE. The mass balance for each of the extraction tests is provided in Table 21, and shows that there is very low concentration of REEs in the extract solution after Type B solvent leaching. Based on these results, it would appear that the REE modes of occurrence in Leonardite are significantly different than in lignite, most likely due to the oxidation process having transformed the REE bonding.

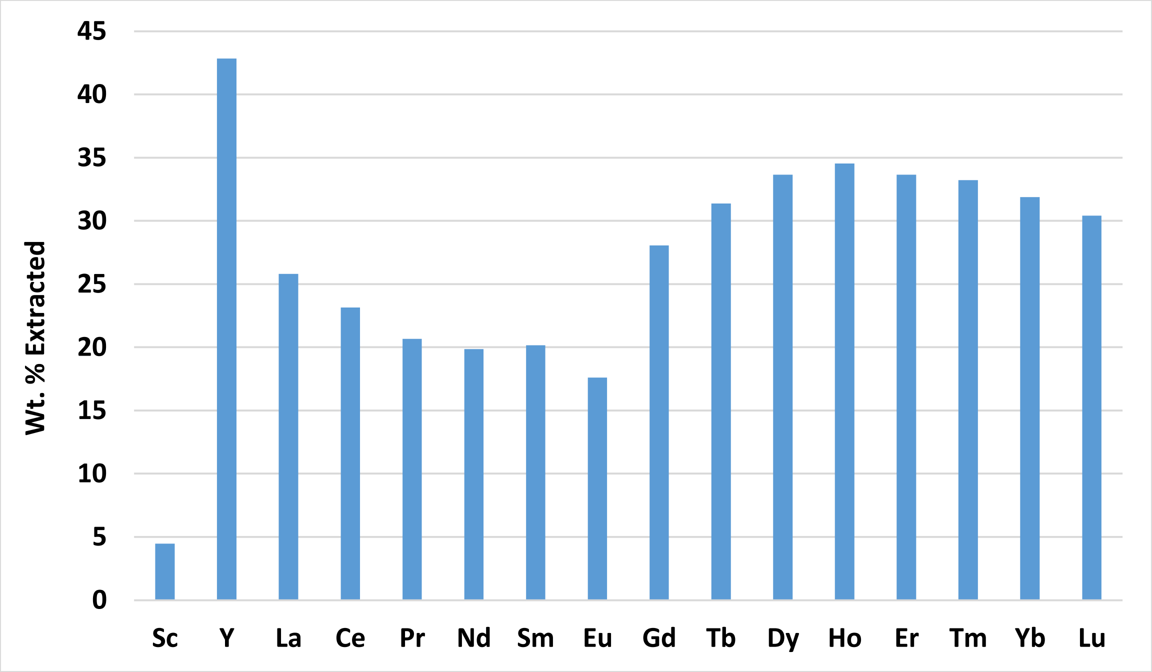


Figure 36. Type B solvent leaching extraction results for Leonardite Fine material

Table 21. Mass balance for Leonardite REE extraction tests

Sample	Ash Content (wt%)	% Ash Reduction	% REE Extraction	REE Concentration (wt%)
Unleached	21.6			
Type D Solvent	20.1	6.9	-	-
Type E Solvent	19.3	10.7	-	-
Type B Solvent	18.0	16.6	25.7	0.05

4.2.2.6 Additional Parametric Testing – Effect of Particle Size Distribution

To determine the role of mass transfer on REE extraction rates, tests were completed using Type B solvent on Hagel B coal at two particle size distributions (PSD) (fine and coarse). Tests were completed with contact times of 1, 2, 4 and 14 hours. Results are provided in Figure 37, which are broken down into groupings of total REE (TREE), total LREE (TLREE), total HREE (THREE) and total critical REE (TCREE). Overall, the results indicated minimal effect for the LREE, with a small effect on the HREE. Specifically, the difference between the 1 hour and 14 hour contact time for the finer PSD was less pronounced than for the coarser PSD. For the fine PSD, extraction increased from 58 to 64% between 1 and 14 hours, but for the coarse PSD, extraction increased from 53 to 71% over the same time frame. The explanation for the higher total extraction at 14 hours for the coarse PSD is not clear. It may be due to a sampling error. These results can be explained by the inherently porous nature of lignite coal that provides good surface area for contacting without fine grinding, as well as the organic associations of the REEs that are bound on the surface of the organic matter in functional groups that are easily accessed through the pore structure. This will allow us to use a coarser coal PSD, which will reduce costs of grinding and will provide larger flexibility in regards to use of the coal byproduct after leaching.

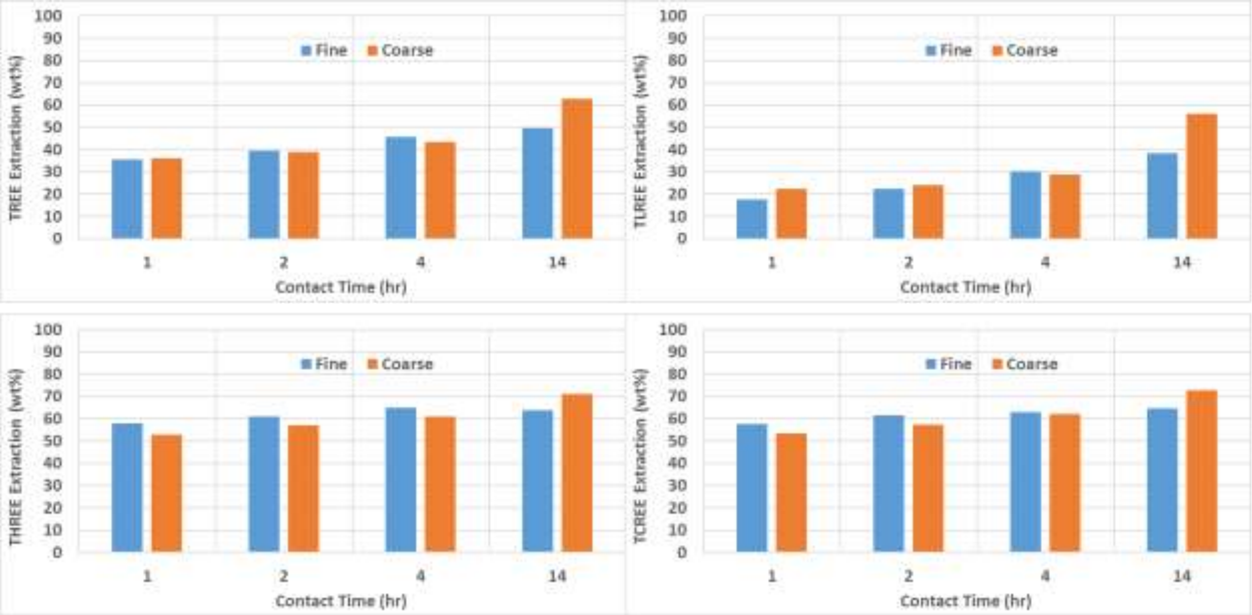


Figure 37. Effect of particle size on REE extraction. Top left (total REE); Top right (total LREE); Bottom left (total HREE); Bottom right (total critical REE)

4.2.2.7 Testing of Additional Solvents

Testing with Type D solvent was previously attempted on the Leonardite materials without success. It was also tested on one of the Harmon-Hansen coal samples as well (NDGS sample 6A-2 with ~40% ash). However, this testing used a modified 2-step leaching approach that consisted of 24 hours of contact time with Type D solvent and then 4 hours of contact time with Type B solvent. The results are summarized by Figure 38. In contrast to the results with Leonardite, a significant quantity of the REEs were extracted with the Type D solvent leaching. In fact, the majority of total REE extraction occurred during this step, and the concentration of REEs in the leachate was 2.05 wt%. A significant quantity of REEs were extracted with one hour of Type B solvent leaching, and then minor amounts with an additional three hours. Table 22 displays the overall mass balance for the test. Overall, the data indicates that the programmatic goal of 2wt% REE was achieved in a single processing step using Type D solvent leaching, but that only 36% REE was recovered in this step. Total REE recovery of 60% was achieved with an additional four hours of contact time with Type B solvent leaching, but this was at the expense of a decrease in REE concentration to 1.24 wt% in the product solution (i.e. mixture of Type D leachate and 4-hour Type B leachate). The data suggests that Type D solvent should be evaluated further.

Table 22. Results of REE concentration in leachates for two-step leaching process using NDGS sample 6A-2

Product Solution	**wt% REE**	**REE Recovery (whole coal)**
Type D Solvent Leachate	2.05	36.0
Type B Solvent - 1 hr Leachate	0.77	21.5
Type B Solvent - 4 hr Leachate	0.78	24.2
Mix Type D + Type B 4 hr	1.24	60.2

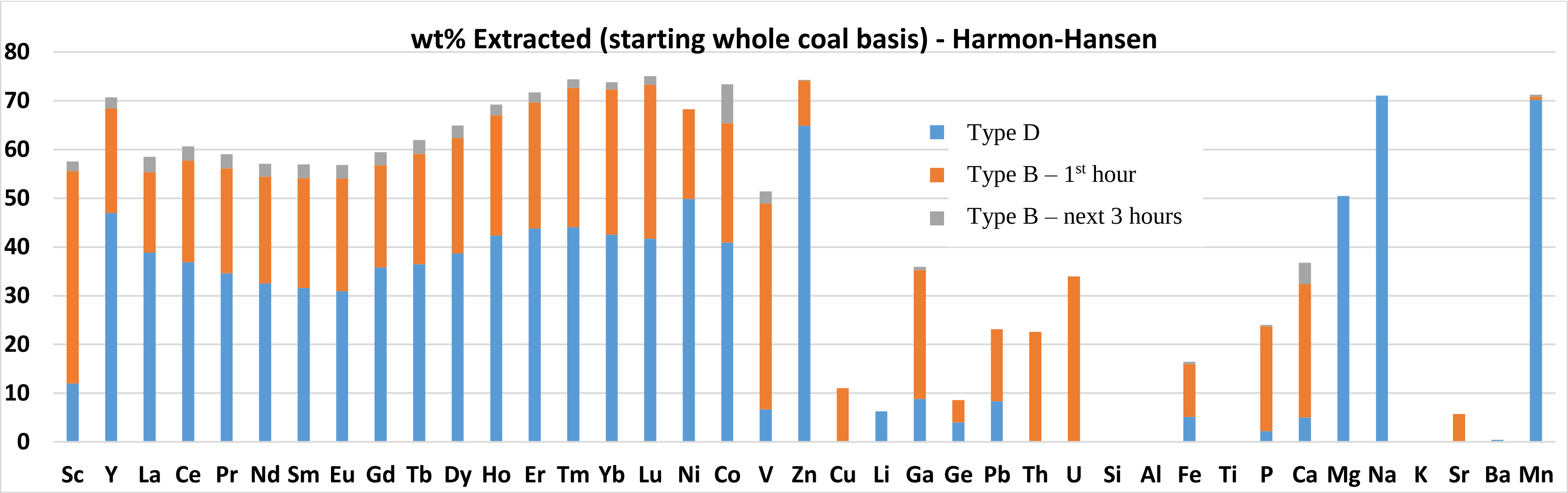


Figure 38. Results of Type D solvent leaching (24 hr) followed by Type B solvent leaching (1 hr and 4 hr) for NDGS sample 6A-2

4.3 Summary and Conclusions

Two types of extraction methods were evaluated that included grinding and classification for roof/floor sediments and combustion fly ash, and solvent leaching for multiple lignite and lignite-related feedstocks. A summary and conclusions are provided below:

- Physical beneficiation processes for concentration of REEs from roof and floor sediments associated with North Dakota lignite coals are likely not feasible either technically or economically due to challenges with separating ultra-fine particles less than 10 microns in diameter. Grinding and classification methods proved ineffective in generating any measurable concentration of the REEs.
- Similarly, physical beneficiation of combustion fly ash is likely not feasible due to challenges associated with the REEs being trapped in the glassy, fused ash materials formed during high temperature combustion. Testing did identify some possible enrichment in the coarse size fraction of the combustion fly ash, but the concentration factor was not large enough to warrant continued evaluation.
- Initial screening identified Type B solvent for detailed testing, which proved highly effective in extracting REEs from the Harmon-Hansen coal and the Hagel B coal, with performance for the Harmon-Hansen being measurably better than the Hagel B coal. However, Hagel B testing showed a favorable selectivity towards extraction of the heavy and critical REEs.
- In addition to REEs, the content and extraction of the bulk ash-forming species and other trace species in the coal were evaluated. Results showed that the coals have strikingly different geochemistry, with the Harmon-Hansen being rich in transition metal elements and the Hagel B being rich in alkali and alkaline earth elements. Overall, in addition to high extraction of the REEs, each coal exhibited co-extraction of a number of other elements of both potentially monetizable value and of low or negative value. Some of the high value elements include Co, Cu, Ga and Ge and the primary impurity forms are iron, alkali and alkaline earth elements. Radioactive Th and U are also extracted with the REEs. The concentration of REEs in the extract solutions were 0.23wt% and 0.8wt% for the Hagel B and Harmon-Hansen coals, respectively when evaluated on a dry basis.
- The kinetics of the REE leaching process were evaluated by varying the contact time for the leaching solution and the coal. For the Hagel B coal, the data showed a strong selectivity towards the HREE, especially at short contact time. After 14 hours a plateau was observed where minimal increase in REE extraction occurred with additional contacting time up to 48 hours. A large step increase in LREE extraction was observed between 8 and 14 hours of contact time, indicating that a significant portion of the LREE are likely bound in soluble mineral forms. The HREE, however,

showed a gradual increase in extraction through 14 hours. With only one hour of contact time, HREE and critical REE extractions were greater than 50%. Overall, the data suggests that an optimal balance between contact time and REE extraction exists when considering economic factors such as equipment sizing and revenues for REEs.

- Kinetics testing for the Harmon-Hansen coal used 2, 14 and 48 hour contact times and both the REEs as well as the other high value monetizable elements and the impurities were measured. Overall, the results show that the kinetics of REE extraction are faster than Hagel B, with about 69% total REE extraction with 2 hours of contact time. Further, the results showed that most of the monetizable elements had similarly fast extraction kinetics, but that many of the impurities, namely iron, thorium and uranium were significantly slower than the REEs. This resulted in a dramatically increased concentration of REEs in the extract solution at the 2 hour and 14 hour contact times, as compared to the 48 hour time. For the 2 hour time, the concentration was 1.36wt% REEs in solution, compared to about 0.8wt% for the 48 hour contact time. This data suggests that with additional optimization, the target of 2wt% REEs may be achieved with only the solvent leaching step.
- Extraction of REEs from Leonardite proved less effective than from the lignite coals, presumably due to a different mode of occurrence resulting from the oxidation of the Leonardite.
- The impact of coal particle size was also evaluated in additional parametric evaluation of the leaching process. PSD was shown to have minimal impact, likely due to the porous nature of lignite and the bonding of the organically associated REEs on surface functional groups.
- In another leaching method tested with the Harmon-Hansen coal, Type D solvent leaching proved capable of generating greater than 2.0wt% REE concentrate in just that single step, but this occurred with only about 36% total REE recovery, compared to the lower concentration with higher yield achieved for Type B solvent (i.e. 70% yield at 1.36wt% REEs concentration).

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PHASE 2 TESTING REPORT

SUBMITTED TO

U.S. Department of Energy
National Energy Technology Laboratory

SUBMITTED UNDER FUNDING OPPORTUNITY ANNOUNCEMENT

DE-FOA-0001202

INVESTIGATION OF RARE EARTH ELEMENT EXTRACTION FROM NORTH DAKOTA COAL-RELATED FEEDSTOCKS

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WORK PERFORMED UNDER AGREEMENT

DE-FE0027006

Signature of Submitting Official: Michael D. Mann
Michael D. Mann Ph.D.

Investigation of Rare Earth Element Extraction from North Dakota Coal-Related Feedstocks

Due to their unique properties, REE are crucial materials in an incredible array of consumer goods, energy system components and military defense applications. However, the global production and entire value chain is dominated by China, with the U.S. currently 100% import reliant for these critical materials. Traditional mineral ores including previously mined deposits in the U.S., however, have several challenges. Chief among these is that the content of the most critical and valuable of the REE are deficient, making mining uneconomical. Further, the supply of these most critical REE is nearly 100% produced in China from a single resource (ion-adsorbed clays) that is only projected to last another 10 to 20 years. The U.S. currently considers the REE market an issue of national security. It is imperative that alternative domestic sources of REE be identified and methods developed to produce them. Recently, coal and coal byproducts have been identified as one of these promising alternative resources. The work presented here focused on the development of a novel technology for REE extraction and concentration from the vast lignite reserves in ND, and is following up on a successful Phase 1 program that developed proof-of-concept at the laboratory-scale.

The overall goal of this Phase 2 project was to test and optimize, at the bench-scale, a novel process to produce a rare earth elements (REE) concentrate greater than 2% by weight (mixed REE) derived from lignite coal and associated sediments. Work conducted during Phase 1 indicated that recovery of REEs from North Dakota lignite and lignite-related materials has been shown to be feasible and worthy of continued evaluation, based on the following:

- Multiple locations in North Dakota have been identified with elevated levels of REEs that are greater than the target of 300 ppm (dry whole sample basis) and the data collected to date provides sufficient evidence to suggest commercially feasible quantities of REE-rich coals are available and worth targeting.
- The weak bonding of REEs in North Dakota lignite allows the use of a novel, highly effective, environmentally benign and extremely low cost extraction technology. The technology is simpler than those being investigated in literature and provides many additional benefits.
- The target of 2wt% REE concentration is achievable in a single processing step and optimization testing in Phase 2 is expected to significantly improve performance

In order to achieve the goal of the project, the Phase 2 objectives included:

- Based on the Phase 1 design, construct and install a bench-scale system that can be used to process a range of feedstocks including coal and associated sediments.
- Obtain large samples of greater than 300 ppm REE content coals from selected locations identified in Phase 1.
- Characterize the samples collected to verify abundances and modes of occurrence and prepare feedstocks for bench-scale testing
- Perform batch parametric testing of the process unit operations to tune process chemistry and optimize conditions and configuration
- Process approximately 1000 kg of feedstock with continuous flow semi-integrated operation at optimized conditions to generate a representative REE concentrate product that would be suitable for further evaluation.
- Update the technical and economic evaluation of the technology based on Phase 2 testing results
- Develop a preliminary commercialization plan

Testing in Phase 2 was accomplished in two stages. The first stage focused on parametric evaluation of each of the process unit operations using batch tests. Once optimization and final process configuration was determined, a second round of testing was performed that processed approximately 1000 kg of lignite coal under optimized conditions in continuous flow operation to achieve the required Technology Readiness Level of 5. Based on the experimental results, the technical and economic feasibility analysis started during Phase 1 was updated. A commercial-scale plant configuration is identified a Class IV (AACE International) design and economic analysis completed. Finally, working closely with industry co-sponsors, a preliminary commercialization plan was developed that identifies opportunities for the application of the technology at existing mines/plants in ND and/or justify the economically viable case for the opening of a new mine in a location with most favorable REE content/distribution.

The technical project team for Phase 2 consisted of the University of North Dakota, Barr Engineering Company, Microbeam Technologies Inc., Pacific Northwest National Laboratory (PNNL) and MLJ Consulting. The cost share partners include North American Coal Corporation, Great River Energy, Great Northern Properties, Minnkota Power Cooperative, the Lignite Research Program of the North Dakota Industrial Commission, the University of North Dakota College of Engineering & Mines, and the North

Dakota University System. North Dakota Geological Survey also supported the project in a technical advisory role.

1. Preliminary Lab-Scale Extraction and Concentration

From Phase 1, dilute mineral acids were identified as a likely candidate for extraction of the REE from pre-combustion lignite coals. Additionally, leaching experiments identified optimal leaching times near 14 hours, as well as the potential for separation of Group 1 and 2 cations away from the REE, further purifying the PLS for the REE. Work at the beginning of the Phase 2 project was targeted towards further increasing the concentration of REE within the final product material, and focused on pre-leaching techniques, selective precipitation, and iron oxidation as a mechanism for separation of the materials. Results of this preliminary work are discussed in this section. Coal for these preliminary tests was sourced from the Harmon seam in the Harmon-Hansen coal zone in southwestern ND (Figure 1.1).

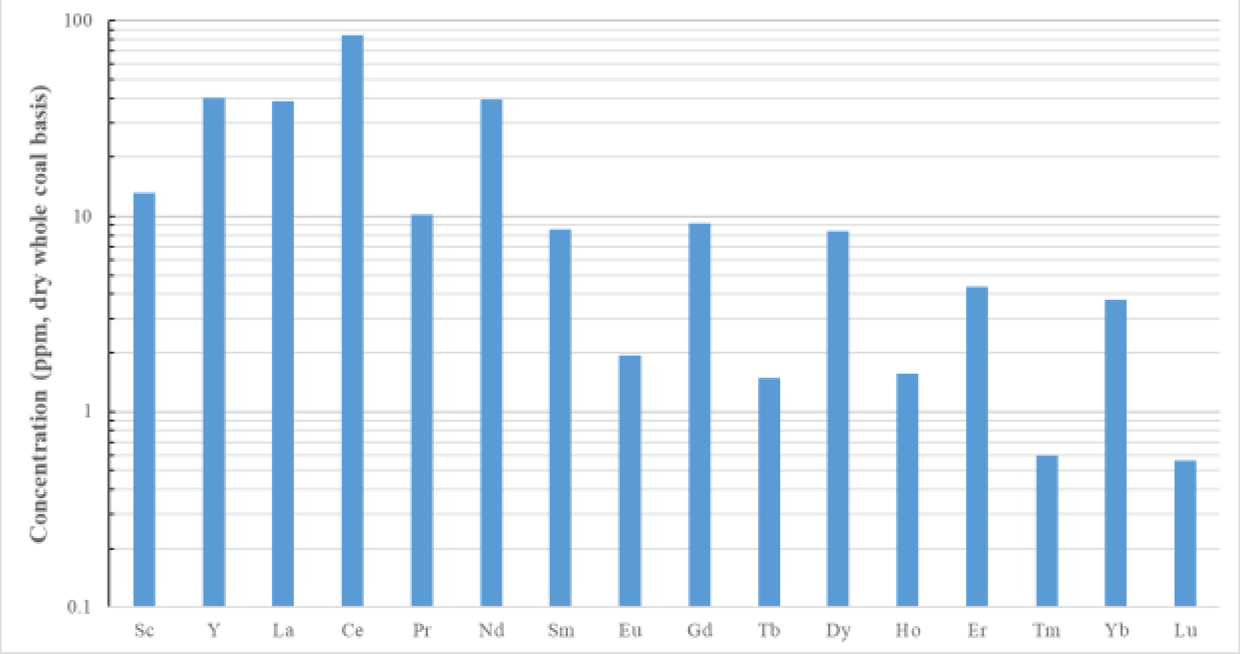

Figure 1.1. *REE Concentration in the Harmon lignite utilized for preliminary lab-scale experimentation.*

1.1. Goals and Methods

<u>Liquid Extraction and Concentration Testing:</u> Recognizing the organic-based nature of the REE within the lignite, as contrasted to the other coal ranks, it was hypothesized that an increased selectivity towards leaching could be achieved. Goals of the preliminary lab-scale testing in Phase 2 were to determine potential pre-leaching setpoints and/or methods for low-cost removal of acid-consuming group 1 and 2 cations (Na,

K, Ca, Mg, etc) from the coal. Ideally, a point with limited REE extraction (<10%) with high alkali and alkaline earth extraction (>80%) would be targeted for initial purification.

Additionally, identification of a purification mechanism for improved REE concentrate purity (above 2 wt%) was targeted. Following the literature survey and discussion with solvent extraction specialists, solvent extraction was not considered prior to generation of a solid REO concentrate, primarily due to the variability in concentrations and ratios of the REEs and impurities within the coal, as well as the high solvent costs incurred in dilute streams. Selective precipitation routes to generate moderate-purity concentrates, followed by either direct refining to separated REE (if possible/economic) or downstream purification (where concentrations of REE may be more conducive to hydrometallurgical separation, such as solvent extraction). Precipitations of the REE based upon pH (through addition of NaOH) as well as the use of oxalic acid ($H_2C_2O_4$) were considered as likely alternatives.

Planned reagents included the use of ammonium lixivants (acetate and sulfate) as well as dilute mineral acids. Planned coal use would be limited to small (< 500 gram) tests, where solid and liquid samples before and after testing would be analyzed. Elemental analysis on solid and liquid samples were conducted by utilizing Inductively-Coupled-Plasma Mass-Spectroscopy (ICP-MS). Solid samples, such as coal, were digested utilizing ASTM trace metal analysis procedures, with liquid samples diluted to specific concentrations for use with known standard solution calibration curves.

Solid Concentration Testing: Testing of physical concentration methods were conducted, primarily based upon removing mineral-based fractions of the coal to concentrate the organic-based REE of interest. Preliminary investigations into density-based separation, as is common with conventional coal cleaning technologies, were conducted utilizing float-sink experiments in heavy organic liquids, for better control over separations.

Small increases in concentration achievable with physical methods, such as classification/density-based separation were anticipated to make significant differences in overall economics. The low cost and ease of scale-up associated with these methods would enable more targeted use of chemical processes as needed, reducing processing costs for similar REE recoveries. However, reject of a significant portion of the coal at lower quality (higher ash content) would result in economic challenges associated with recuperated mining costs, as the reject coal may not be usable in further downstream operations (such as coal-fired electric utility systems).

Following the fractionation of the coal by density fractions, extraction testing of each fraction was conducted using the extraction chemistry and methods identified in Phase 1 to evaluate REE and major element extraction performance as a function of density fraction. These coal samples were representative mixtures of each size fraction of material, and were leached in 60g tests under lab-scale conditions. Evaluation of the change in extractability of multiple elements, including the REE, and any correlations between the major elements and the rare earths were of significant interest, as well as determining potential liquid-phase concentrations of the impurities to improve downstream process tuning.

1.2. Results of Testing, Analysis, and Conclusions

Extraction and Concentrate Testing: Preliminary testing at multiple pH units for pH-based separation from the UND pregnant leach solution was performed, with liquid solutions analyzed for total removal efficiency of multiple elements at each level (Figure 1.2). While significant recovery of the REE was possible utilizing pH-based precipitation mechanisms, and with relative high purity, significant precipitation of a valuable REE, Sc, occurred during a pH level at which another major impurity precipitated (Al). This would result in a very low concentration of Sc, and a potential challenging recovery process for the valuable material.

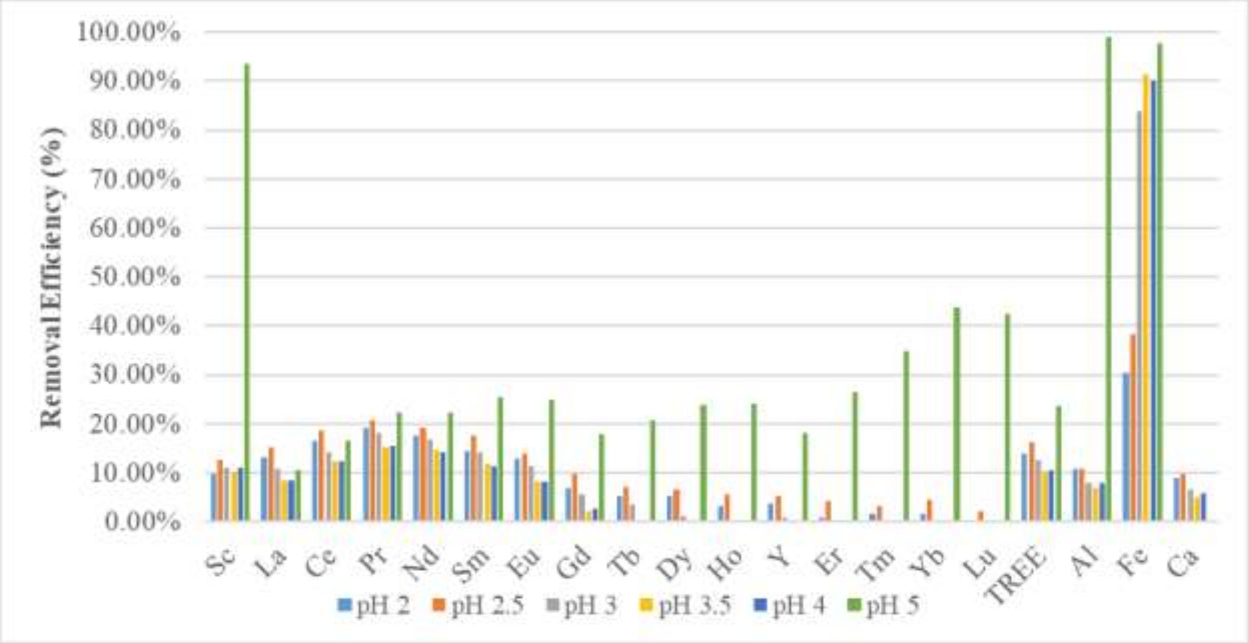

Figure 1.2. *Removal efficiency of REE, CM, and other major elements as a function of pH on the UND PLS*

Previous literature pointed towards an equilibrium pH of near 2 for effective REE oxalate precipitation [1]. To control to this pH value, a 10M solution of NaOH was added. Concentration of oxalic acid precipitant was varied to determine the requisite amount required for high REE recovery (Figure 1.3). As shown in the figure, significant excess was required to precipitate the REE, far more than literature had suggested. After further evaluating literature, evidence towards Fe^{3+} and Al^{3+} complexation of the oxalate ion was discovered, particularly surprising given the expected ferrous ion state (as in pyrite). Additionally, Ca was identified as an impurity of significant concern, as this was the only low-value impurity of note contained in the REE-oxalate solids produced.

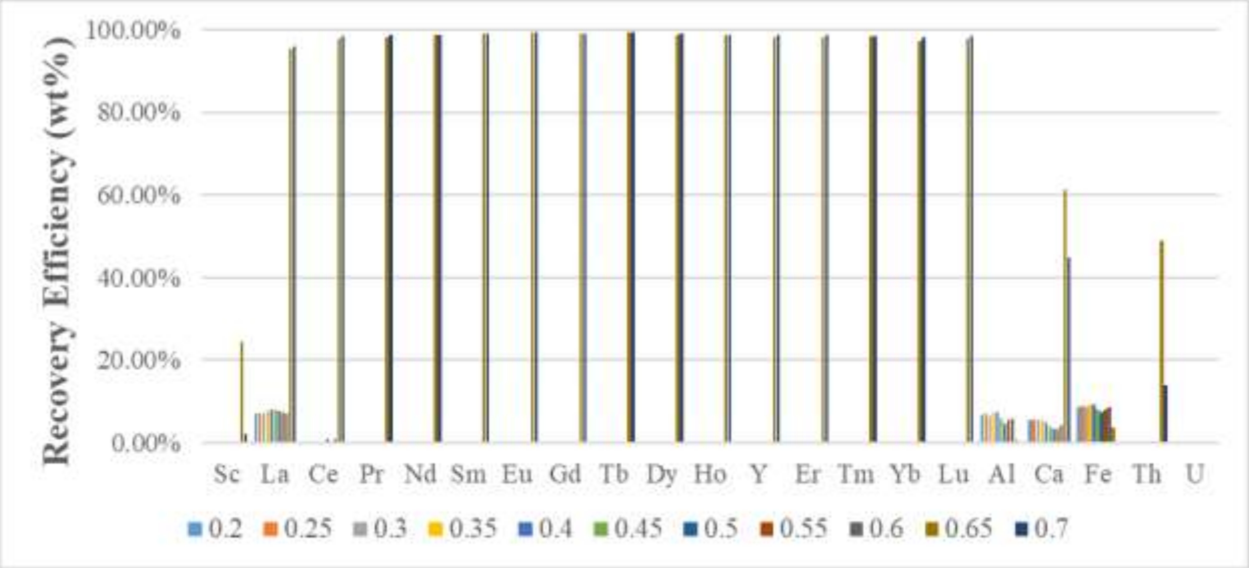

Figure 1.3. *Recovery efficiencies of REE's and major elements with multiple oxalic acid concentrations (M in solution).*

This information significantly added to process development efforts, as pre-leaching was given a specific target to remove Ca, and further Fe removal steps were needed, and would require a mechanism other than air oxidation (due to the ferric ion). Al removal would also be preferred, but pH-based removal schemes had already identified co-precipitation with Sc, an element of strong economic potential to the process. Additionally, the low recovery of Sc, coupled with the high oxalic acid concentration required to have complete precipitation of the REE, warranted further investigation into required improvements. This could include the removal of the complexant species (Al and Fe), removal of Ca as a co-precipitant, and other chemical controls.

Pre-leaching Testing: From Phase 1 of the project, evidence pointing towards REE complexation within organic structures, such as with the humic and fulvic acids indicative of low rank coals, had been made [2]. However, the forms of the alkaline and alkaline earth metals, while believed to have organic associations, were unclear as to whether mineral encapsulation, organic complexation, or ion-adsorbed behaviors dominated these elements (Na, Mg, Ca). Testing to identify this source, and to leach these acid-consumer/diluent elements prior to REE leaching was conducted in two parts, one under the assumption that these materials would be leachable by an lixiviant-based system (ammonium acetate) under various concentrations [3], and another where these elements are chemically complexed and acid is required (utilizing dilute mineral acid) [4]. These results are found in Figures 1.4 and 1.5, respectively.

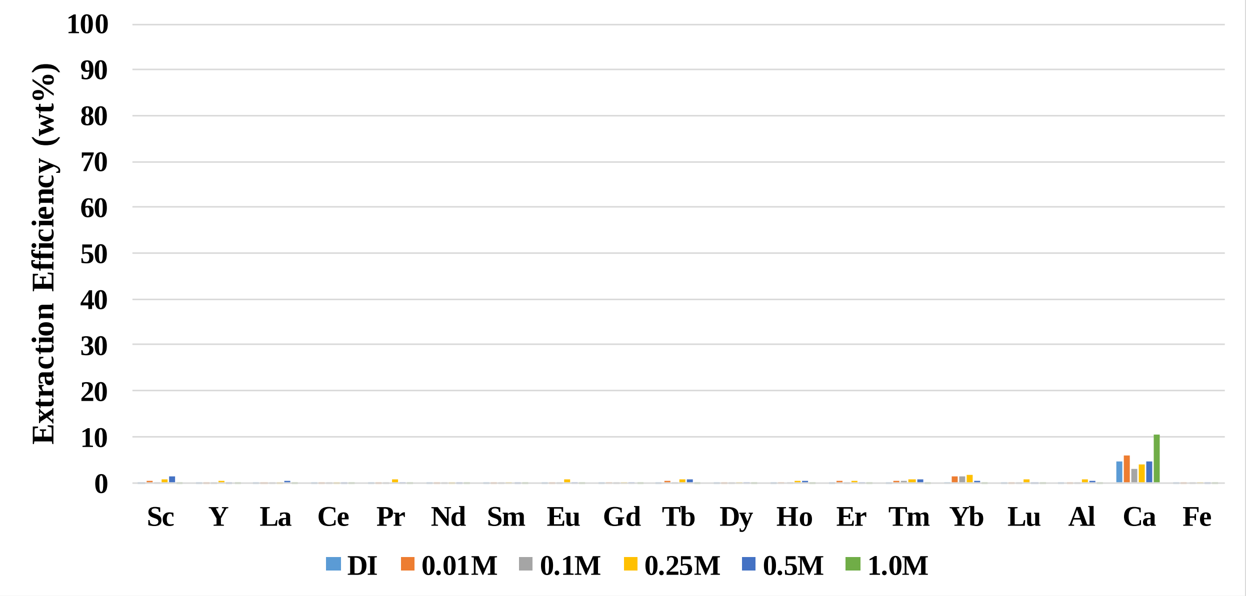

Figure 1.4. *Ammonium Acetate leaching of Harmon lignite coal.*

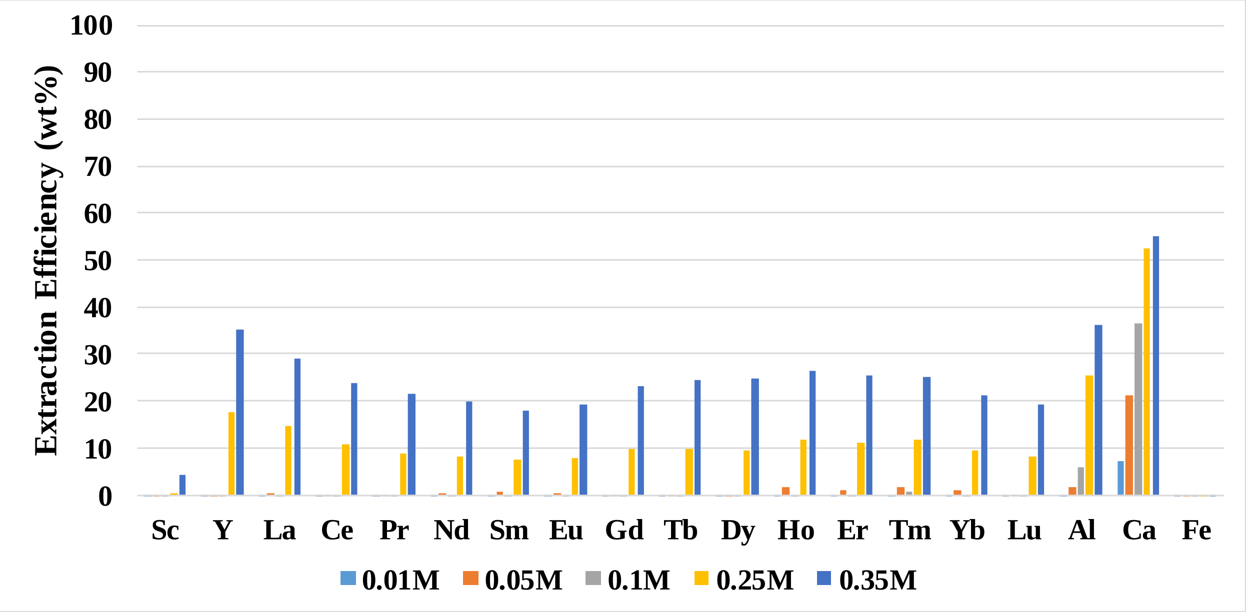

Figure 1.5. *Dilute mineral acid leaching of Harmon lignite coal.*

Based upon the data, the alkali and alkaline earth metals were predominantly complexed in the organic matrix, preventing the ammonium ion from adequately mobilizing these into a liquid solution. Further, removal of only 50-60% of the Ca was only achievable in concentrations where REE leaching was > 10%, minimizing the potential benefits achievable through this mechanism. Bench testing of this mechanism and planned tests was still recommended, primarily to determine if other variables beyond concentration would affect the leaching separation of the two elemental groups, including slurry density and slurry contacting time. Surprisingly, significant Al extraction occurred, despite the expectation of aluminosilicate clays as the primary mode of occurrence [4]. This revelation, pointing towards a highly-soluble fraction of the Al in a separate form (such as organically associated or as soluble minerals), is key in understanding potential impurity elements leachable into the PLS, and affects potential impurity removal requirements and/or oxalic acid usages. Expanding on this, the variability of the extractability of Al in the Harmon vs the H-Bed coal (data shown later in Figure 3.2) demonstrates additional attributes to understand in each coal material, outside of the leachable REE content, to determine final process parametrics and conditions.

Physical Concentration Testing: In addition to the chemical concentration pathways pursued, physical concentration utilizing float-sink density methods was employed to determine the potential benefit (Figures 1.6-8) to the process economics. Float/Sink analysis was conducted on multiple size fractions (4x20 US Mesh, 20x40, and 40x60). As demonstrated, significant REE concentration may be achieved (from 265 ppm average to > 350 ppm for the lightest fractions, dry whole coal basis) with coal cleaning, particularly on an ash basis (>2,500 ppm for the float material at 1.3 SG). Slight concentrating effects were found between the sizing of the coal with float sink, and are anticipated to be a result of improved liberation of mineral matter through fine grinding. However, further process testing would confirm the detrimental effects of fine grinding, particularly upon the leaching liquid recovery from the coal as a result of the material. For this reason, finer grinding, despite the REE concentration improvement, was neglected.

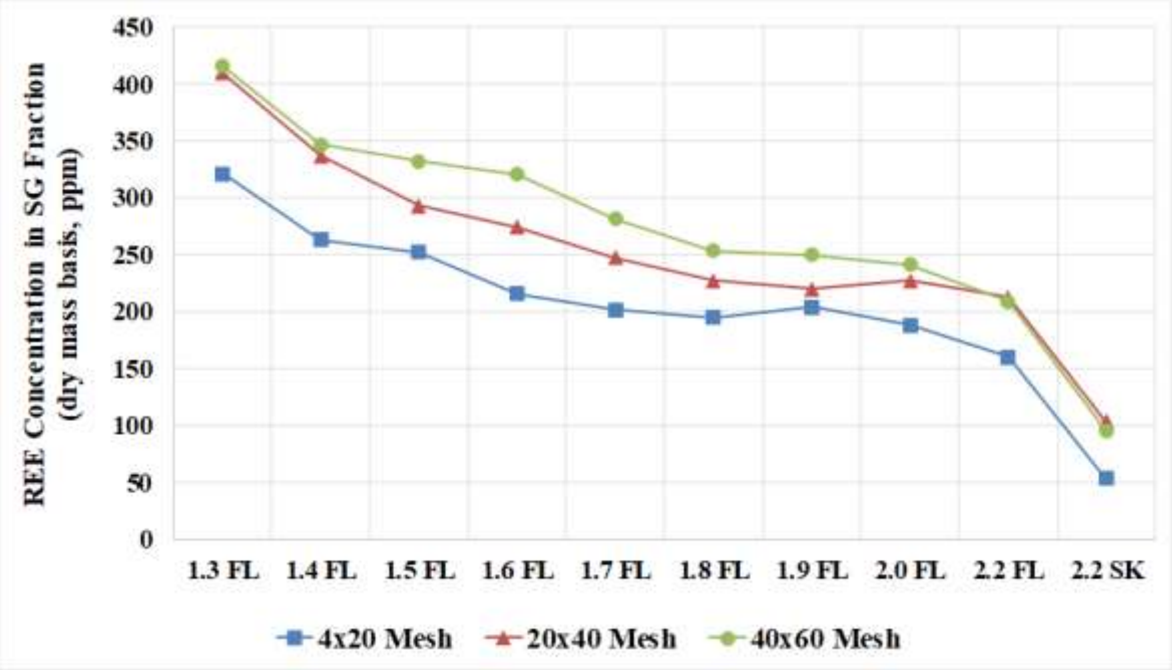

Figure 1.6. *Total REE concentration on a dry, whole coal basis by specific gravity fraction and coal size.*

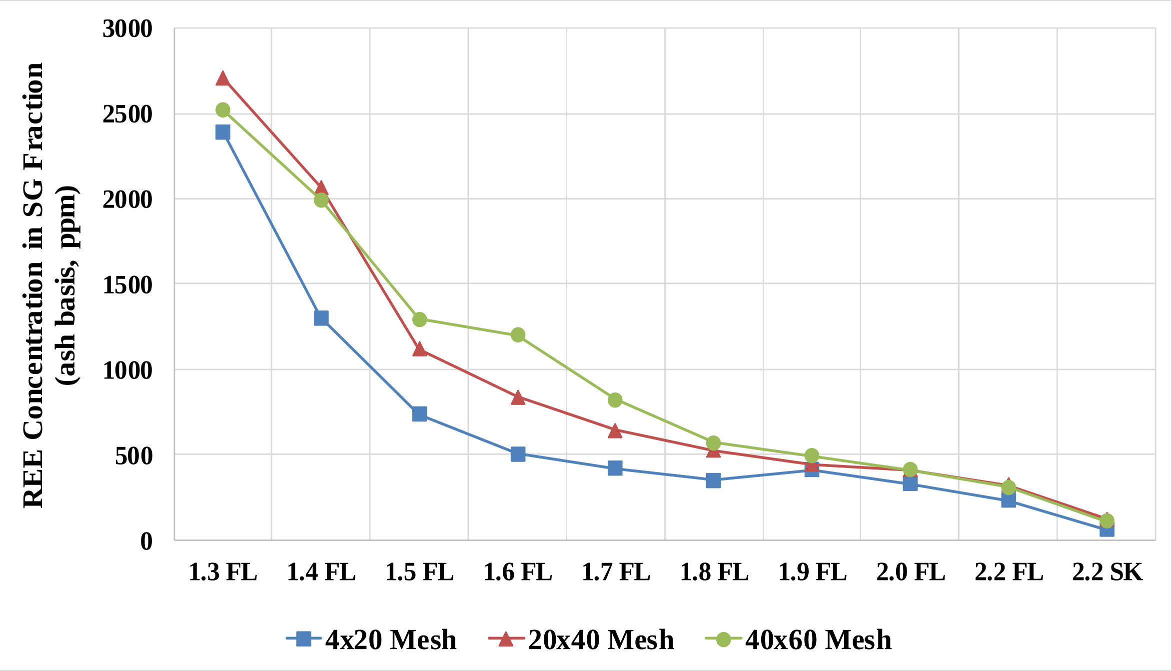

Figure 1.7. *Total REE concentration on a dry, ash basis by specific gravity fraction and coal size.*

As shown in Figure 1.8, REE concentrations show a marked affinity towards the organic-based fractions *on a whole coal basis*, as compared with the heavier fractions identified in prior work on higher-rank coals [5], [6]. This enables coal cleaning technologies to simultaneously improve REE concentrations and improve value of the resultant coal.

Figure 1.8. *Cumulative coal, ash, and REE composition and mass by specific gravity fraction.*

Based upon this data, a SG cutpoint for coal cleaning operations was chosen at 1.7 SG, a point for the Harmon coal tested to retain 80% of the REE within the overall coal, receive a coal feedstock > 300 ppm, and reduce the ash content of the leached coal by 12 percentage points. This was chosen to maximize potential cost-savings for REE processing, while retaining a sizable fraction of the coal (70%) for recovery of mining costs (through upgraded product sale). Additionally, the removal of dilute-acid-soluble mineral matter improved potential liquid-phase concentrations of REE vs other contaminants, decreasing concentration/purification costs.

Leachability of the REE and major elements were evaluated utilizing the conditions for PLS generation identified in Phase 1 (Figures 1.9-10). Extraction efficiency peaked near Tb and Dy for all lanthanides across all specific gravity samples, with consistent improved HREE/LREE extraction. While extraction efficiencies are lower for the lower SG fractions for a number of elements, overall extracted mass is higher given the significant concentration increases.

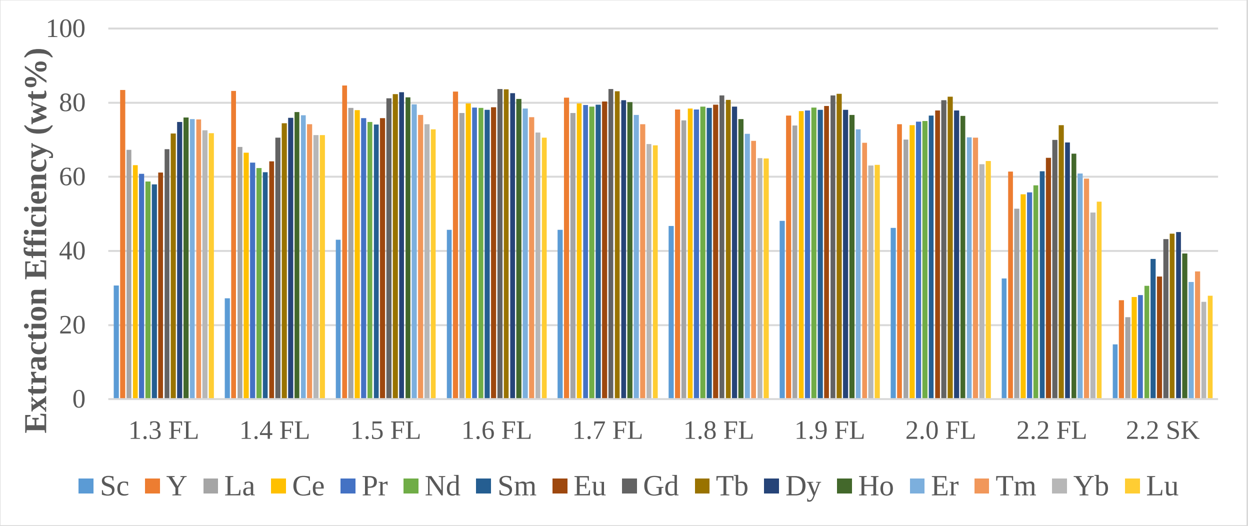

Figure 1.9. *Extractability of the REE from SG-fractionated Harmon Lignite samples.*

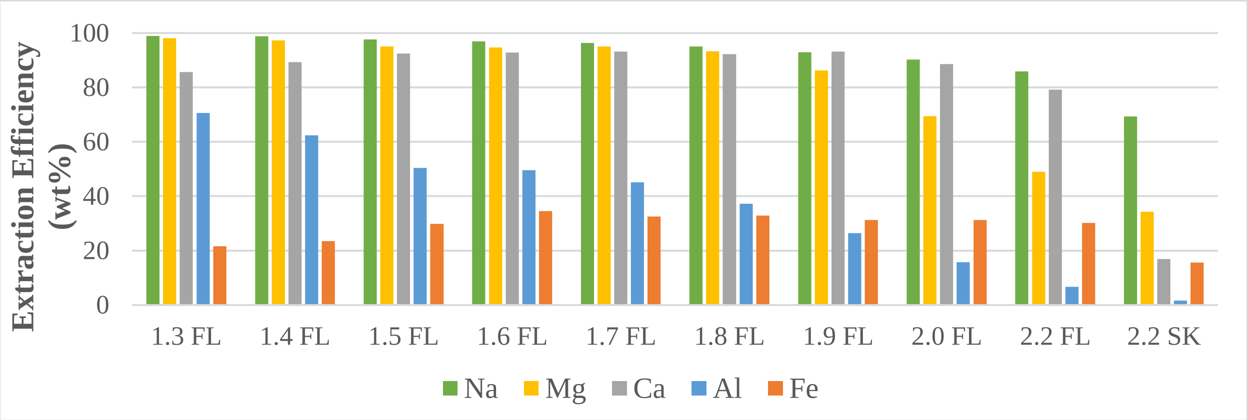

Figure 1.10. *Extractability of major elements from SG-fractionated Harmon Lignite samples.*

Across the SG fractions, the REE (with the exception of Y) and Fe show a trend of increasing extractability towards the middle SG fractions (peaking near 1.9 SG). This trend is postulated to be a result of higher organic binding site density, and therefore potential strength of organic binding at the lower SG. However, the mineral-rich phases of the high SG fractions (> 2.0 SG) have significantly lower leachability of all elements as compared with the peak leaching, pointing towards a weaker organic binding site in these middle fractions. This trend appears to have the largest effect on Sc, Fe, and the LREE (La-Eu), with a diminished effect as compared with the HREE.

Addressing the outlier trivalent materials from this trend (Al and Y), significant leaching is demonstrated at the lowest SG fractions, and decreases, albeit slowly for Y, across the entire SG series. This significant deviation from the other trivalent elements analyzed in this study, may point towards a separate, or weaker binding of these materials as compared with the REE and Fe, and rules out ionic radius effects (due to Y's place between Ho and Er within the ionic radius series). The other major elements (Na, Mg, and Ca) show a negative extractability trend with increasing density fractions, a point towards the limited mineral dissolution occurring in the system in question. These elements have been shown to contain significant organic affinities within ND lignite [3].

In conclusion, this testing period showed potential benefits of physical concentration, both to the REE concentrations and to the usability of the feedstock for post-REE use; demonstrated the required processing efforts needed to improve REE product quality, reduce costs, and improve yield; and evaluated potential impacts of preliminary leaching steps to reduce acid usage/improve REE process costs. Overall, this testing set the stage for the further evaluation throughout the project for improving REE concentrate purity, reducing overall processing costs, and increase the understanding of the leaching process and the effects/advantages of the REE organic-associations with the lignite coals.

2. Bench-Scale Pre-Leaching

The bench-scale system designed and constructed for these tests consisted of 4 mixing tanks, each set up in the same configuration which is shown in Figure 2.1. The system for each tank consisted of a coal hopper with a double-dump valve system to feed the coal into the tanks, an acid hopper with a manual valve for acid addition, a gas scrubber, the tank mixer, and a vacuum filtration system to separate the coal from the liquid after leaching. Thermocouples and pH probes were added to each tank to monitor the process conditions during testing. Coal utilized for this testing was sourced from the Falkirk Mine (Hagel B seam), and contains a REE distribution found in Figure 2.2.

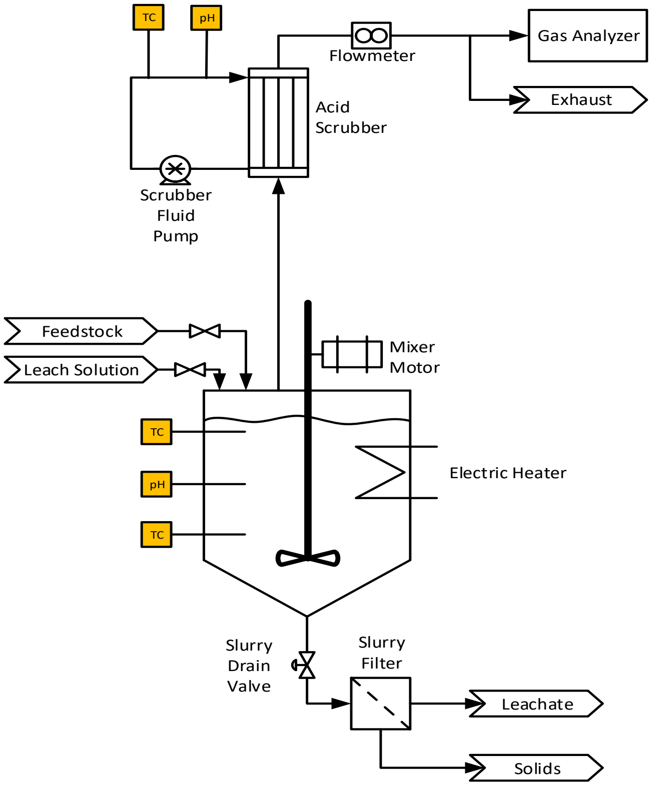

Figure 2.1. Diagram of bench-scale batch testing setup.

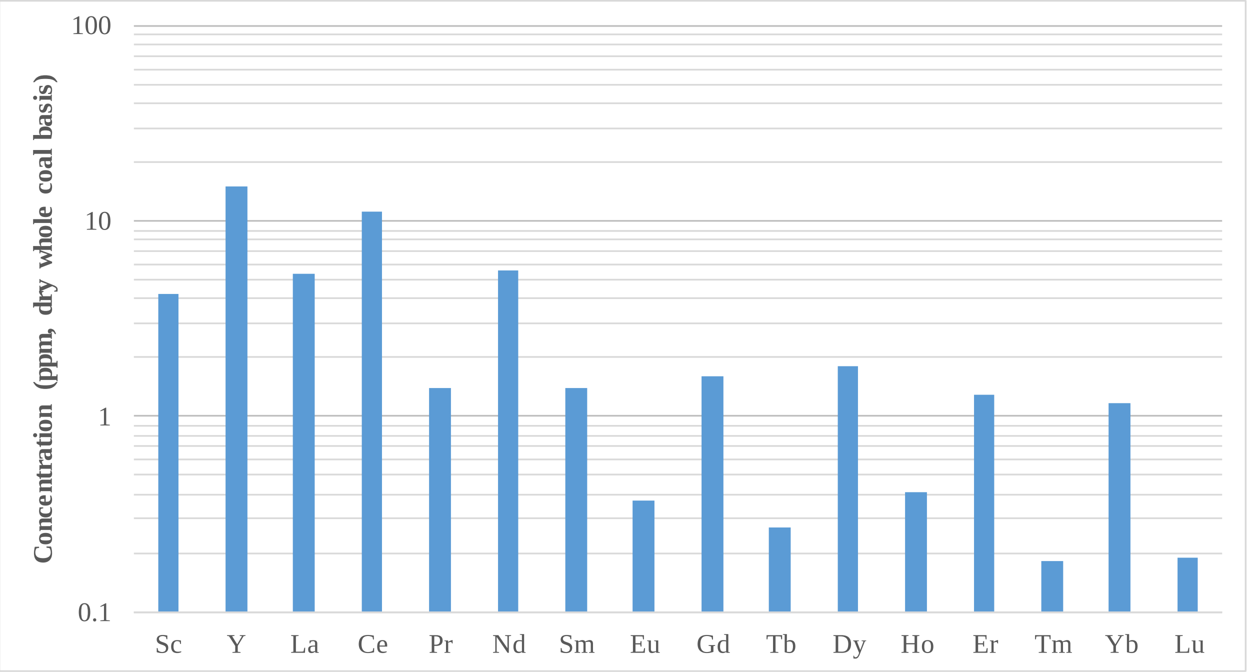

Figure 2.2. *REE distribution of the coal utilized in bench-scale pre-leaching and system commissioning (overall 54 ppm).*

2.1. Goals and Methods

The goal of the bench-scale pre-leaching parametric tests was to evaluate the efficacy and optimize conditions of a processing step prior to leaching which would extract impurities from the coal. These impurities included elements such as sodium, magnesium and calcium. Additionally, minimization of REE loss during pre-leaching was considered when determining optimal conditions. The coal used for this testing was a run-of-mine lignite with relatively low REE concentration (54 ppm) and was sourced from the Hagel B seam of the Falkirk Mine (Underwood, ND). The purpose of using this coal with relatively low REE concentration was to determine the factors which had the greatest impact on pre-leaching extractions. Utilizing this information, additional factors would be tested with the 300 ppm coal feedstock selected for production testing. For this testing, several factors that could affect pre-leaching efficiencies were identified in the testing plan. Factors to be tested included acid type, concentration, starting pH, residence time, and slurry density. An initial parametric testing plan, which included 12 tests, was developed. For cost-reduction purposes, analysis of only one REE from each grouping (LREE, MREE, HREE) was measured.

The batch size for each pre-leaching test utilized 10 gallons of liquid in the tank for the tests with the highest coal to liquid slurry ratio, this batch size was scaled up for any tests which required more liquid (lower coal to liquid ratios). For each of these tests the appropriate amount of DI water was added to the mixing tank, after which the acid required for the test was also added to the tank. After all of the liquid was added to the tank, the coal was fed into the hopper, the double-dump valve system used to add the coal to the tank, and the slurry stirred in the tank for the residence time required. After the test was concluded, the slurry was drained from the tank to the vacuum filtration system, the filtered coal re-added to the mixing tank with DI water to wash the coal, and this slurry filtered.

After the initial 12 tests in the parametric testing plan, Test 13 was added to the testing plan. The testing method used for this test was changed slightly compared to the method used for the initial 12 tests, in that acid was added periodically throughout the test to maintain the pH of the slurry in the mixing tank. This test was included to test the theory of additional acid providing more active reagent and preventing complete consumption of H^+ ions throughout the test. By maintaining the leaching driving force, additional material could be leached from the coal.

2.2. Results of Testing, Analysis and Conclusions

The results of the pre-leaching tests which investigated the effect of acid concentration of acid Type 1 are shown in Figure 2.2. Contact time and coal/liquid ratio were constant for these tests. Improved extraction of impurities was observed for increased acid concentration, but extraction of REEs also increased with increasing concentration.

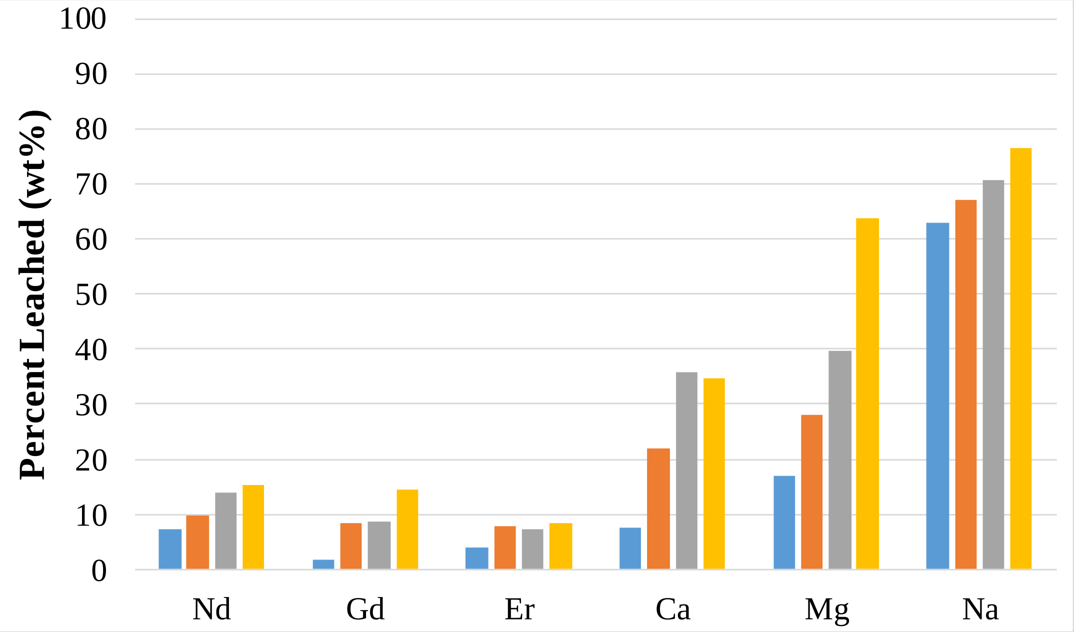

Figure 2.2. *Pre-leaching results as a function of increasing concentration of acid Type 1 (concentration increasing from left to right).*

The effect of acid Type 2 concentration on leaching efficiency is shown in Figure 2.3. Contact time and coal/liquid ratios were constant for all tests, and the acid concentrations used for these tests were the same as the concentrations used for acid Type 1 shown in Figure 2.2. Better extraction of impurities was observed with higher concentration of acid Type 2. As with acid Type 1, the extraction of REE also increased with increasing concentration. In comparison to acid Type 1, the leaching efficiencies of acid Type 2 were lower for identical concentrations. Interestingly, sodium extraction reached a similar maximum point as compared with acid Type 1, indicating a stronger-bound occurrence of Na making up the ~20% non-extractable fraction.

A decreased leaching of magnesium and sodium was observed as the contact time increased, while for REE and calcium there does not appear to be a trend with changing contact time (Figure 2.4). This phenomenon was explained through a continuous consumption of acid, and a re-complexation of organically-bound materials as time progressed Because of this re-complexation pathway, goals of reducing potential contact time for future extractions was identified (discussed further in section 3) . For these tests acid type 1 was used with consistent concentration and coal/liquid ratio.

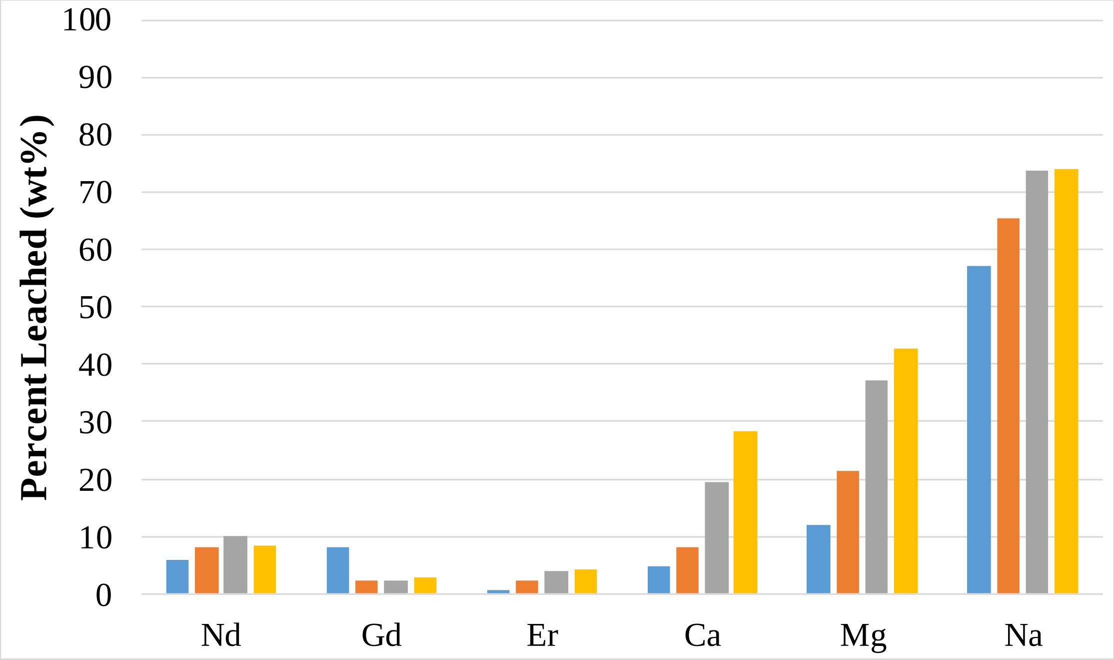

Figure 2.3. *Pre-leaching results as a function of increasing concentration of acid type 2 (concentration increasing from left to right).*

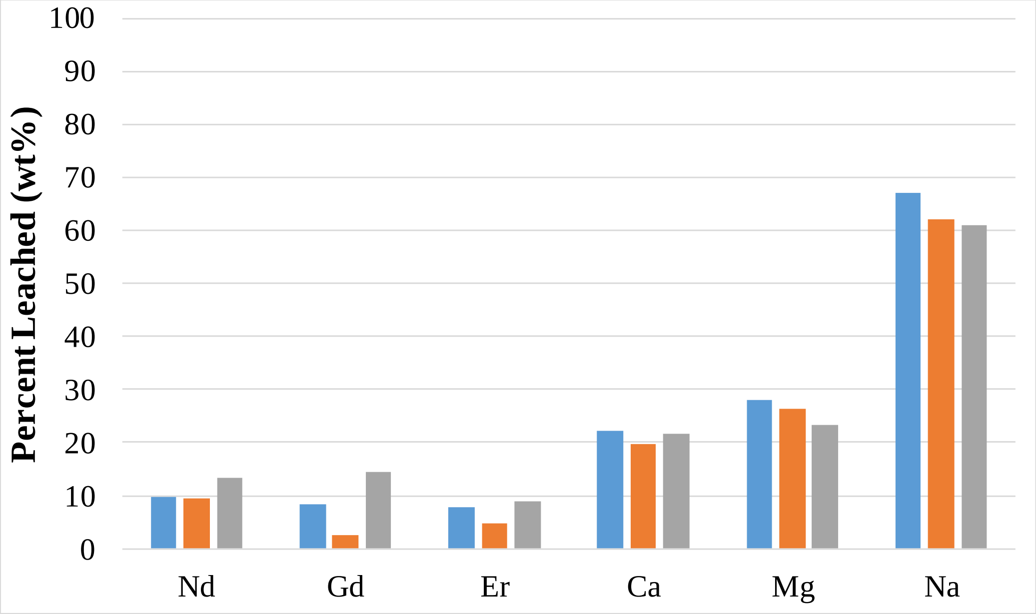

Figure 2.4. *Pre-leaching as a function of coal/acid contact time (time increasing from left to right).*

Figure 2.5 shows the effect of the coal: liquid ratio of leaching efficiency. In these tests, a higher extraction of Ca, Mg, and Na was observed with the lower coal/liquid ratio, while the leaching of the REE was either the same or slightly lower for the test with the lower coal/liquid ratio. The acid concentration of acid type 1 and the contact time were kept constant for these tests. The lower coal/liquid ratio was theorized to provide more moles of H^+ per unit mass of coal during leaching, permitting a prolonged leaching driving force. As these tests pointed out, the driving force for extraction was diminishing without constant acid addition, and pointed towards additional acid-utilization mechanisms for driving force maintenance.

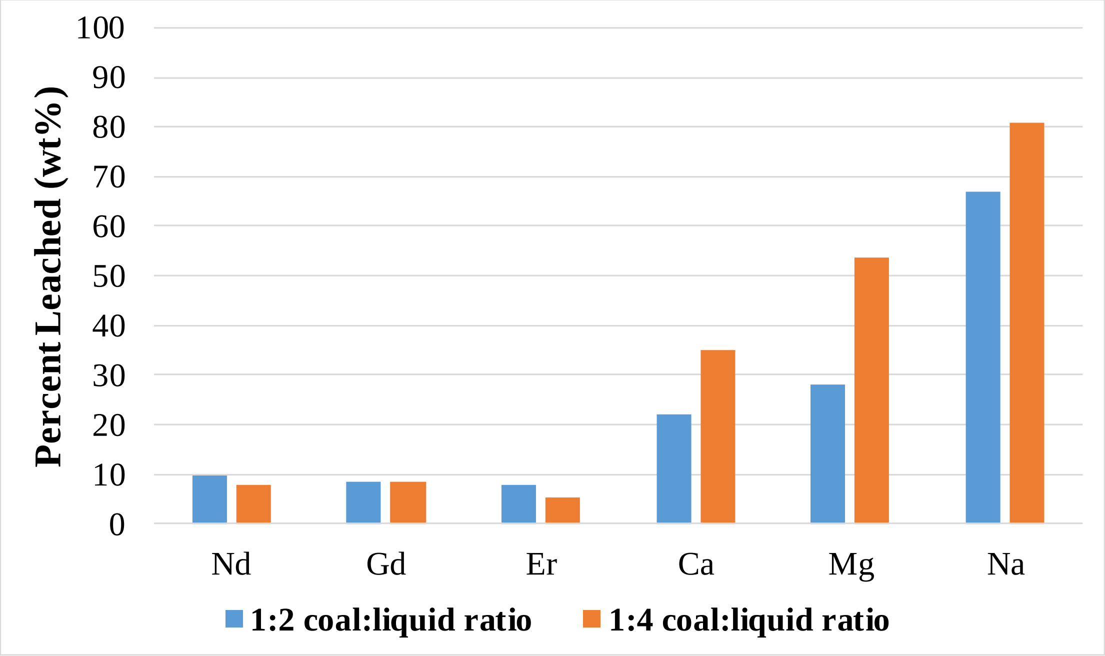

Figure 2.5. *Pre-leaching as a function of coal/liquid ratio.*

A pH-based pre-leaching test was run to investigate this theory of continuous acid addition throughout the test, with the hypothesis of increasing extraction from the coal during leaching by providing more active reagent and preventing complete consumption of H^+ ions. The pH was monitored throughout this test, and is shown in Figure 3.6. During this test, a setpoint pH was determined, with acid additions occurring should this rise above the target. After the coal was added to tank, the pH rapidly increased. As additional acid was added, the rate of pH increase slowed. As the leachable material was extracted from the coal, the rate of consumption of H^+ ions decreased.

The extraction results of the pH-based pre-leaching test compared to a concentration-based pre-leaching test, which both had the same initial acid concentration, acid type, contact time, and coal/liquid ratio, are shown in Figure 2.7. Extraction of all elements was higher in the pH-based pre-leaching test. However, losses of over 20% were observed for the REE in the pH-based leaching test, and future testing to optimize conditions of pH-based pre-leaching will be discussed in Section 3.

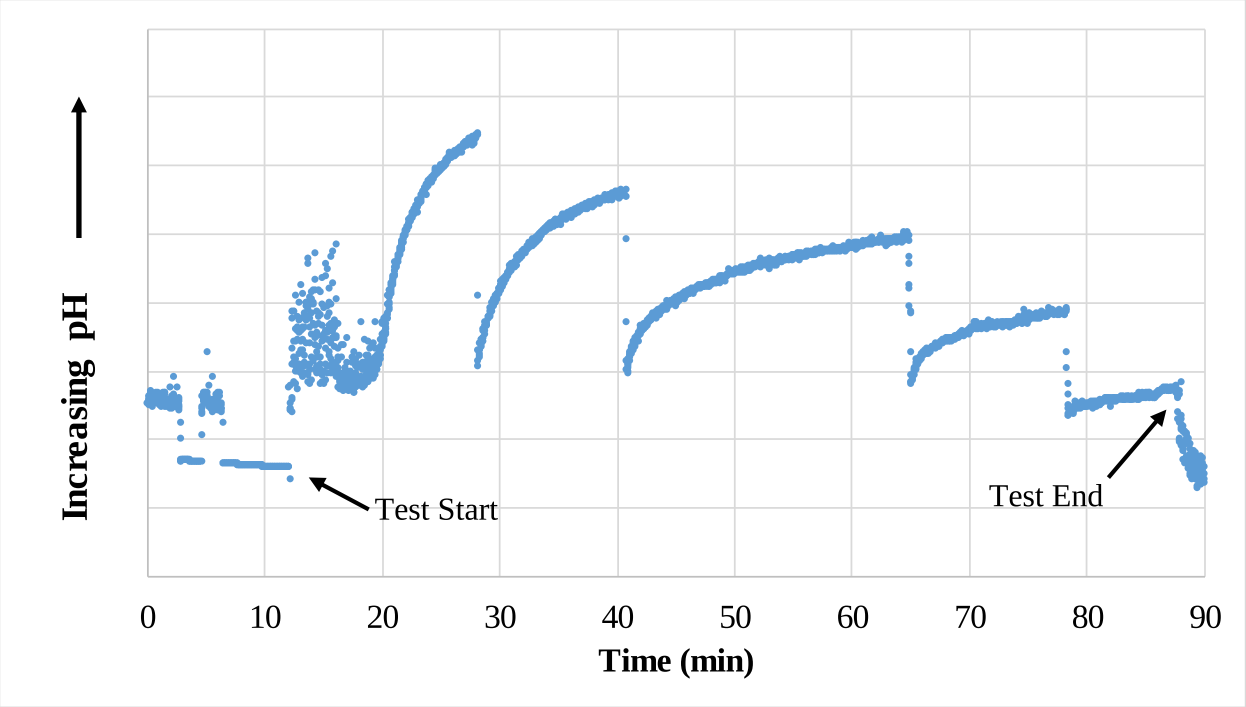

Figure 2.6. *The pH over time during pre-leaching test with periodic acid addition to maintain pH.*

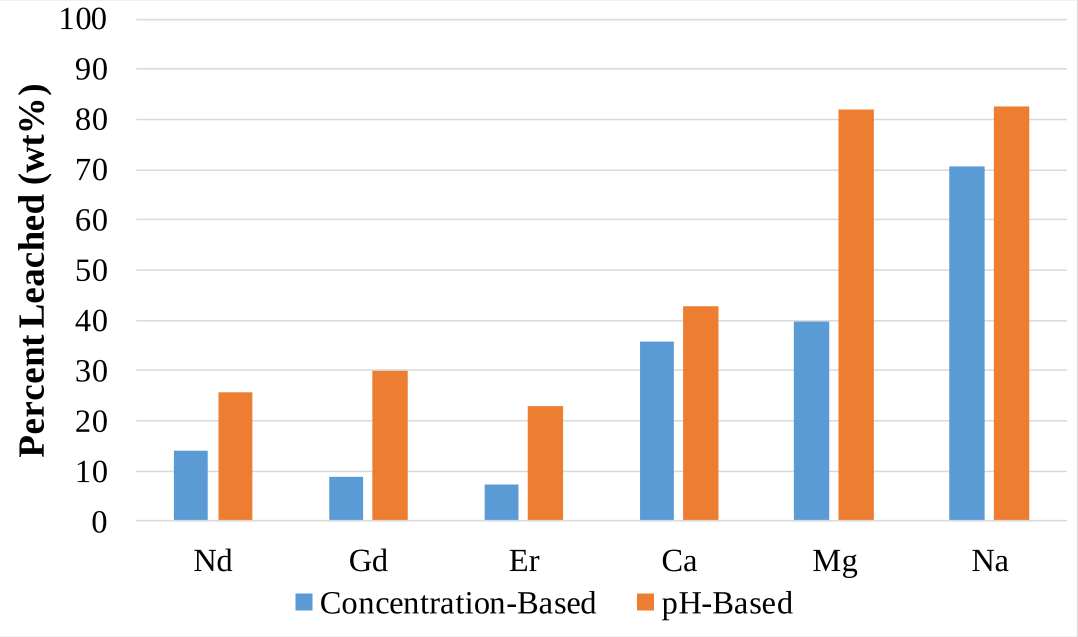

Figure 2.7. *Pre-leaching results for concentration-based and pH-based pre-leaching tests with the same initial acid concentration.*

In conclusion of this testing, pre-leaching was not identified to bring significant economical enhancement, primarily due to the low leachability of the impurities noted previously of most concern (Ca, Al, Na), in addition to the negative economic effect of increasing processing time, capital, and separations for this step. However, the testing did point towards a pH-based mechanism as a leaching driving force, similar to mechanisms found with other cation-exchange carboxylic acid media and humic acids (present in lignite, extraction as inverse of capacity factor) [7], [8], [9]. Evaluation of different equilibrium pH levels, as compared with acid concentrations, would be further explored in lab-scale tests.

3. Lab-Scale pH-Based Leaching

3.1. Goals and Methods

Coal utilized for this testing was the gathered average 647 ppm H-Bed lignite from the ~7,000-pound sample mined from Slope county, with REE concentrations found in Figure 3.1.

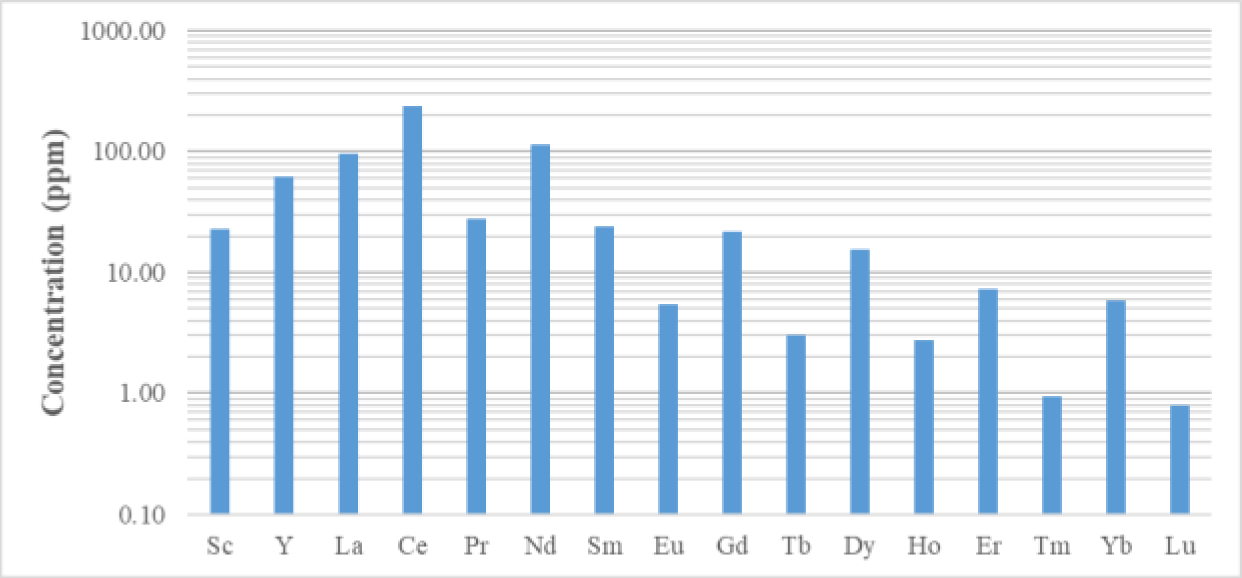

Figure 3.1. *REE concentrations of the H-Bed lignite sample used for testing.*

<u>Leaching:</u> Based upon the results of testing conducted at the bench-scale in regards to pre-leaching, particularly the revelation of a pH-based leaching response (as compared with a solubility-based system, Test 13 – section 2), experimentation into the leachability of separate materials held at constant pH, rather than an initial acid dosage, was planned. Continuous monitoring and control of pH through staged reagent/acid additions was conducted at the lab-scale (< 500g coal per test). Time-dependent samples were taken from larger leaching tests and filtered during the test using large-mouthed pipettes, and were taken at various intervals from 1 minute to 60 minutes within each test, to allow high-resolution analysis at the beginning, while maintaining relevant samples as the test progressed.

Expectations of the use of semi-continuous acid addition, as compared with use of a single starting solution, included significantly improved leaching kinetics (due to the maintenance of driving force associated with maintaining H^+ concentration), reduced impurity leachability, and significantly reduced water/acid usage. These were expected to reduce both leaching and downstream processing costs, while also reducing potential environmental challenges associated with high NORM levels within the PLS stream.

Goals of this experimental testing included answering the following questions: 1) Do different elements generate similar, but off-set leachability curves, similar to carboxylic-based cation-exchange resins? 2) What are the kinetics of a maintained driving-force reaction, and do these change for each element? 3) How much is the liquid concentration improved by utilizing the staged acid addition method?

Following leaching, due to the expectations of a significantly different solution (lower impurity leaching, higher REE concentrations), downstream processing would need to be re-evaluated to ensure similar workability. This includes the impurity removal mechanisms, REE precipitation, and potential post-purification steps.

Impurity Removal: A similar pH-based deposition mechanism for Fe and other low-solubility impurities was planned. Leachate generated through the use of pH-controlled leaching was utilized in these downstream tests. Tests were conducted at the lab scale (<1 L of solution) in beakers, with pH continuously monitored and various reagents added as necessary to attain and hold the pH at specified levels. Additionally, the specific alkaline reagent was varied to target the lowest cost, while maintaining the highest Fe removal and the lowest REE deposition. These included NaOH, $Ca(OH)_2$, $Mg(OH)_2$, and Na_2CO_3.

Goals of this testing included determining the most cost-effective reagent (both on a $/$H^+$ neutralized and Fe removal/REE recovery basis), as well as determining the pH-dependency of the various elements within the pH-controlled leachate solution. Further, downstream effects of each base chosen, such as potential interactions with the REE precipitation step, were critical in determining optimal reagent choice. Expectations pointed towards the highest impurity removal/REE loss ratio of NaOH, with the most cost-effective base at either $Mg(OH)_2$ or Na_2CO_3, depending on reactivity in downstream REE-precipitation steps.

REE Precipitation: Utilizing the optimal solution developed from the previous impurity removal testing, concentrations of oxalic acid dosing, both in terms of effects on non-REE constituents and on the REE as a function of concentration, were tested. These included co-precipitation mechanisms and oxalate-complexation. With the reduced impurity leaching achieved through the pH-controlled approach and the improved Fe removal efficiencies through the prior processing step, reduced oxalate usage was expected.

Additionally, effects from the increased liquid concentrations of the REE were anticipated to result in purer products.

Goals of this testing included the determination of the minimum and optimal oxalic acid dosing concentrations, potential impurity-control mechanisms to improve product purity, and effects of the heightened REE and lowered impurity concentration on the generation of these product streams.

Aluminum Concentrate Production: The Al content of the REE-depleted solution represents a potential value-creation from a waste source, and could effectively pay for the water treatment costs if generated at a salable grade and with effective recovery. Further, the reagent used (whether the same as the previous impurity removal mechanisms or a separate reagent) and the materials co-precipitated with this Al stream (for added value/environmental costs) required testing. This testing plan included determination of the mechanism for Al production with water treatment, identification of a reagent for Al capture without increasing water treatment burdens, and evaluation of the product for addition potential value.

3.2. Results of Testing, Analysis and Conclusions

Leaching: Equilibrium testing of the H-Bed lignite with various pH levels was conducted (Figure 3.2). As shown, at the highest pH value chosen, REE and Fe leaching is negligible, with slight Al leachability. However, as the equilibrium pH of the leaching solution is decreased, leaching efficiency increased to specific levels, finally leveling off at the lowest pH values tested. As pH is logarithmic with acid concentration (and therefore dictating significant acid consumption increases with each reduction), an optimization based on economics may be made (increasing cost for minimizing benefits).

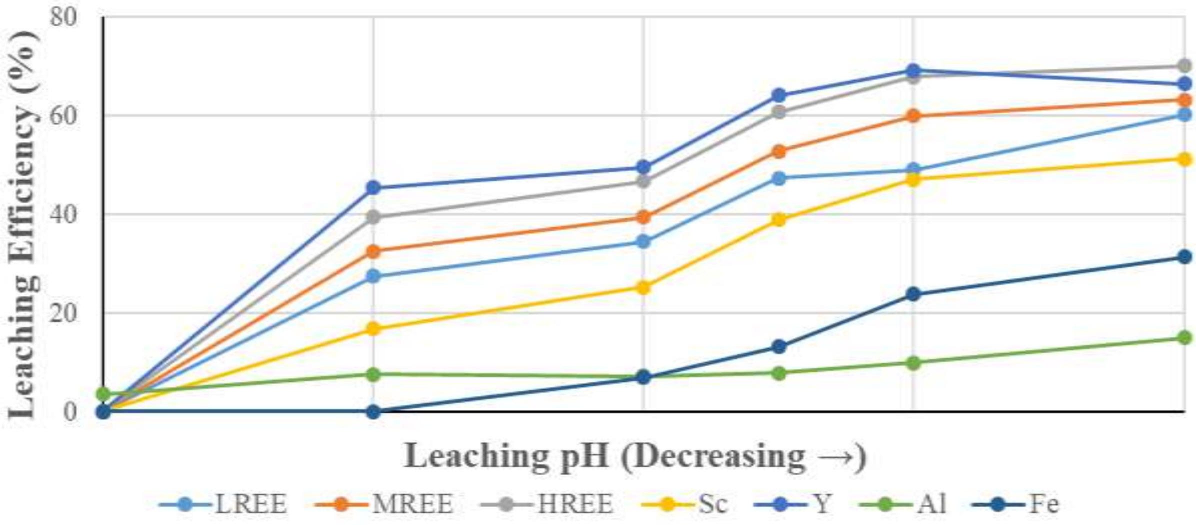

Figure 3.2. *Equilibrium-pH curves for H-Bed lignite pH-controlled leaching.*

While the pH-based leaching did not result in significantly more leachability of the REE as compared with the static-concentration testing conducted in Phase 1 (both >60% for all REE minus Sc), there were reductions in leachability of impurity elements. In particular, leaching of Fe, Th, and U were significantly lower as compared with the leaching experimentation in Phase 1, with percentage point reductions of 17, 54, and 50, respectively. This enabled significant impurity removal and potential environmental abatement cost reductions, improving economics.

Even though equilibrium leaching of the REE was not improved as compared with Phase 1 results, leaching kinetics were substantially improved. As shown in Figure 3.3, kinetics of leaching of a trivalent ion (Fe used as tracer for the REE) was rapid, with 80-90% of equilibrium leaching occurring within the first 15-30 minutes. Fe was chosen as the tracer for this experiment, as the pH values in question and the residence time utilized were unlikely to dissolve iron-based minerals expected in the coal, such as pyrite.

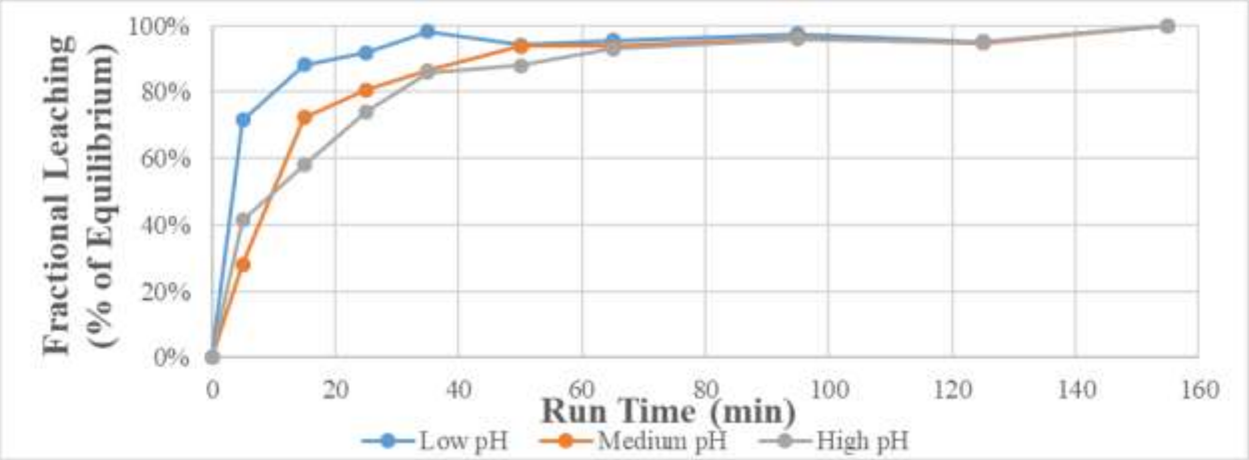

Figure 3.3. *Leaching kinetics (Fe) for three pH values.*

As shown and compared with static-leaching conducted in Phase 1, leaching kinetics under constant driving force conditions (pH) are minimally affected by the pH value in question, with a non-mineral dissolution mechanism predicted. The improved kinetics, particularly the faster kinetics noted here as compared to that observed in Phase 1 [2], resulted in significant cost-savings of capital equipment (reduction from 14-hour residence time tanks and conversion to 45-minute residence time). Further, the water and acid usage were reduced by 40% and 22%, respectively utilizing the pH-controlled approach.

<u>Impurity Removal:</u> Utilizing the more concentrated REE solutions with reduced Fe content, as compared with prior testing, a significant reduction in overall H^+ neutralization was required (20% reduction as compared with Section 2 testing). Testing of each reagent was conducted to determine the most cost-effective reagent for Fe removal (Figure 3.4, conducted at pH 3). $Mg(OH)_2$ and $Ca(OH)_2$ were removed

from the testing matrix, as these were found to co-precipitate with the REE preferentially during the next step, causing substantial purity loss. From the remaining three alkaline reagents, Na_2CO_3 was identified as the optimal base of use, primarily due to the retention of the REE in the liquid, with substantial Fe removal.

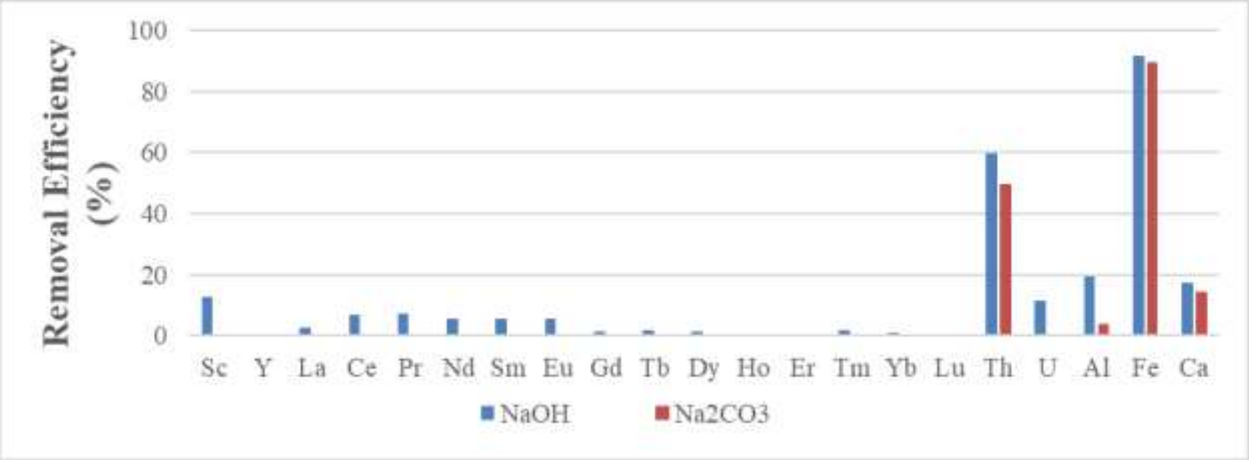

Figure 3.4. *Removal efficiency of the REE and impurities as a function of alkaline reagent species.*

Additionally, Na_2CO_3 was determined to be a lower-cost H^+ neutralization feedstock (given prices at the time for both bulk-quantity materials). Testing into Na_2CO_3's performance as a function of solution pH maintained was performed (Figure 3.5). A pH value of 3 was chosen as the target for impurity removal testing, due to the minimal REE losses (particularly Sc), in addition to a > 80% Fe removal efficiency. Due to the slow nature of the pH-response during precipitation, residence times in excess of 2.5 hours were used in this testing (to ensure equilibrium, no pH response after additional base addition).

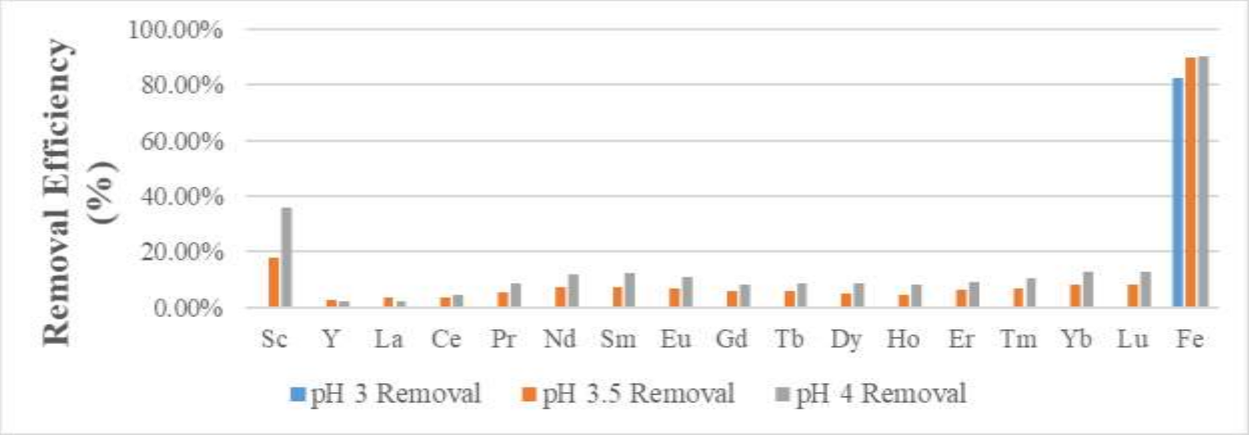

Figure 3.5. *Removal efficiency of the REE and impurities as a function of pH (Na_2CO_3).*

<u>REE Precipitation:</u> Following the impurity removal step optimized above, oxalic acid concentrations were evaluated to determine optimal oxalate concentrations based upon the Fe-depleted PLS, as well as

determining potential pre-concentration/separation pathways for the REE and downstream processing. Three specific oxalic acid concentrations were tested, with varying recovery and/or purity in each (Figures 3.6-7). Within the concentrations tested, significant speciation and separation of the REE occurred, namely with the division of the SEG (Sm, Eu, Gd) group with the HREE and LREE, in addition to the significant speciation of Sc. Additionally, this low-concentration product was of > 80% purity, containing 70% of the total REE mass contained within the Fe-depleted PLS. However, for economics, a greater recovery (particularly of Sc) was required, prompting the use of a higher oxalate concentration (such as the medium or high concentration, in series with the high-purity product.

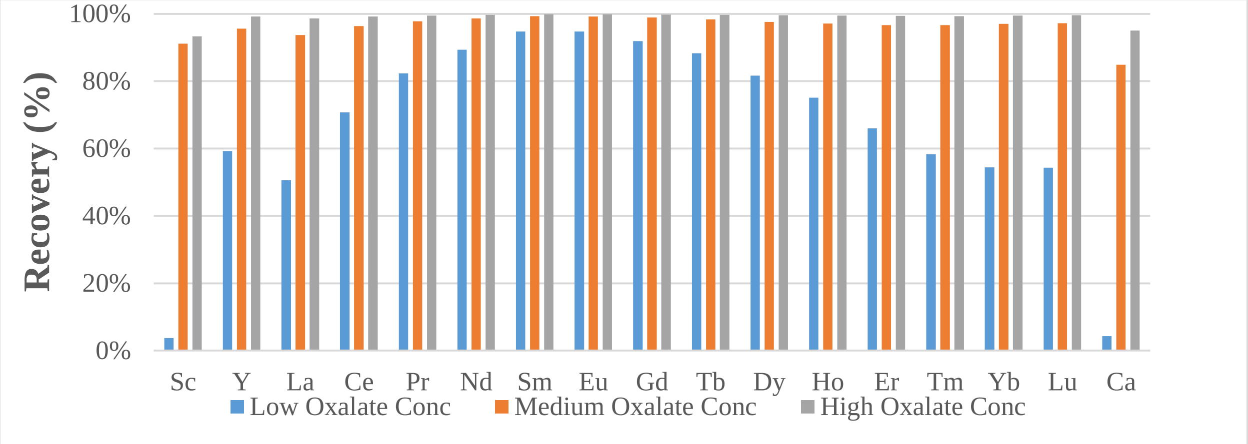

Figure 3.6. *Recovery of REE and impurities as a function of oxalic acid concentration.*

The REE concentrations generated from the sequential precipitation (low → medium → high oxalic acid feed rates) were measured to determine if there are advantages in using a three-step precipitation method. In this case, purities of 84.9%, 3.9%, and 15.7% REE's were obtained, respectively, and containing 70.0%, 26.4% and 3.5% of the REE mass, respectively.

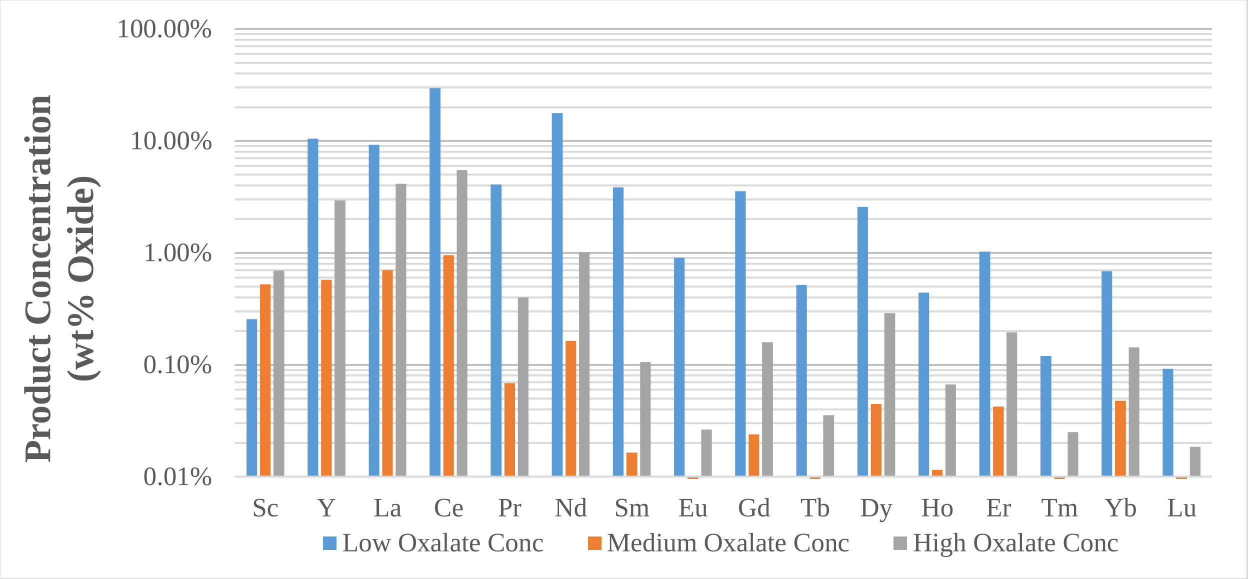

Figure 3.7. *REE concentration within each oxalic acid concentration product (sequentially).*

<u>Aluminum Concentrate Production:</u> Following REE precipitation utilizing the oxalic acid, additional valuable materials are contained with the now REE-barren liquid, with Al being foremost in concentration. Additionally, with liquid pH values below 3, water treatment through use of an alkaline material, such as $CaCO_3$ or NaOH, is needed. If a strategy could simultaneously recover this value while moving along the path for water treatment, a significant economic improvement could be made. To this end, utilization of a mixture of Na_2CO_3 and NaOH (with the mixture being determined by the $/$H^+$ ion ratio) was utilized, with multiple pH levels identified as potential.

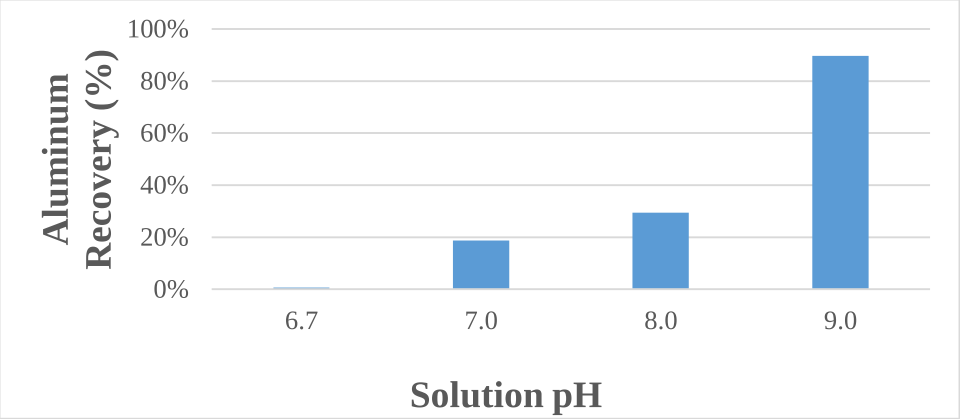

Figure 3.8. *Recovery of Al as a function of pH.*

In conclusion, these lab-scale pH-controlled leaching tests were critical in determining water, acid, and downstream reagent savings, in addition to an understanding of key parameters to target for bench-scale parametric testing. Further, identification of potential product separation/purification efforts through control over complexing species made significant strides to improving overall product purity and recovery from the testing conducted in Section 2 of this report.

4. Bench-Scale pH-Based Leaching Parametric Testing

The coal used for this testing was collected from an outcrop in Slope County in western North Dakota. The North Dakota Geological Survey (NDGS) had previous sampled this coal, and was found to have a high concentration of REE (average of ~650 ppm, maximum of > 1,300 ppm). Approximately 7,000 lbs of coal was excavated from the outcrop in 18 55-gallon drums. This coal collection effort was completed with the assistance from the North Dakota Geological Survey, and Barr (Figure 4.1).

Figure 4.1. *Members of the UND and Barr team during collection of the H Bed lignite in Slope County, ND (Nov, 2018).*

Once at UND, the coal was dried to remove excess moisture before crushing to a particle size of less than 10 US mesh. After crushing the coal, a sample was taken from each of the 18 drums to analyze for REE content using ICP-MS. To ensure representative samples, each drum was coned and quartered twice, and sectioned using a riffle splitter to collect the final sample for analysis. Figure 4.2 shows the REE concentration for all of the drums with a black line indicating the 300 ppm requirement. As the REE concentration in each of the drums was above 300 ppm, all of the coal was kept for future testing. The average distribution of the REE is found in Figure 4.3.

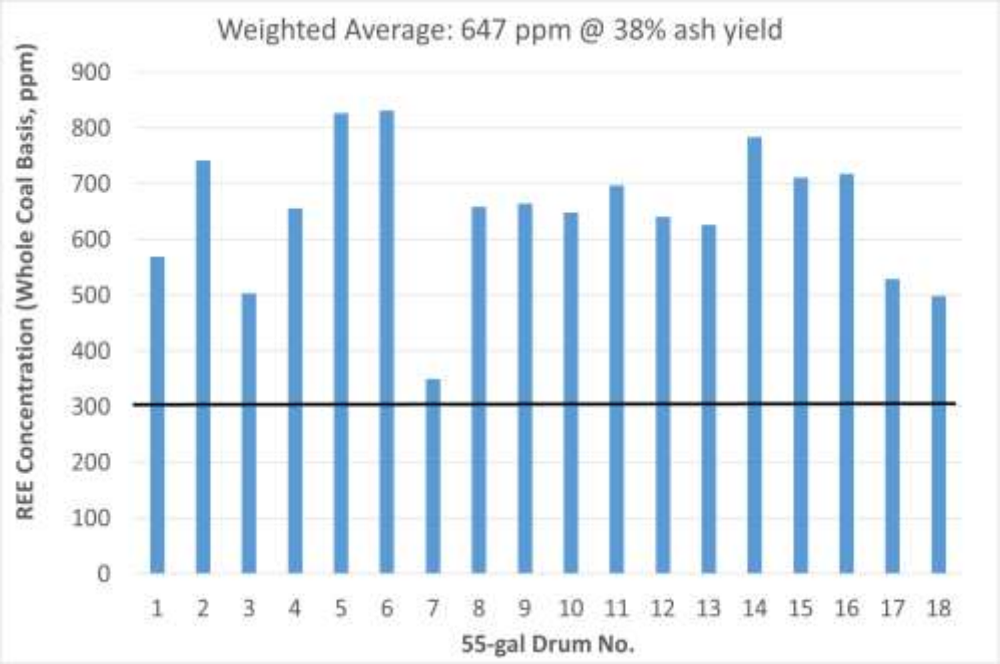

Figure 4.2. *REE concentration on a dry, whole coal basis for each of the 18 drums collected from Slope County, North Dakota.*

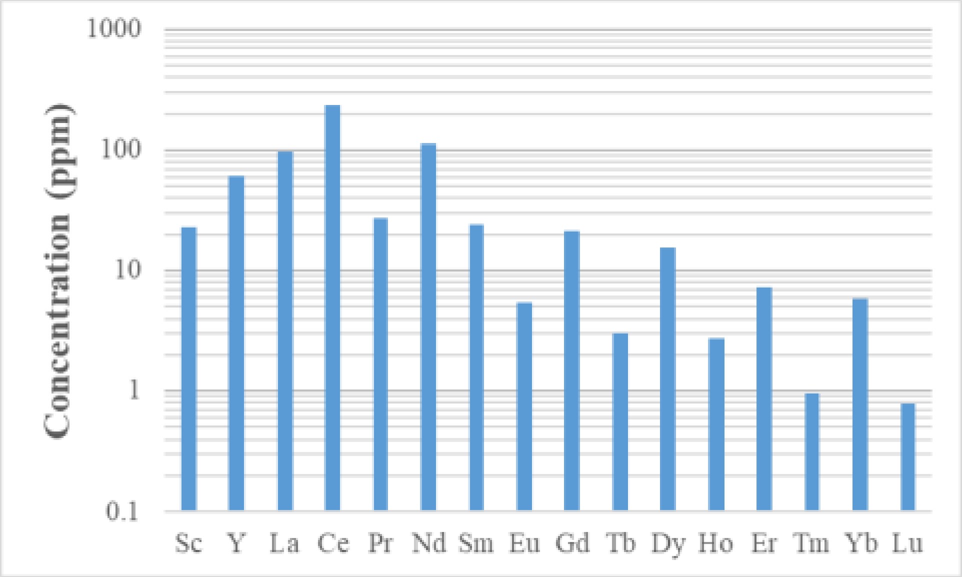

Figure 4.3. *Average REE distribution of the 18 drums of coal collected from the H-Bed outcrop.*

After crushing, the coal was sent to Hazen Research Labs for further processing. The coal was first wet screened to remove any -100 mesh particles in the process is shown in Figure 4.3. The coal was fed to a series of screens to remove to first removal any large particles, and then to remove any particles smaller than 100 mesh. The -100 mesh particles were collected in a filter press, and the remaining coal exiting the wet screening process was collected in drums.

The screened material was then further processed in coal spirals to separate the material into different density fractions (Figure 4.3). The purpose of this process was to remove the high density, high ash material “tails”. As discussed in Section 1 and 2, the REE in North Dakota lignite has been found to be associated with the organic fraction of the coal, with density-based separation shown to improve REE concentrations in the light fractions (Figure 1.6).

The coal was spiralized and divided into a concentrate (low density), middlings, and tailings (high density) fraction. The middlings fraction was then reprocessed through the spirals to further separate the high and low density materials, in a scavenger mechanism[10], further separating into a scavenger concentrate, scavenger middlings, and a scavenger tailing fractions. Table 4.1 summarizes the characteristics of each fraction from the spiraling density separation process. Based on the REE and ash content of each fraction of the coal, the concentrate, scavenger concentrate, and the scavenger middlings were chosen as the fractions to be used for processing, and these fractions were blended to create the upgraded coal feedstock for REE extraction. The new blended coal feed, highlighted in green in Table 4.1, had an average REE concentration of 658 ppm and an ash content of 19.3%, which had decreased significantly from the raw coal ash content of 35.5%.

Figure 4.3. *a.) The wet screening process used to remove all particles -100 mesh from the coal, b.) the spiraling system used for density separation of the coal.*

Table 4.1. *Abundance of REE from H Bed sample spiral fractions. Orange highlighting indications fractions combined to create the upgraded blended coal, which is highlighted in green.*

Sample ID	**Mass Fraction (wt% of Feed)**	**Ash Content (wt%)**	**Total REE (ppm)**	**Total REE, ash basis (ppm)**	**HREE/ LREE**
Raw Coal	100	35.45	646	1822	0.28
Concentrate	35.6	15.09	657	4357	0.30
Scavenger Concentrate	8.2	19.5	679	3483	0.30
Scavenger Middlings	5.4	47.26	630	1333	0.28
Scavenger Tailings	2.1	59.34	550	927	0.26
Tailings	12.0	70.31	353	502	0.26
Fines	36.7	47.37	826	1743	0.26
Blend	49.2	19.34	658	3881	0.3

Of the initial raw coal mass, 36.7% was lost as fines in the process. This accounted for the most significant fraction of the material not included in the final upgraded coal, and occurred as a result of un-staged coal crushing. Potential changes to the crushing process could decrease the amount of fines generated, resulting in reduced material loss as fines and a higher fraction of the initial material retained in the final coal product.

4.1. Goals and Methods

The goal of this testing was to optimize process conditions and identify the most efficient configuration of the process units at the bench scale. Each of the process units was evaluated over a range of conditions to optimize performance. The testing was sequenced such that the first unit operation was optimized prior to testing of the next unit operation. Previous lab-scale testing results were used to focus the parameters and conditions for this bench-scale parametric testing and to help maximize testing efficiency. The results of this testing were to be used to develop testing conditions for the semi-continuous testing discussed in Section 5.

All tests for this task were performed as batches using the bench-scale system described in Section 2.

<u>Coal Leaching:</u> The operating conditions for coal leaching were evaluated based on the goal of optimizing REE extraction considering the cost of additional acid required to extract any additional REE. Leaching efficiency was tested at several different pH set point to determine the optimal extraction conditions. During previous lab scale testing (Sections 1 and 3) the effect on leaching efficiency of other factors such as acid type, residence time, slurry density, and pH set point were investigated. The results from these previous

tests were used select acid type, residence time and slurry density for this parametric testing, and also to narrow down the range of pH values to be tested for leaching. Previous testing had shown the optimal pH for leaching varying slightly based on the slight changes in composition between different seams of lignite. However, the previous tests of pH-based leaching were used to determine a range of pH values to be tested for this bench-scale parametric testing.

The method used for this process was to mix coal and recycled coal wash water in a tank at a 2:1 liquid to dry coal ratio. Before the coal was added to the tank, the pH of the wash water was adjusted to the pH set point being used for that test by pumping concentrated acid into the tank. The acid feed pump was controlled by a programmable logic controller (PLC) that would turn the pump on if the pH was above the set point, and turn the pump off if the pH was below the set point. This allowed for the pH to be maintained throughout the test.

After the pH of the wash water was adjusted, coal was added to the mixing tank, and acid was fed via the acid feed pump to maintain the pH value. The coal was mixed with the acid for at least 1 hour, or until a constant pH value was maintained for at least 15 minutes without additional acid addition. After the test completed, the slurry was drained to a vacuum filtration system where the coal and the leachate were separated. The coal was collected from the Buchner funnel and added to water in the tank to wash the remaining acid off the coal. The water and coal were mixed using a ratio of 3:1 water to coal for 15 minutes, before the slurry was again drained to the vacuum filtration system where the coal and wash water were separated. This recycled wash water was used as the starting liquid for the next leaching test.

Impurity Removal: The goal of this testing was to optimize the pH set point for the impurity precipitation. The optimal pH for this step would result in minimal REE loss while maximizing impurity removal. The cost of additional base to increase the amount of impurities removed was also a factor in determining the optimal pH. Results from previous testing (Section 4) were used to select sodium carbonate to be used as the base in this step, and also to determine the residence time to be used (at least 2 hours). The range of pH values to be tested was selected based on previous testing.

For this step, the pregnant leach solution (PLS) was added to a mixing tank, and sodium carbonate was slowly added using a screw feeder to maintain the pH required for the test. After the pH set point was reached initially, the solution was mixed in the tank for 2 hours with pH controlled by a PLC tied to the Na_2CO_3 screwfeeder. The slurry was drained from the tank and placed into buckets to allow settling time, before filtering the liquid using the vacuum filtration apparatus described above.

REE Precipitation: The REE precipitation parametric testing matrix was designed to evaluate the feasibility of generating two separate REE products. The criteria for the first product being minimal impurities to dilute the concentration of REE, and the second product being maximum REE recovery from the PLS. The oxalic acid concentrations for precipitation both of the REE products would be tested in this step. Oxalic acid concentrations to be used for REE precipitation were tested during previous lab scale tests discussed in Section 4. The results of these tests were used to determine the range of oxalic acid concentrations to be used for this parametric testing. Sodium carbonate was used as the base in this step for pH adjustment, and the pH being used for precipitation was chosen based on literature information.

The process used for this step was to add the mass of oxalic acid required to meet the desired concentration to a tank, which already contained the PLS. After the oxalic acid was completely dissolved, sodium carbonate would be added to increase the pH and precipitate a REE oxalate solid. This would be stirred in the tank for 2 hours, before the solution was drained from the tank and filtered using a vacuum filtration apparatus. After the filtering the first REE product, the solution would be added back into the tank for the second oxalic and sodium carbonate addition to precipitate additional REEs. The solids would again be collected through filtration.

Aluminum Recovery: The goal of the aluminum recovery step was to produce a saleable byproduct that was concentrated in aluminum. After REE extraction, the pH of the remaining solution is low and would require pH adjustment as part of the wastewater treatment process before disposal. By increasing the pH slightly above the minimum requirement for treatment, an aluminum concentrate product can be generated with a minimal increase in processing cost.

The process for aluminum recovery had previous been tested in the lab (Section 4), and the results of these tests were used to develop a testing plan for this parametric testing. The method of using sodium carbonate first, up to a pH of 6, then using sodium hydroxide for any additional pH increases was previously tested in the lab, and the benefits of this process are described in Section 4, and was utilized for this bench-scale parametric testing.

For this processing step, the pH at which aluminum would precipitate was the operating parameter selected for testing. The remaining PLS after REE extraction was added to a mixing tank, where sodium carbonate was added to the solution to increase the pH of the solution to 6. After the pH had stabilized at 6, sodium hydroxide was then fed into the tank using a pump to increase the pH of the solution to the final set point for that test. After the pH stabilized, the solution was mixed for 1 hour, and the slurry mixture was then drained from the tank, and the solids were filtered from the solution using vacuum filtration. After filtering and collecting the solids, the solution was added back into a mixing tank where additional sodium hydroxide was added to bring the pH to the second testing value for aluminum precipitation.

4.2. Results of Testing, Analysis and Conclusions

<u>Coal Leaching:</u> The results of the coal leaching parametric tests are shown in Figure 5.4, with pH A being the highest pH tested, pH B being in the middle, and pH C being the lowest pH tested. These results show the extraction efficiency for the REE was the lowest when using pH A as the set point. As pH A was the highest pH value of the three tested, this was the expected result. The extraction efficiencies for pH B and pH C were similar for all of the REE, with pH B having better extraction than pH C for some of the elements.

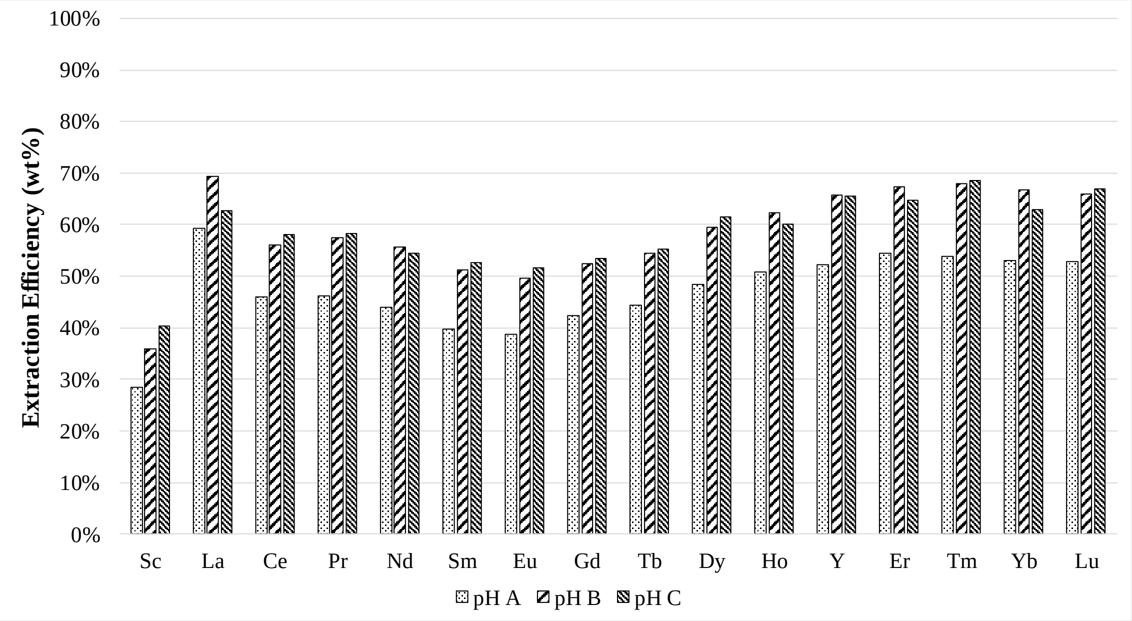

Figure 4.4. *Extraction efficiency of REE from lignite coal using a pH-based leaching process at various pH values, with pH A being the high pH, pH B being the medium pH, and pH C being the low pH.*

Based on the similar leaching efficiencies between the middle and low pH set points, the pH B set point was chosen as the set point to be used for further testing. Although the acid consumption during this testing was the highest for pH B, this was expected to be the result of an issue with the pH probe during the test, and the acid consumption was expected to decrease in future tests.

<u>Impurity Removal:</u> After the leaching conditions were selected, two different pH values were tested to determine impurity removal efficiencies. As shown in Figure 4.5, the first test was completed at a pH of 3 and removed 82% of the iron from solution. In the pH 3 test, a loss of approximately 10% was observed for all of the REE. The pH 3.5 test showed an 87% removal of iron and a significantly higher thorium removal than was observed in the pH 3 test, but also removed an additional 10% of most of the REEs compared to the pH 3 test. The scandium loss in the pH 3.5 test was 35% compared to the 10% loss in the pH 3 test. While the sodium carbonate requirements for the pH 3.5 test were not significantly higher than the pH 3 test (36 g Na_2CO_3/L solution for pH 3 and 37.6 g Na_2CO_3/L solution for pH 3.5), the additional losses in REE and an improvement of only an additional 5% removal of iron made the pH 3.5 test less

optimal. Based on these results a pH of 3 was chosen as the set point to be used for further impurity removal testing.

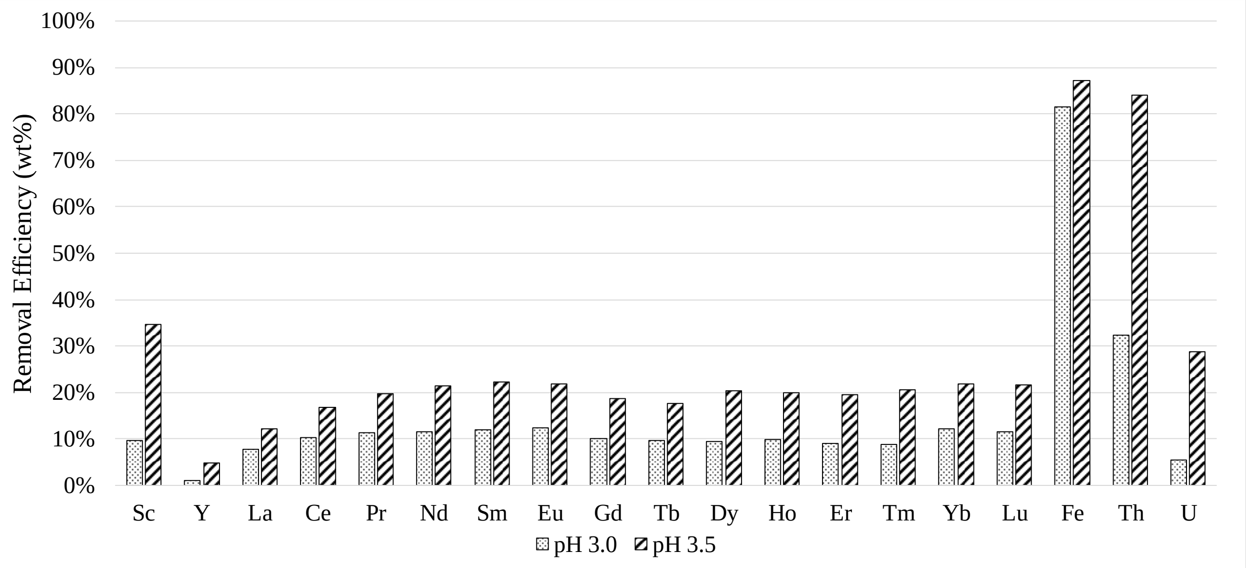

Figure 4.5. *Removal efficiencies of REE, iron, thorium, and uranium in the impurity removal step at both pH 3 and pH 3.5.*

<u>REE Precipitation: </u>The recovery efficiencies of REE at the oxalic acid concentrations tested are shown in Figure 4.6, with the oxalic acid concentrations increasing from left to right (Concentration A being the lowest and Concentration D being the highest). The figure shows the cumulative REE recovery at each concentration. It was observed that at Concentration D 95% or higher recovery was achieved for most of the REE.

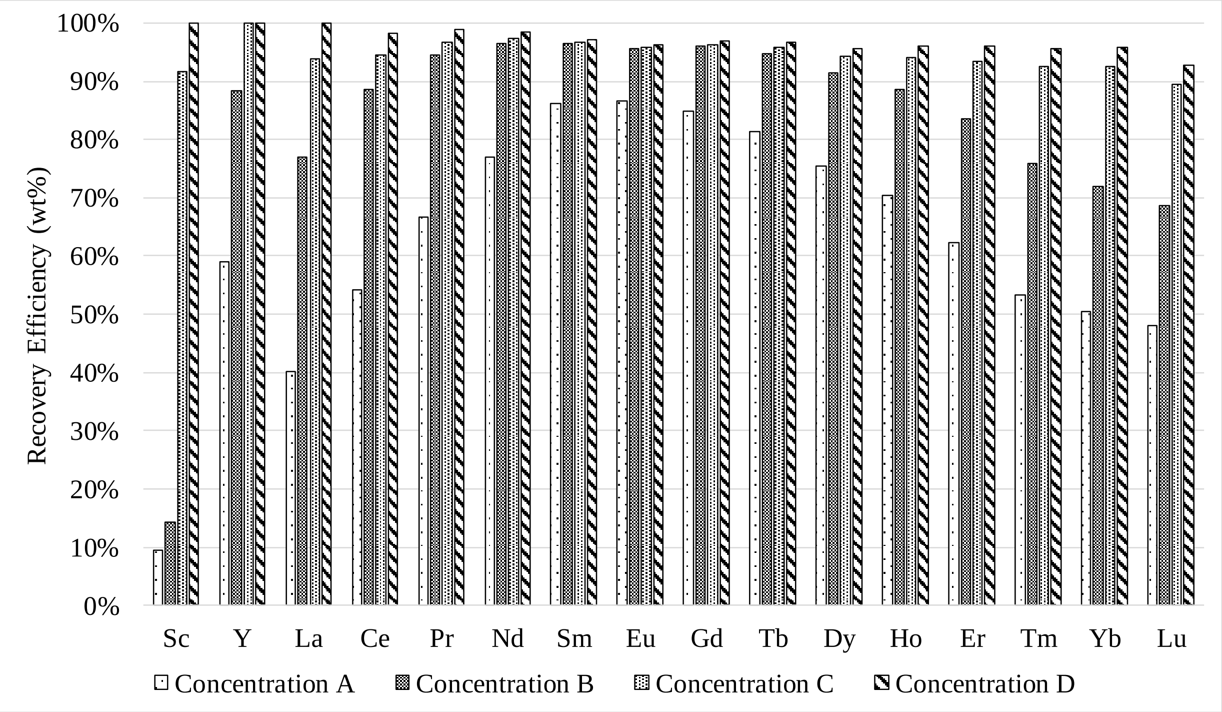

Figure 4.6. *Cumulative recovery of REE at different oxalic acid concentrations. Oxalic acid concentration increases from left to right (Concentration A is the lowest and Concentration D is the highest).*

In this testing, two REE products were generated from each test completed. The first REE precipitation test used Concentration A of oxalic acid for precipitation of the primary product, and Concentration C to generate the secondary product. The second REE precipitation test used Concentration B of oxalic acid for the primary product, and Concentration D for the secondary product. The purities of the REE in each of these products are shown in Figure 4.7. The purity of the Concentration A product is the highest of all of the products, and Concentration D has the lowest. The lower concentration of oxalic acid allows for a more selective precipitation of the REE, by utilizing the low solubility of the REE compared to the other elements, such as calcium, which can also precipitate in this reaction and dilute the final product. The precipitation of calcium is the most significant diluent in these products, and accounts for the significant loss in purity between the Concentration A and the Concentration D products. The purity of the Concentration A product on a total REE oxide basis was 68%, while the Concentration D product had a purity of 1.6% REE (Figure 4.7).

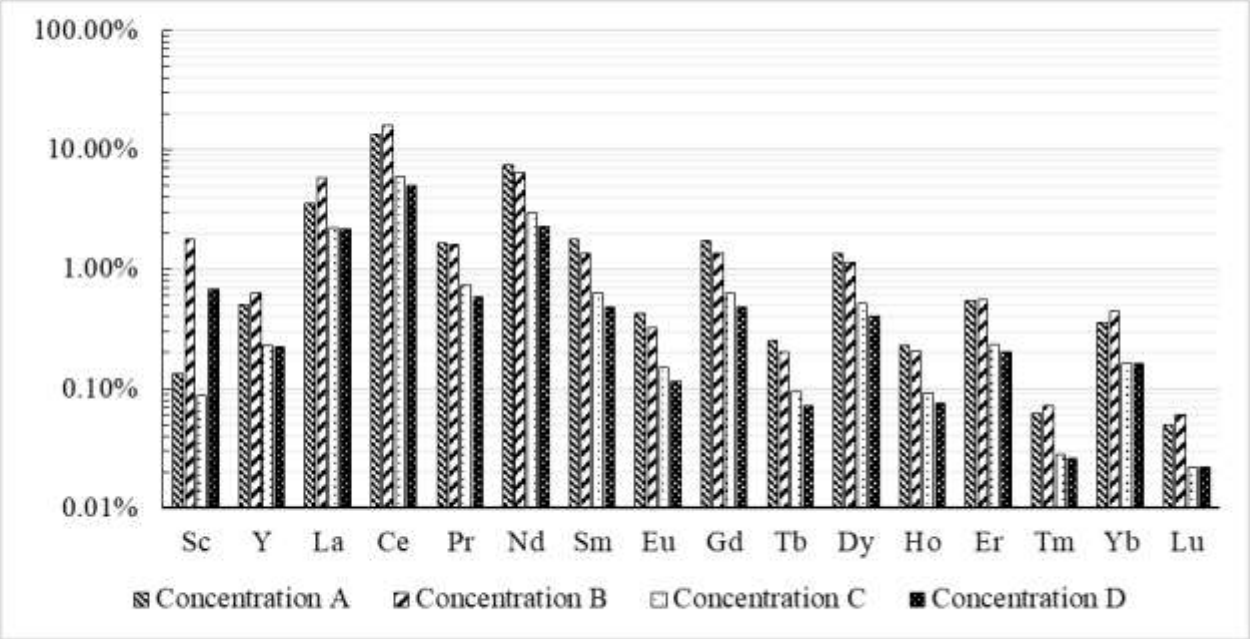

Figure 4.7. *Purity of REE products on an oxide basis, which were precipitated at various oxalic acid concentrations. Oxalic acid concentration increases from left to right (Concentration A is the lowest and Concentration D is the highest).*

Based on these results, the oxalic acid concentration selected for the primary REE product was Concentration A. This would provide a primary REE product with the high purity. The concentration chosen for the secondary product was Concentration D. This was chosen in order to recover the maximum amount of REE from the PLS.

<u>Aluminum Recovery:</u> The results of the aluminum precipitation tests showed a significant increase in aluminum recovery from pH 8.5 to pH 9. As shown in Figure 5.8, a 22% increase in recovery was observed by increasing the pH to 9. In this test, 8 g Na_2CO_3 per L of solution was used to bring the pH of the solution up to a pH of 6. Bringing the pH of the solution up to a pH of 8.5 required 12 mL of 50wt% NaOH per L of solution. The additional NaOH required to increase the pH to 9 was only 3 mL NaOH/L solution. The pH 9 set point was selected to be used in future testing due to the minimal increase in NaOH requirements to achieve over 20% improvement in recovery of aluminum.

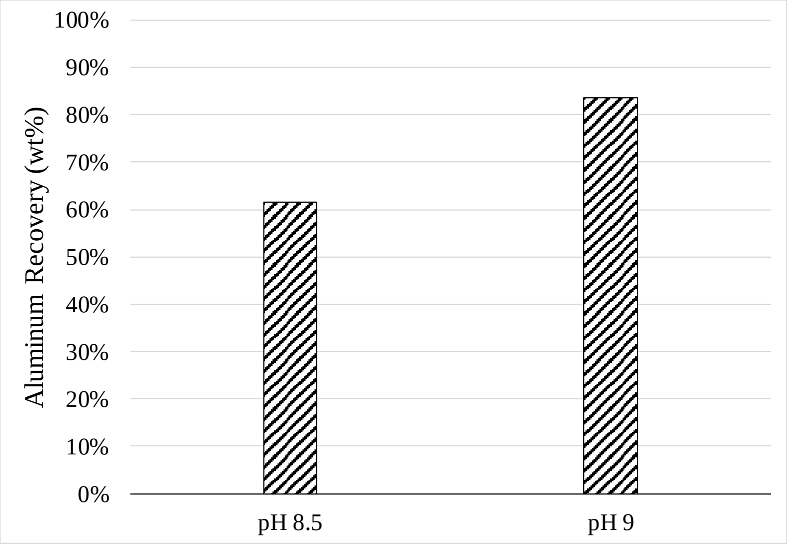

Figure 4.8. *Recovery efficiency of aluminum at a pH of 8.5 and a pH of 9.*

5. Bench-Scale Semi-Continuous Testing

For this testing, the mixing tanks used for previous bench-scale testing were modified to run in semi-continuous operation. The semi-continuous system with all of the modifications can be seen in Figure 5.1. The previous system design for the bench-scale mixing tanks had each tank operating independently of each other, while this design connected the tanks and allowed for flow between them. The H Bed coal from Slope County, ND described in Section 4 of this report was also utilized for this testing.

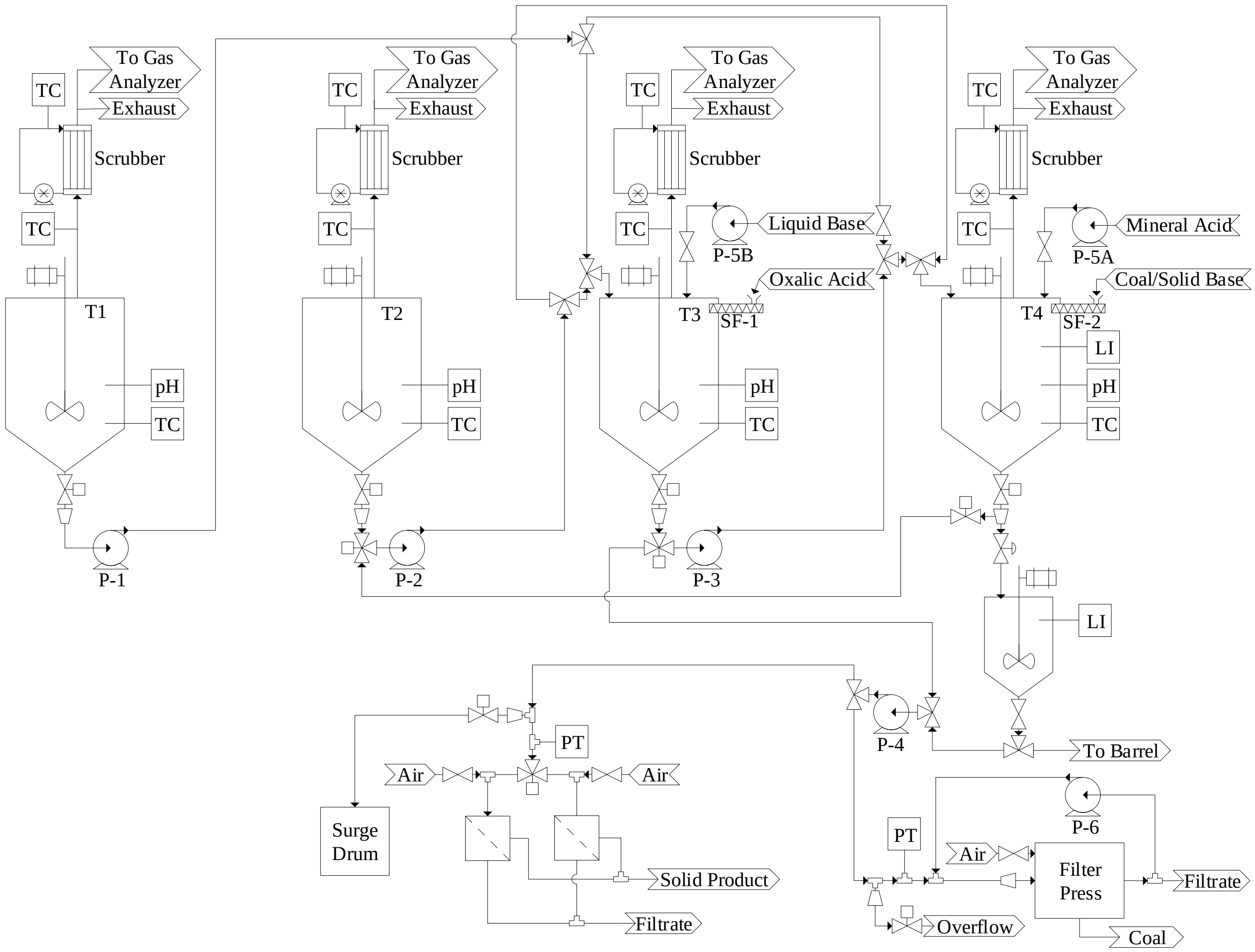

Figure 5.1. *Piping and instrumentation diagram for the as-installed semi-continuous bench-scale system for REE extraction process.*

The modified semi-continuous system is shown in Figure 5.2. Modifications made to the prior batch-type system included new piping, valves, and pumps to allow for flow between mixing tanks. Two screw feeders were added to the system to allow for continuous feed of solids into tanks 3 and 4; the first screw feeder being used for oxalic acid addition, and the second used to feed coal and sodium carbonate.

Additionally, the vacuum filtration systems which had previously been used for filtration of solids during earlier testing was removed and replaced by a new filtration system. The modifications to the filtration system included a surge tank and slurry pump which could feed the in-line filters or a filter press. The two in-line filters were installed to allow for continuous operation in a duplex configuration, with one filter being in use while the other was cleaned and prepped for use. The filter press for this system had a capacity of 4 cubic feet, and was sized to hold approximately 100 kg of coal (wet).

Figure 5.2. *Semi-continuous system as-installed.*

The pumps and screw feeders were all calibrated before operation of the system to determine appropriate flow and feed rates for the process. However, challenges were encountered with the calibrations of some of the equipment, particularly involving the flow rates associated with the liquid metering pumps. The initial calibration testing revealed significant variations in flow rate at one setting in day-to-day activities (by up to 20%), and the cause could not be determined. As a result of this, calibration tests were run for each pump before starting every test. This was done to ensure accurate flow rates while testing.

The initial method for calibrating the pumps involved disconnecting the pump from the system at the exit of the pump. This method was used for the leachate generation testing and system shakedown testing. The method was changed after it was determined that the fittings between the pump and the tanks were providing substantial pressure drop, resulting in lower flow rates than anticipated. To correct this error, the pump calibration method was changed to disconnect at the inlet to the tank. This method was used for Week 1, Week 2, and the leaching and impurity removal tests of Week 3. At this point it was determined that the fitting for the tubing entering the tank was also restricting flow. For the REE Extraction and Aluminum Tests of Week 3 and all of Week 4, the method for calibration used involved no disconnection of the pump from the system, but rather opening the valves under the required tanks, and calibrating the flow exiting the mixing tanks. This method was shown to produce the most accurate pump calibrations, and was checked using a known amount of liquid in a tank and the calibrated flow rate to calculated the amount of time required to drain all of the liquid from the tank.

Throughout testing, inconsistencies were discovered in the feed rate of coal into the tank from the screw feeder. The feed rate of the coal had some variation between tests from the 25 kg/hr feed rate calibration (up to 20%). The rate was also observed to vary within some of the experimental runs. This was determined to be a result of the slight differences in moisture content of the coal from one coal drum to another. These differences in moisture content caused slight changes in the density of the coal between barrels, and can explain the observed changes in the mass feed rate while the volumetric feed rate was constant.

Figure 5.3 shows the observed feed rates for a low, medium, and high moisture coal, as well as a test where coal was used from two different barrels which had significantly different moisture contents. The differences in feed rates for each test can be correlated to the changes in the moisture content of the coal impacting the density of the coal.

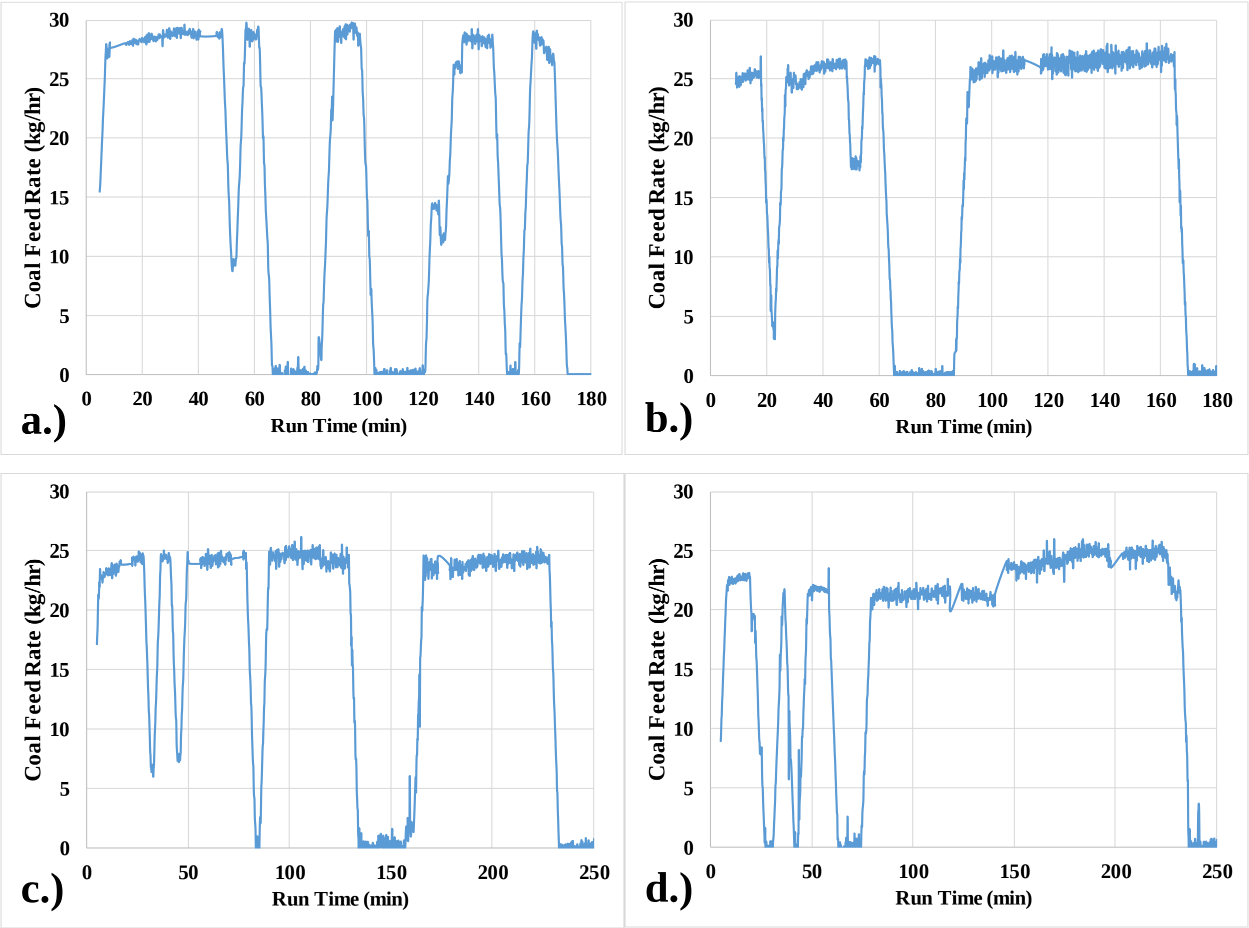

Figure 5.3. *Coal feed rates during various leaching tests. a.) Week 4, Leaching Test 2, coal moisture = 29.4%; b.) Week 2, Leaching Test 2, coal moisture = 31.1%; c.) Week 3, Leaching Test 2, coal moisture = 32.4%; d.) Week 2, Leaching Test 1, coal moisture 1 = 34.1%, coal moisture 2 = 31.8%.*

5.1. Goals and Methods

The goals of the bench-scale semi-continuous testing were to process 1000 kg of feedstock, produce an REE concentrate product in sufficient quantity to be suitable for evaluation for further processing, and provide further data for the refinement and analysis of the techno-economics of the process. The H Bed coal collected from an outcrop in Slope County, North Dakota was used as the feedstock for this testing. This coal contained an average of 647 ppm REE, which exceeded the project requirement of a 300 ppm REE feedstock. Processing conditions for the semi-continuous testing were chosen based on results of the bench scale parametric testing discussed in Section 4.

<u>Leachate Generation:</u> During equipment shakedown testing, it was determined that recirculation of leachate through the filter press while it was being filled with coal would be required to prevent plugging in or before the filter press. Before this recirculation could be implemented, the leachate for recirculation needed to be generated. A blanking plate was used in the filter press, which allowed for the tail plate to be moved up and shorten the number of plates being used in the filter press. This resulted in a decreased capacity of the filter press.

The initial leachate generation test was run with only 4 center plates, rather than the entire 26 plates which were available in the press. This size was chosen based on where plugging had previously occurred in the filter press when no recirculation was used. After the initial leachate generation test, the recirculation of leachate was used when filling the press. As more leachate was generated, the amount of center plates used was slowly increased. A total of 9 tests of varying scale were completed to generate a total of 35 gallons of leachate. This volume of liquid would fill the entire filter press if there was no solid inside, guaranteeing a constant recirculation loop for operation.

<u>Coal Leaching:</u> Before the coal was leached, a sample was taken from each barrel of coal. These samples were dried to determine the moisture content of the coal in each barrel, and the coal was kept to be used as the feed coal samples for each leaching test.

The amount of coal processed for each leaching test was based on the capacity of the filter press, which could hold the wet equivalent of 50 kg of dry coal (roughly 100 kg wet at 50% moisture). A total of three leaching tests at this size were run, with the liquid combined from each to ensure sufficient volume of the PLS was generated for further processing.

Each leaching test was conducted by feeding recycled wash water and coal into one of the mixing tanks in a ratio of 2:1 liquid to dry coal mass. Coal was added to the tank using a screw feeder, which had been calibrated to feed the coal at a rate of 25 kg/hr. The flow rate of wash water pumped into the tank was calculated based on the moisture content of the coal and the pH of the wash water. Acid addition to the tank was controlled by the pH measured in the tank. When the pH in the tank was above the set point, the acid pump would turn on, and feed acid at a rate of 24.5 mL/min, and the pump would turn off when the pH was below the set point.

A residence time of one hour was used for the leaching process; after one hour of adding material to the mixing tank, continuous operation would begin: the slurry would be allowed to start flowing out of the mixing tank and the pump to the filter press would be turned on to begin filtering the coal from the leachate. The recirculation pump would be turned on at this time, to prevent plugging in the filter press inlet line. The flow rate of the slurry pump feeding the filter press was set to match the flow rate of materials into the mixing tank and maintain levels in the tanks. This flow rate was calculated using calibration curves generated using a coal-water mixture and flow rate of material entering the mixing tank, as well as checks utilizing level sensors. The recirculation pump was a fixed flow pump, operating at the maximum flow potential to ensure high velocities and effective solids dilution in the filter press.

Material was added to the filter press until the pressure reached approximately 50 psi, or until all of the coal from the test was fed into the filter press. Although the maximum pressure rating for the filter press was 100 psi, this pressure limit was chosen based on the dead-head pressure of the recirculation pump. The recirculation pump would shut-off at approximately 50 to 55 psi, generating a plug in the filter press if the slurry pump was not also stopped. The consequence of not reaching maximum pressure on the filter press was that maximum dewatering efficiency was not achieved in the filter press, a critical economic parameter to evaluate in further studies.

After the pressure reached 50 psi, flows were stopped to the filter press, and any remaining coal slurry was drained from the tanks. The leachate was then recirculated through the filter press to remove any coal fines from the liquid. Due to the extensive cake of material in place on the near-full filter press, significant reductions in small particulate matter (<40 µm) were achieved.

After the leachate was cleaned, an air blowdown was started on the filter press to expel any remaining liquid from the coal in the filter press. Once the flow of liquid out of the filter press stopped, the coal was washed in the filter press. Water was run through the filter press to wash the coal via the recirculation pump. The amount of water used to wash the coal was calculated based on a ratio of 2.2:1 liquid to dry coal mass. After flowing the water through the press, another air blowdown was started to collect all of the wash water, which would then be recycled into the next leaching test where it would be mixed with the coal in the leaching tank. Recycling the wash water helped to reduce acid consumption by recovering additional acid when washing the coal, and also improved REE recovery efficiencies.

Samples were collected from each leaching test of the washed coal, leachate, and wash water. It was not possible to collect a sample from the leached coal before washing, because the coal was not removed from the filter press between the leaching and washing steps. One composite sample was made of the feed coal for every set of three leaching tests and from the samples taken of the washed coal, leachate and wash water.

Impurity Removal: After three leaching tests were completed, the PLS was collected for impurity removal. In this step, sodium carbonate it added to the liquid to precipitate impurities (i.e. iron) which if they remained in solution would negatively impact REE recovery (see section 1, 3). The PLS was pumped to a mixing tank at a flow rate of 1 L/min. The sodium carbonate was fed into the tank using a screw feeder, and the feed rate for this was set using a PID control loop based on maintaining the pH value in the tank which was required for precipitation of the impurities. A residence time of two hours was used for this step. The slurry exiting the tank was sent to a barrel where it sat for 9 to 12 hours to allow for the precipitated solids to settle to the bottom of the barrel.

After the settling time, the liquid was pumped off the top of the barrel into one of the tanks, from which the liquid was pumped through in-line filters as a final clarification step. Some liquid was not separated from the solids at the bottom of the barrel during this step, this liquid was separated from the solids using a vacuum filtration apparatus in the lab, and the filtered liquid was reintroduced to the process. In this step, samples were taken of the precipitated solid and the liquid after filtering.

REE Precipitation: The REE precipitation was completed in two steps to produce a primary and secondary REE concentrate product. The goal of this was to produce a primary product that was high in concentration of REE, and a secondary product that maximized recovery of REE from the solution. Both REE precipitation steps utilized the same procedure, including oxalic acid addition feed rate and pH set point.

The PLS was fed into a mixing tank at a flow rate of 1 L/min, and oxalic acid was fed into the tank using a screw feeder which had been calibrated to the feed rate required. The residence time in this tank was one hour, after which the solution was pumped into a second tank where sodium carbonate was fed via a screw feeder to precipitate the REE. The feed rate of sodium carbonate was determined by a PID control loop which used the measured pH in the tank to set the speed of the screw feeder. After a 90-minute residence time in the tank, the mixture was pumped to the in-line filters where the solid was separated from the solution. This process was then repeated for the secondary REE precipitation step. Samples of the primary and secondary REE products were collected, in addition to liquid samples from each step after filtration.

Aluminum Recovery: After the REE products have been recovered from the PLS, the remaining solution is at an acidic pH and would require water treatment before it could be disposed of. By bringing the pH of the solution to a value slightly higher than the minimum required for disposal, but still within the pH limits for disposal, aluminum can be precipitated to generate an additional product stream.

The solution was pumped into a tank at a flow rate of 1 L/min, and sodium carbonate used to adjust the pH of the solution. The sodium carbonate is fed into the tank using a screw feeder at a rate which is set to maintain a pH of 6 based on a control loop using the pH measurement in the tank. After a residence time of 45 minutes the solution is pumped into another tank, where sodium hydroxide is added to complete the remainder of the pH adjustment and precipitate the aluminum concentrate. The sodium hydroxide is pumped into the tank at a rate of 24.5 mL/min when the pH is below the set point, and the pump is turned off when the pH is above the set point. A residence time of 1 hour was used in this tank to allow time for the solids to precipitate. From the tank, the slurry was pumped into a barrel where the solids could settle out of solution. A sample was collected of the filtered barren solution and the precipitated aluminum solid.

6.2. Results of Testing, Analysis and Conclusions

The testing completed during the semi-continuous processing was broken down into testing “weeks.” The initial phase of semi-continuous testing involved generating a sufficient volume of leachate to allow for the recirculation of leachate through the filter press. This is referred to as Leachate Generation or Week 0. Each of the following weeks of testing consisted of three leaching tests and the processing of the PLS generated from those leaching test to remove impurities, precipitate REE, and recover aluminum. There were a total of 4 weeks of semi-continuous testing.

<u>Coal Leaching:</u> The leaching efficiency of the REE for each week of testing is shown in Figure 6.4. For the Leachate Generation testing, the overall REE extraction from the coal during these tests was just over 35%, and lanthanum had the highest recovery at 46%. The Leachate Generation tests had the lowest overall recovery of REE from the coal out of all of the semi-continuous testing. This is likely due to poor dewatering efficiency in the filter press, especially during the initial testing where no leachate recirculation was used and plugging was likely to occur. These challenges in addition to pump calibration may have also factored into the low extraction, as less liquid was being fed into the tanks, which changed the liquid to solid ratio during mixing and may have resulting in lower extraction during leaching.

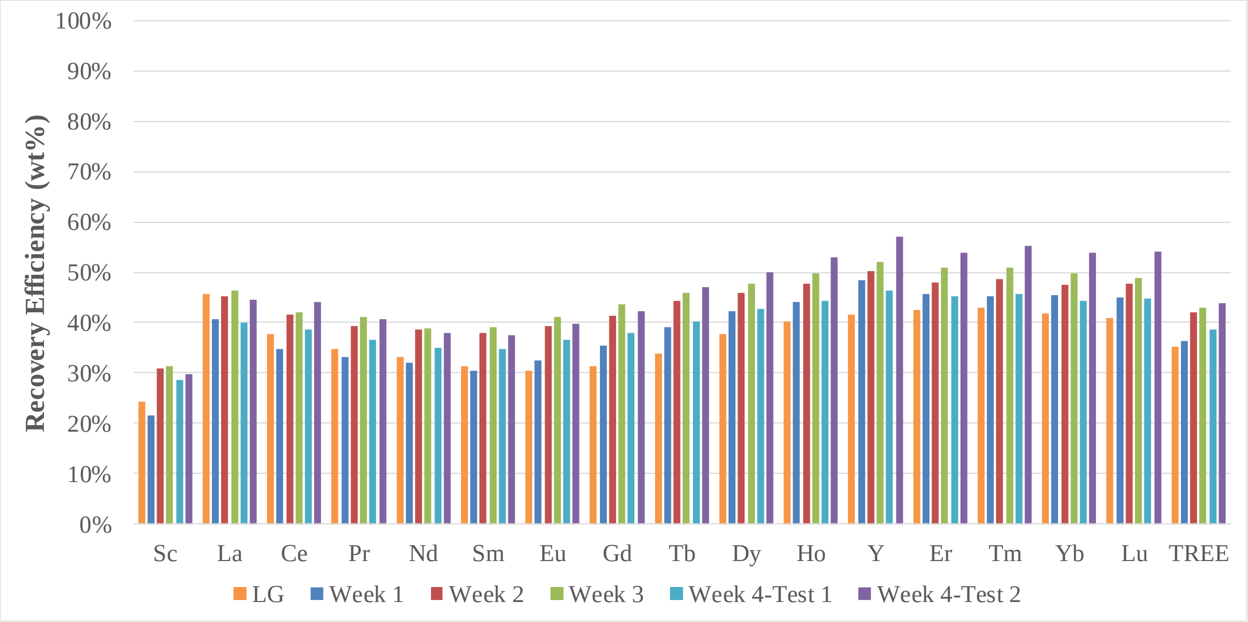

Figure 5.4. *REE recovery from coal during leaching tests.*

The leaching efficiency for Week 1 shows an overall REE extraction from the coal of 36%, with higher extraction was achieved for the HREE compared to the LREE. Week 2 had improved extraction for all elements compared to Week 1 with an overall leaching extraction for Week 2 of 42%, and Week 3 had an overall REE extraction efficiency of 43%.

In Week 4, the pH for leaching was decreased slightly to attempt to improve the leaching of the REE from the coal. Additionally, the first leaching test was run using the same process as all of the previous leaching tests with only one water wash (Week 4-Test 1), but for the second test in Week 4 (Week 4-Test 2) the coal was washed a second time with additional water. The purpose of this was to determine if additional washing of the coal could improve the REE recovery. As shown in Figure 5.4, the Week 4-Test 2 coal was able to recover an additional 5% of the REE from the coal compared to Week 4-Test 1 where the coal was only washed once. This shows that additional washing for future tests should be performed to improve REE recovery from the coal, and may be involved in a multi-step washing circuit. Further, dewatering efficiencies were poor for Week 4 Test 1, (10-20% less than previous weeks), and likely accounts for the loss in extraction efficiency.

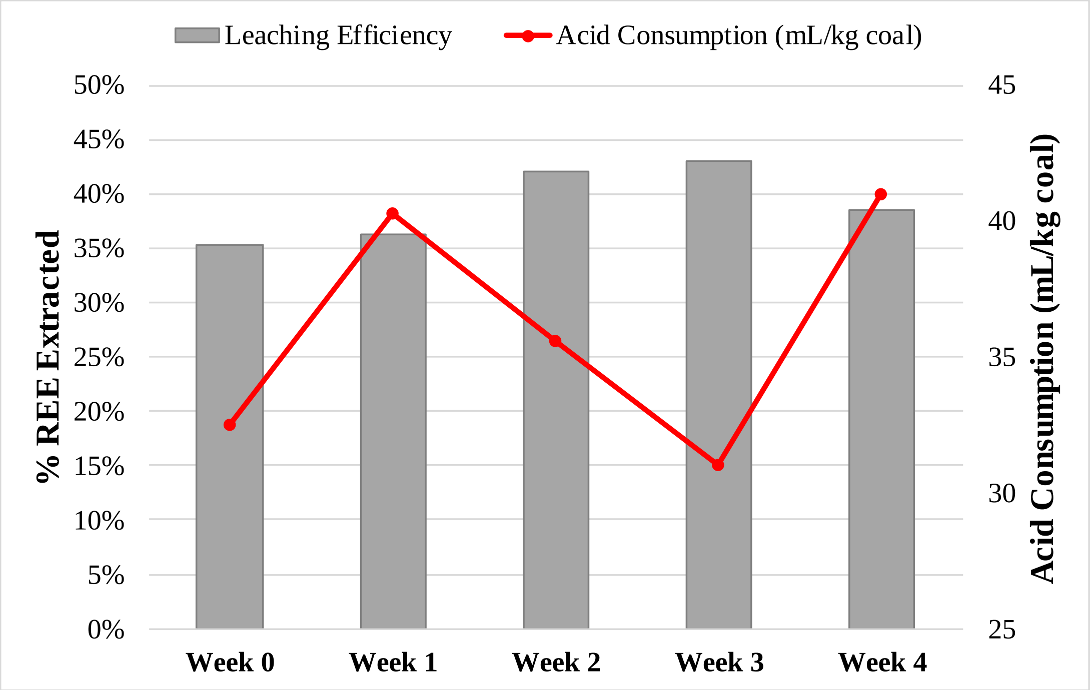

Figure 5.5. *Overall REE extraction from the coal and acid consumption during leaching tests.*

The overall extraction efficiency of REE for each of the leaching tests is shown in Figure 5.5. This figure shows an increasing trend in REE extraction for Weeks 0 through 3, and then a decrease in extraction in Week 4. The trend of increasing extraction efficiencies may be a result of leaching improvements due to recycling the wash water and weakly bound REE exchanging with elements that can form stronger bonds with the coal. This may also be the reason for decreasing NORM concentration which was observed in the PLS (Figure 5.6). The NORM concentration decreased from Week 0 to Week 3, but then increased again in Week 4. This increase in Week 4 is likely due to the lower pH used for the Week 4 leaching tests.

The low acid consumption in the Leachate Generation period (Week 0 in Figure 5.5), was likely due to the use of previously produced wash water of a significantly lower pH level than additional water produced during this test. In general, and particularly involving the consistent week-to-week testing of 1-3, REE extraction improved and acid consumption decreased, likely as a result of concentrating recycle stream (the wash water).

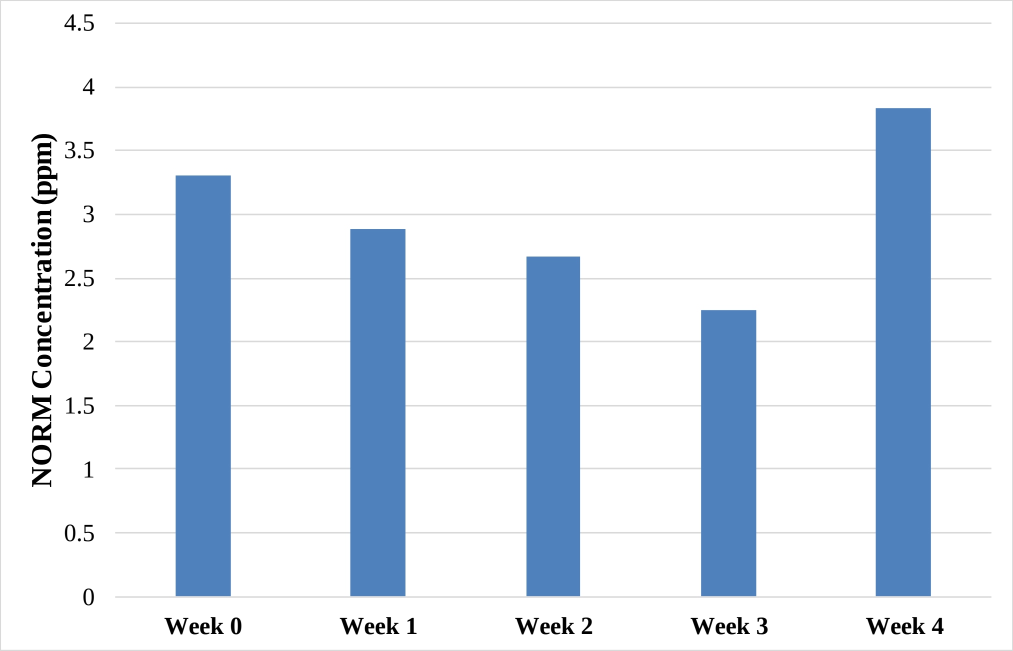

Figure 5.6. *Concentration of NORM (thorium and uranium) in the PLS after leaching from the coal in each week of testing.*

Impurity Removal: Loss of REE during the impurity removal step was minimal for most testing weeks (Figure 5.7), except for Week 3. In Week 3, about 15% loss of REE was observed. This was likely due to equipment issues which resulted in a much shorter residence time than the other testing weeks. The residence time in Week 3 was less than 1 hour, while the residence times in the other weeks were all over 2 hours. The Week 3 test likely did not reach equilibrium, which resulted in the higher loss of REEs and the lower removal of iron from the solution. Based on the shorter residence times which caused losses of REE in Week 3, future testing should use a minimum residence time of 2 hours to optimize this step.

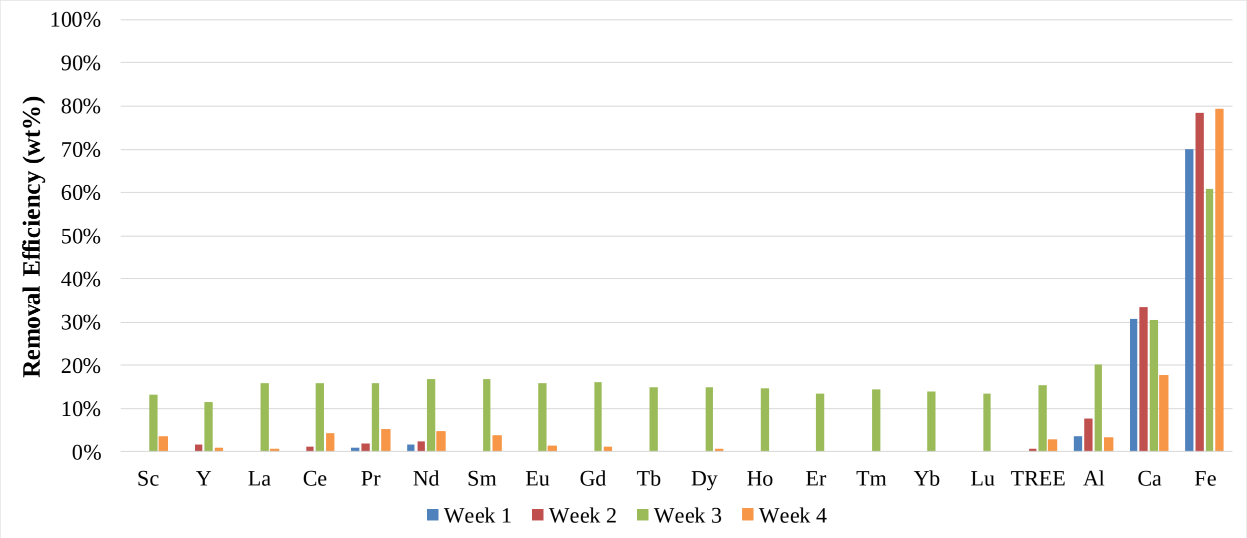

Figure 5.7. *Extraction of elements during the impurity removal step for each testing week.*

In all other testing weeks, minimal losses of REE were observed, with elements such as praseodymium and neodymium showing some losses in this step for all of the testing weeks. After Week 3, the highest loss of REE in this step occurred in Week 4 with a loss of less than 3% total REE. Iron removal efficiencies in Weeks 1, 2, and 4 were all at least 70%.

Sodium carbonate consumption for this step ranged from 31 to 39 g Na_2CO_3/L solution.

REE Precipitation: The total recovery of REE from the PLS is shown in Figure 5.8. This recovery is based on the remaining concentration in the PLS after impurity removal. Due to the challenges with pump calibrations discussed previously in this section, the flow rates of liquid being fed to the tank for oxalic acid addition was lower than anticipated for Weeks 1 and 2. With fixed oxalic acid feed rates, this resulted in higher oxalate concentrations in the liquid than desired for some of the tests. The REE precipitation for Week 3 was completed after the pump calibration method was corrected, and therefore the Week 3 oxalic acid concentrations were at the correct set points for these tests. As shown in Figure 6.8, the recovery of REE from the PLS was the lowest in Week 3, this was due to Week 3 having the lowest total oxalic acid concentration added, as all of the other weeks had total oxalic acid concentrations that were above the desired amount.

For all of the elements besides scandium, nearly 100% recovery from the PLS was achieved in Weeks 1, 2 and 4. Based on this information, higher oxalic acid concentrations, such as the final concentrations in Weeks 1, 2, or 4, should be used in future testing to maximize extraction of REE from the PLS. The higher-than-expected oxalic acid concentrations required is likely a result of higher REE and Al concentrations than anticipated, based upon the recycle.

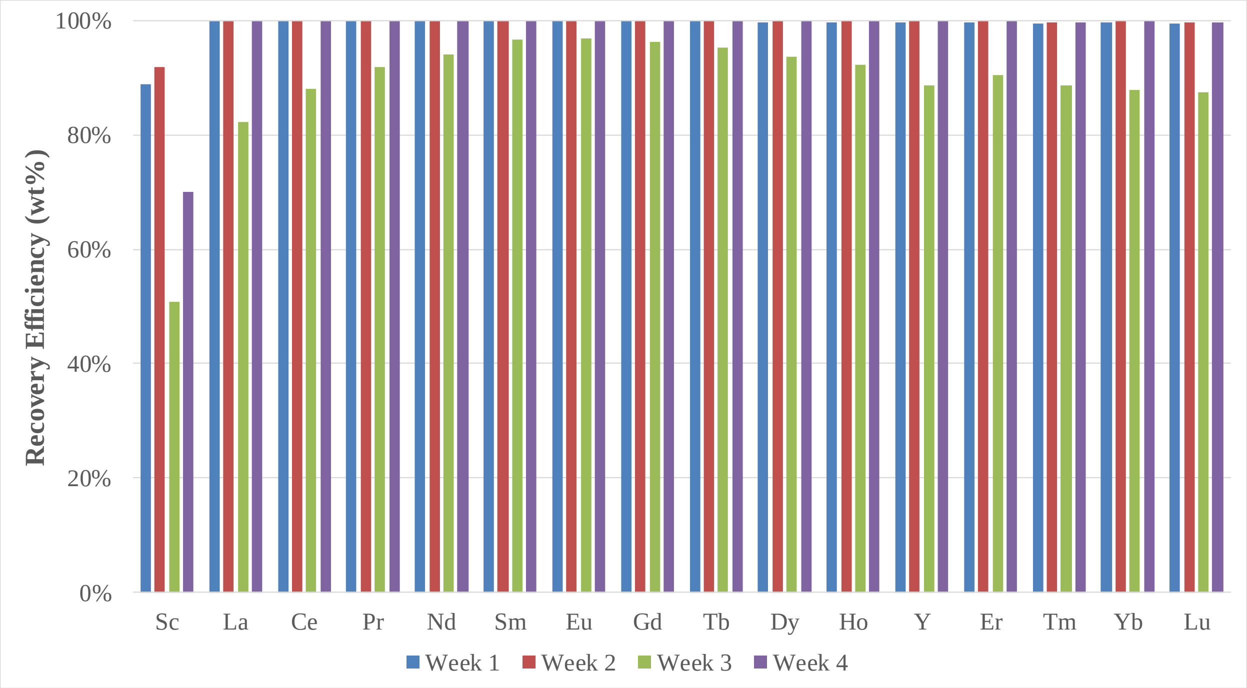

Figure 5.8. *Recovery of REE from the PLS for each of the weeks of testing.*

The concentration of the primary REE solids produced during the REE precipitation testing is shown in Figure 5.9. The highest purity (percent REE oxides present in the product) achieved in the primary product was observed in Week 4 of testing, with a 54% purity. Week 3 had the lowest purity in the primary REE product, but this is likely due to the lower iron extraction in the impurity removal step. In Weeks 1 and 2, the oxalic acid concentration was slightly higher than desired, and this caused the lower purity in these products compared to Week 4. As shown in Table 5.1, purities of the primary product ranged from 27% in Week 3 to the highest purity in Week 4 of 54%.

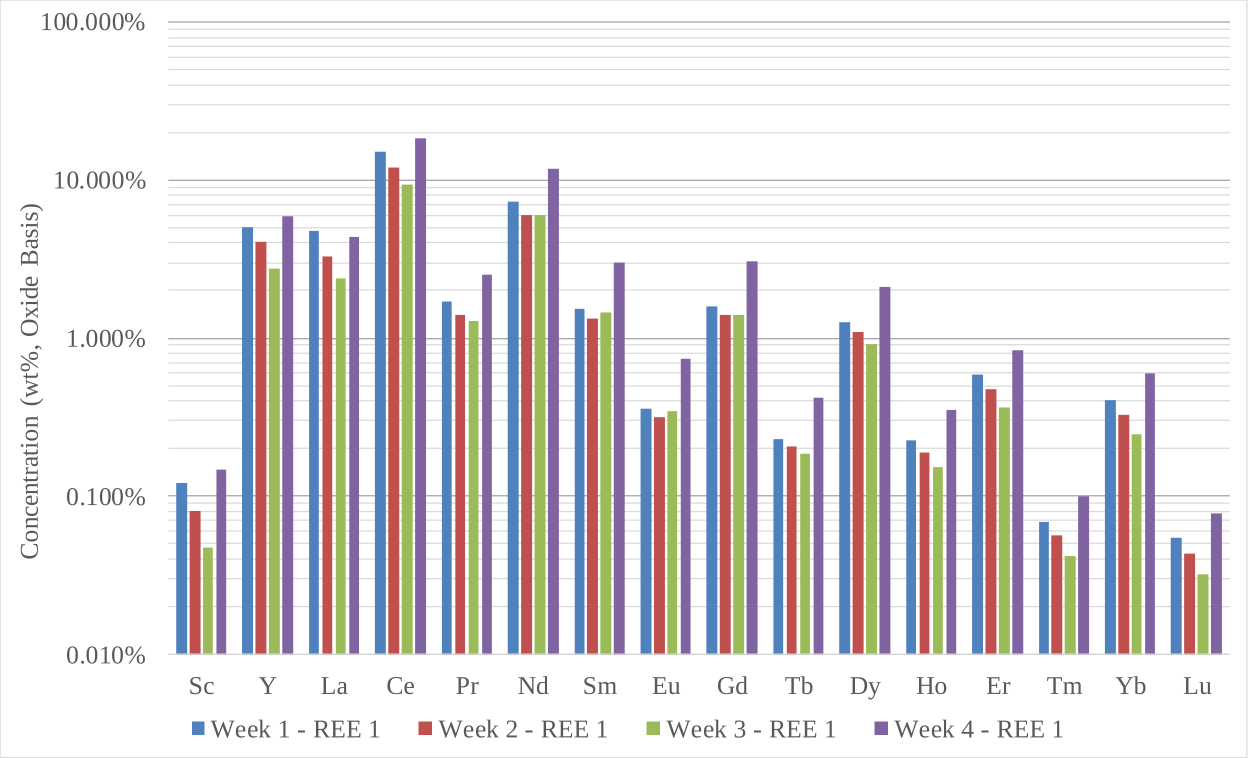

Figure 5.9. *Concentration of the primary REE products (oxide basis) from each week of semi-continuous testing.*

The concentrations of the secondary REE product is significantly lower than the primary product (Figure 5.10). This was expected, as the goal of collecting the secondary product was to maximize recovery of REE from the PLS and not to produce a high purity product, as was the goal with the primary product. Purities of the secondary product ranged from 3.5% REE Week 1 up to 8.6% in Week 3 (Table 5.1).

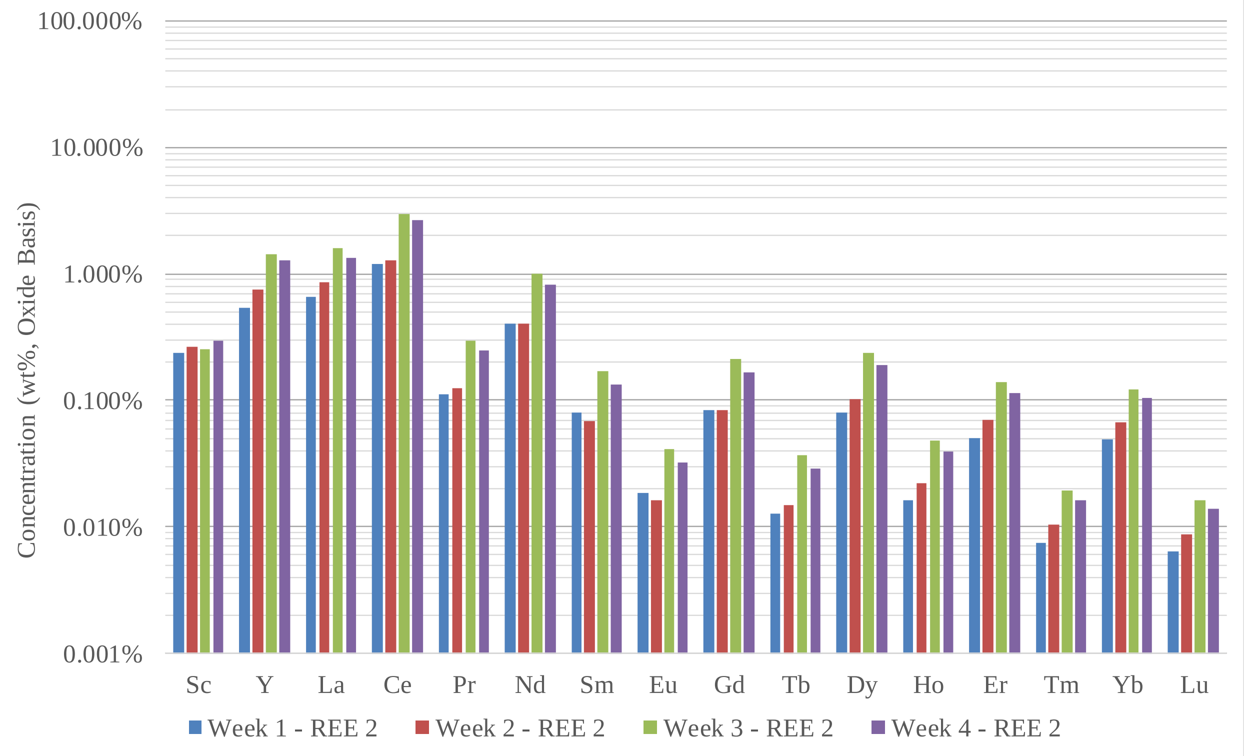

Figure 5.10. *Concentration of the secondary REE products (oxide basis) from each week of semi-continuous testing.*

Table 5.1. *Purity of the REE products produced during each week of testing on an oxide basis.*

Test	Primary REE Product Purity (wt%, oxide basis)	Secondary REE Product Purity (wt%, oxide basis)
Week 1	40.3%	3.5%
Week 2	32.3%	4.1%
Week 3	27.0%	8.6%
Week 4	54.4%	7.5%

<u>Aluminum Recovery:</u> The extraction efficiency of the aluminum recovery step is shown in Figure 5.11. The aluminum extraction from the solution was highest in Week 2 and lowest in Week 1. There is a correlation in these tests between the amount of sodium hydroxide used per liter of solution to reach pH 9 and the efficiency of aluminum extraction. In Week 1, 7.3 mL of 50wt% NaOH was used per L of solution, compared to 10.1 mL of 50wt% NaOH/L of solution for Week 2. This same correlation is also followed in Weeks 3 and 4 where 9.0 mL/L and 8.2 mL/L were used respectively for each test. The amount of sodium

carbonate used each week to reach pH 6 did not vary significantly, ranging from 7.9 to 9.6 g Na_2CO_3/L solution.

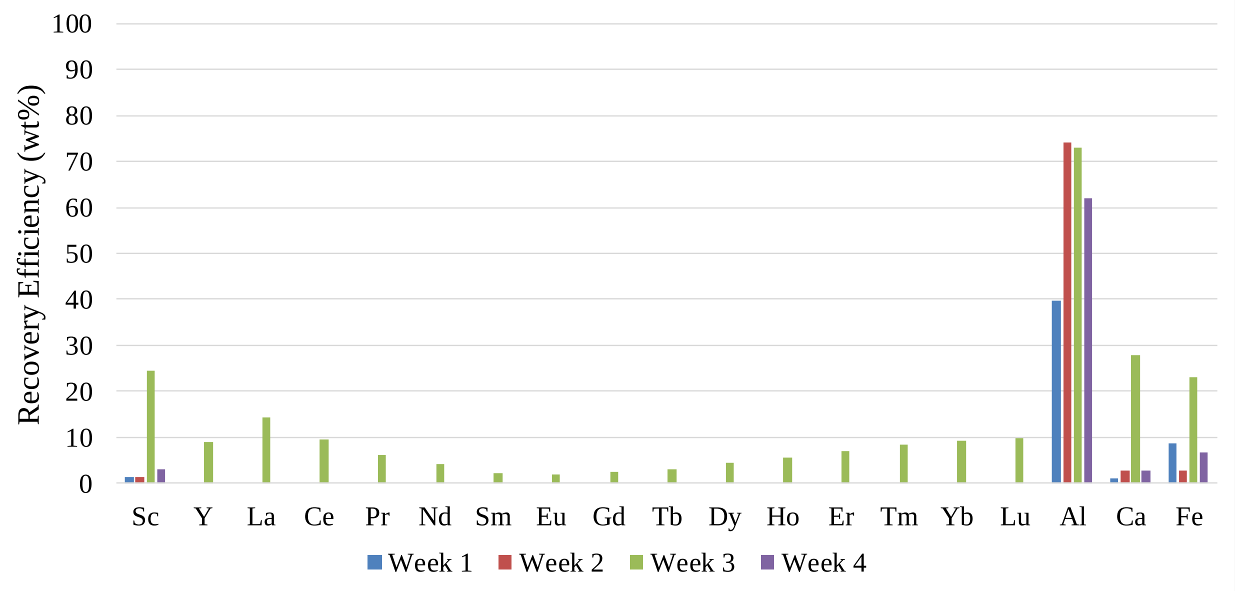

Figure 5.11. *Percent of the elements leached from the coal which were recovered in the aluminum product.*

The higher recovery of REEs in Week 3 (Figure 5.11) is a result of the lower recovery of REE during the REE precipitation step. For Weeks 1, 2, and 4, nearly 100% of the REE had previously been removed from the PLS during the REE precipitation step, and therefore were not available in solution to be extracted in this step. Additionally, any scandium remaining in the PLS was recovered from the solution in this step, along with a large fraction of the remaining calcium and iron in the solution.

6. Summary and Conclusions

Over the course of the Phase 2 testing, which included lab-scale, batch bench-scale, and semi-continuous bench-scale tests conducted on a number of coals, a number of key observations and technical determinations were made: i) the discovery of the pH-based leaching mechanism similar to cation exchange extractants, ii) identification and methods of control of impurities of purity/economic impacts, and iii) the impact of engineering-scale impacts, such as dewatering efficiencies and flow control mechanisms on the chemistry of the process. As a result, the planned processing method for the REE from lignite underwent multiple iterations of design adjustments, including the deletion and addition of unit operations to account for the lack of alkaline-earth separation found in planned pre-leaching steps. Purities of REO concentrates were increased from 2 wt% on a dry, solids basis within the PLS (Phase 1) to greater than 50% on a dry, whole sample basis by the end of Phase 2 at the bench scale in semi-continuous testing.

The identification of the pH-based mechanism, similar to cation-exchange extractants and resins, allowed for development of equilibrium-based separation and significantly faster kinetics than previously thought, primarily of a control mechanisms developed. Kinetic improvements from 8-14 hours (Phase 1 kinetic testing) to 30 minutes (Figure 3.3) significantly reduced the size of the equipment required, and substantially reduced potential costly impurity extraction (NORM reductions by more than 50% for actinides). The effects of this leaching mechanism scaled well from lab-bench scale testing.

Impurities such as Ca, Fe, and Al were identified as key challenges for process economics, impacting the purity of the REO concentrates and the reagent usage required to generate these. Methods of control, such as by utilizing equilibrium-limited leaching and targeted removal through pH-swing, were identified and tested with positive results. As technology scale-up occurs, use of on-line monitoring systems for these elements and evaluation of improved separation mechanisms will be evaluated.

Engineering-scale challenges, such as dewatering of the leached lignite for larger-scale testing and recapture of liberated REE ions, allow testing in future, larger-scale facilities to be focused towards addressing these issues. Additionally, identification of potential recycle stream up-cycling effects, as well as key process parameters to be measured and controlled, further enable better utilization of resources as technology progression continues.

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TECHNICAL AND ECONOMIC FEASIBILITY STUDY

SUBMITTED TO

U.S. Department of Energy
National Energy Technology Laboratory

SUBMITTED UNDER FUNDING OPPORTUNITY ANNOUNCEMENT

DE-FOA-0001202

INVESTIGATION OF RARE EARTH ELEMENT EXTRACTION FROM NORTH DAKOTA COAL-RELATED FEEDSTOCKS

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WORK PERFORMED UNDER AGREEMENT

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Investigation of Rare Earth Element Extraction from North Dakota Coal-Related Feedstocks

Technical and Economic Feasibility Study

Prepared for
The University of North Dakota
Institute for Energy Studies

March 9th, 2020

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Investigation of Rare Earth Element Extraction from North Dakota Coal-Related Feed Stocks

Technical and Economic Feasibility Study

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Acronyms

Acronym	Description
AACE	Association for the Advancement of Cost Engineering International
AC	Activated Carbon
AOI	Area of Interest
Barr	Barr Engineering Co.
CAPEX	Capital Expenses
DOE	Department of Energy
FOA	Funding Opportunity Announcement
HA	Humic Acid
IRR	Internal Rate of Return
NDSU	North Dakota State University
NDUS	North Dakota University System
OPEX	Operating Expenses
PFD	Process Flow Diagram
PLS	Pregnant Leach Solution
PNNL	Pacific Northwest National Laboratory
PPMW	Parts per Million Weight
REE	Rare Earth Element
ROI	Return on Investment
TEA	Technical Economic Analysis
UND IES	The University of North Dakota Institute for Energy Studies
UND	University of North Dakota
VCSU	Valley City State University

I. Executive Summary

The University of North Dakota Institute for Energy Studies (UND IES) has teamed with Barr Engineering Co. (Barr), Microbeam Technologies Inc. (MTI), Pacific Northwest National Laboratory (PNNL), MLJ Consulting, and the North Dakota Geological Survey (NDGS) to determine the technical and economic feasibility of extracting and concentrating rare earth elements from North Dakota lignite coal-related feedstocks, for a project submitted under US Department of Energy Funding Opportunity Announcement DE-FOA-0001202 in Area of Interest (AOI) 1 - Bench-scale Technology to Economically Separate, Extract, and Concentrate Mixed REEs from Coal and Coal Byproducts including Aqueous Effluents. The project is supported by cost-share partners North American Coal Corporation, Great River Energy, Minnkota Power Cooperative, Great Northern Properties, North Dakota University System, Valley City State University, and the North Dakota Industrial Commission/Lignite Research Council.

The work described in this report identifies conditions for an economically viable and environmentally benign process to produce an REE concentrate. The effort includes feedstock identification and procurement, construction and testing of a bench-scale system, separation and concentration methods development and testing, production of an REE concentrate product, and technical and economic feasibility evaluations of the complete system. Background and introductory information can be found in Section 1.0 of this report.

Section 2.0 of this report summarizes the following considerations regarding the design basis and approach:

Table EX-1. Summary of the REE Extraction process modeled within this TEA.

Feedstock	**H Bed Lignite Coal**[1]
Plant Size	Activated Carbon – 10,000 lb/hr (coal feed rate) Humic Acid – 40,000 lb/hr (coal feed rate)
Lignite Feedstock REE concentration	• 650 ppm REE+Y and Sc, (dry coal basis), 1350 ppm REE+Y and Sc, (ash basis)
Process and Concentrating Sequence	• **Crushing -** (to -4 mesh) • **Spiraling –** Remove high ash material • **Leaching -** (dilute mineral acid) • **Separate** – Residual coal for Activated Carbon or Humic Acid Processing • **Remove Fe Impurity** – pH Adjustment • **Recover REE –** Selective Precipitation (oxalic acid) • **Al Precipitation –** pH Adjustment • **Transport** REE concentrate to processor/buyer
Concentration Results (dry solid oxide basis)	**Primary – 54 wt% REE oxide** **Secondary – 7.5 wt% REE oxide**
Environmental Considerations	• Ambient temperature and mild leaching solution w/ zero acid discharge methodology • Byproducts processed to create either saleable syngas/activated carbon or humic acid • Waste heat used to reduce energy of drying materials.

1 Selectively mined coal from the H Bed in ND.

Section 3.0 - Process Design and PFDs: This section describes the systems to be considered for full scale production. Section 4.0 discusses the evaluation of the mass and energy balances of the total system used in the economic evaluation. Section 5.0 discusses the technical and economic evaluation results. These Class 5 estimate results are based on mining and minerals processing industries and are summarized below:

Table EX-2. Summarized Base Case Economics for Activated Carbon and Humic Acid Cases.

Byproduct	Plant Size (lb/hr coal feed)	CAPEX	Annual OPEX	Net Annual Revenue	Simple Payback (yrs)	ROI[1]		IRR[1]		NPV[1]	
						10 yrs	20 yrs	10 yrs	20 yrs	10 yrs	20 yrs
Activated Carbon	10,000	$36,800,000	$9,980,000	$7,300,000	5.1	10 %	15%	15%	19%	$4,200,000	$17,400,000
Humic Acid	40,000	$50,700,000	$69,100,000	$10,400,000	4.9	5%	10%	8%	14%	$8,200,000	$27,200,000

1.0 Introduction

Background of Funding Opportunity Announcement DE-FOA-0001202

This project addresses the technical area of interest as defined by DOE in DE-FOA-0001202: AOI 1 – Bench-scale Technology to Economically Separate, Extract, and Concentrate Mixed REEs from Coal and Coal Byproducts including Aqueous Effluents.

The DOE program objective for this FOA is as follows:

- Demonstrate a bench-scale, high performance, economically viable, and environmentally benign concentrating technologies for coal-related feedstocks to produce a two weight percent REE concentration

The specific objectives of this Phase 2 Project included: feedstock identification and procurement, construction and testing of a bench-scale system, development/testing of concentrating methods, technical and economic evaluation of the concentrating process, production of an REE concentrate product, and development of a strategy for commercialization.

Project Team

The University of North Dakota Institute for Energy Studies (UND IES) has teamed with Barr Engineering Co. (Barr), Microbeam Technologies Inc. (MTI), Pacific Northwest National Laboratory (PNNL), MLJ Consulting, and the North Dakota Geological Survey (NDGS) to determine the technical and economic feasibility of extracting and concentrating rare earth elements from North Dakota lignite coal-related feedstocks. The project is being conducted with the support of cost-share partners North American Coal Corporation, Great River Energy, Minnkota Power Cooperative, Great Northern Properties, North Dakota University System, Valley City State University and the North Dakota Industrial Commission/Lignite Research Council.

1.1 Purpose

The overall goal of the project was to demonstrate at the bench-scale, a high performance, economically viable, and environmentally benign technology to recover rare earth elements from local lignite coal or lignite-related feedstocks.

In order to meet the goal, the following are specific objectives in Phase 2:

- Based on the design of the bench-scale system developed in Phase 1, construct a bench-scale system with a REE-rich feedstock throughput of about 10 kg/hr to produce a mixed REE stream of >2% by weight on a dry, elemental basis
- Obtain large samples (~2000 kg) of coal and associated sediments containing >300 ppm total REE dry whole sample basis for testing
- Conduct parametric testing of the bench-scale system to determine optimum conditions required to concentrate REE to >2%

- Conduct continuous testing of the bench-scale system at optimized conditions/configuration to produce a representative REE concentrate that is suitable for evaluation for further processing
- Provide split samples of the final product produced from the Phase 2 testing to NETL for independent analysis and verification of the quantity of REE present
- Update the technical and economic analysis of the REE recovery process conducted in Phase 1 with the results of testing obtained in Phase 2
- Identify opportunities for commercialization at existing mines/plants locally and/or build the commercially feasible case for opening a new mine in an area with most favorable REE content
- Work with industry supporters to develop a technology development and commercialization strategy

1.2 Scope and Technical Basis

The scope and basis for the technical and economic feasibility analysis is derived from the results of testing and analysis conducted in this project. Sampling and analysis conducted in Phase 1 of this project indicated that the bulk of the REE in the lignite coals are organically associated, loosely bound to the clays, and in mineral grains less than 10 µm. A majority of the REE forms are present as weakly bonded and are extractable using a mild acid leaching process. This hypothesis has been supported by additional testing and analysis done in Phase 2.

The UND REE extraction process involves a mild acid leach at ambient temperature of the pre-combustion coal to extract the REE, Y and Sc, and other valuable elements. The mild leach is made possible by the weak association of the REE within the lignite coals. The resulting residual coal has a lower ash content and higher heating value and can be beneficially utilized in other processes such as activated carbon manufacturing or humic acid production. The pregnant leach solution (PLS) is pH adjusted to remove impurities (i.e. iron) before the REE extraction step where REE's and critical minerals (CM) are precipitated using oxalic acid and sodium carbonate. The remaining PLS may then be processed to recover aluminum by base addition to the barren solution.

The overall concept for commercial implementation of this REE recovery process is to combine the REE recovery with an additional value-added process, which utilizes the residual coal, such as activated carbon production co-located at a combined heat and power plant, or at a purified humic acid production facility. The integration of activated carbon production with steam generators is a concept developed at the University of North Dakota to replace aging district heating systems at North Dakota University System (NDUS) campuses with systems that co-produce activated carbon and steam. The activated carbon will be sold for municipal water treatment and mercury capture at coal-fired power plants. The steam will be used for district heating and for activating the carbon. The concept will be first implemented at Valley City State University (VCSU) in North Dakota, which has constructed a new steam generation plant and is in the process of obtaining funding for the activated carbon plant. The overall concept that has very favorable economics and has generated tremendous support within the State of North Dakota. Allocation of funding for the activated carbon plant through a revenue bond or other funding scenarios to build the integrated plant was unanimously passed in the ND State legislature. Adding a REE recovery system to the integrated carbon/steam plant has the potential to increase revenue through the production of REEs and improve the properties/value of the produced carbon.

Letters of support from both NDUS and VCSU have been gathered for this Technical and Economic Analysis (TEA) as a statement of their support for investigation of the REE recovery addition to the VCSU facility, along with more information on the current status of the existing projects.

Humic acid production was also considered as an alternative value-added opportunity to be integrated with the REE recovery process. Humic acid can be produced from the residual coal after leaching, and then used for pharmaceutical purposes or as fertilizer. Benefits to the humic acid extraction and recovery process following the REE leaching process include: Significant improvement in recoverable product (15% → > 25%), significant purity enhancement (ash content from >4% → <0.5%), and minimal additional permitting (due to the existence of all chemical required for the process utilized in the REE process – acids and bases. Further, use of the humic acid in potential growth markets, such as specialty carbon electronics and battery anode materials would be permissible due to the significant purification afforded the material from the acid stripping performed within the REE processing.

For this TEA, the scope of economic modeling is shown in Figure 1-1 and Figure 1-2. Major assumptions include:

- Selectively mined coal from the H Bed seam in North Dakota is purchased (additional locations for selective mining have been identified, but the H Bed seam is used as the base case in this evaluation)
- Iron precipitates generated in the process is sold for the cost of transportation (no revenue or cost)
- Concentrated REE solid is sold to a commercial processor for final separation
- If optional aluminum concentrate is produced, it is sold as a bauxite equivalent material
- In the case for activated carbon production:
    - Fuel gas generated via the activated carbon production process is sold to the VCSU steam plant
    - Activated carbon is sold wholesale to a distributor
    - Steam for activation is purchased from the VCSU steam plant
- In the case for humic acid production:
    - Humic acid is sold for fertilization or pharmaceutical use

The above concept has numerous benefits that are summarized as follows:

- Uses smaller quantity of fuel than large-scale power plant (i.e., 1100 MW Coal Creek Station), which will enable selective mining to prevent dilution of the REE content in the feed coal.
- Extraction of other valuable minerals such as cobalt, copper, gallium, germanium, manganese, and zinc.
- In the case of activated carbon production:
    - The REE extraction process reduces the inorganic content in the coal, thus resulting in a high purity activated carbon product that can be sold for a premium price.

  - Co-location of the REE, activated carbon, and steam plant components offers synergies such as sharing of coal handling infrastructure, transportation mechanisms, and heat integration opportunities.
  - The combustible fuel gases produced via activated carbon production are hydrogen-rich, and with carbon being permanently sequestered in solid form as activated carbon, CO_2 emissions from the steam plant are dramatically reduced (~40-45% reduction).
  - The VCSU plant can be considered a first-of-a-kind demonstration. With successful implementation at VCSU, support is expected for installation at additional campuses in North Dakota that offer significant scale-up opportunities.

- In the case of humic acid production:
  - The REE extraction process reduces the inorganic content in the coal, thus reduces potential impurities in the humic acid product
  - Co-location of the REE and humic acid components offers synergies such as sharing of coal handling infrastructure, transportation mechanisms and acid and base handling infrastructure.
- Technical, environmental and economic benefits of the REE extraction/concentration process include: (i) ambient temperature and mild leaching of the raw coal, (ii) minimal NORM extraction from the coal, (iii) minimal production of waste, and (iv) simple, highly effective and industrially proven processing steps. Additional details are located in Section 2.4.

This study evaluates integration of REE recovery with either the activated carbon and steam production plant at VCSU or with a humic acid production plant; however, it is important to note that the residual coal resulting from the leaching processes, with lower ash content/higher value than the feed coal, can be utilized in an array of value-added coal utilization processes to augment overall economics.

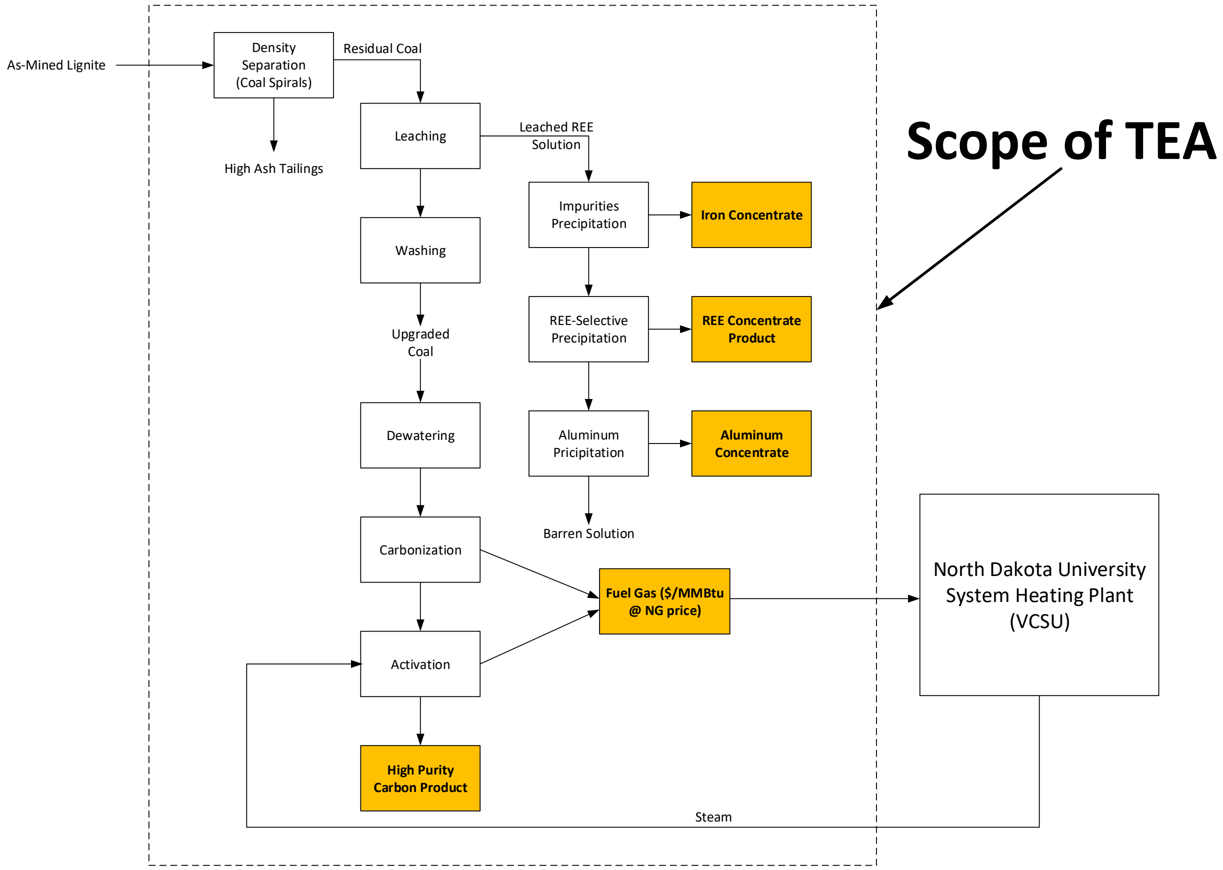

Figure 1-1 Schematic of the scope of economic modeling for the Technical and Economic Assessment

2.0 Design Basis/Approach

2.1 Feedstock Identification

Selectively mined coal is sourced from the H Bed seam of the Harmon-Hanson coal zone in North Dakota (650 ppm REE+Y and Sc, whole coal dry basis and 1,350 ppm REE+Y and Sc, ash basis) and assumed to be purchased. The relevant REE content basis for the concentration methods evaluated in this study is whole coal (dry basis), but ash basis is also presented as a baseline for comparison with other resources. Mass and energy balances for the activated carbon production process have previously been developed by UND as part of a non-DOE-funded project (North Dakota Department of Commerce Award Number 16-05-J1-125; Venture Grant Phase I). To be consistent with the separately funded activated carbon/steam plant project, this evaluation assumes a bulk coal composition (proximate / ultimate) that is an 'average' ND lignite. Hence, the carbon/ash balances presented here will not correspond to the actual composition of the H Bed coal for this study. An 'average' ND lignite was also assumed for the humic acid production case. This does not have a significant impact on the economics of the overall process. Detailed analysis of the H Bed coal can be found in Section 2.3. According to the USGS,[1] The Harmon-Hanson coal zone covers an approximate area of 5500 square miles in southwestern ND and into portions of Montana and South Dakota (Figure 2-1). It consists of multiple coal seams ranging from 4 to 42 feet thick, portions of which have been mined as recently as 1997 at the Gascoyne Mine that produced about 2.5 Million tons/year between 1975 and 1995. Samples of this coal zone were collected from an exposed portion of a seam in Slope County, ND and analyzed in this project.

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[1] Flores, R.M., Keighin, C.W., Ochs, A.M., Warwick, P.D., Bader, L.R., Murphy, E.C. "Framework Geology of Fort Union Coal in the Williston Basin." Chapter WF in U.S. Geological Survey Professional Paper 1625-A. 1999 Resource Assessment of Selected Teriary Coal Beds and Zones in the Northern Rocky Mountains and Great Plans Region.

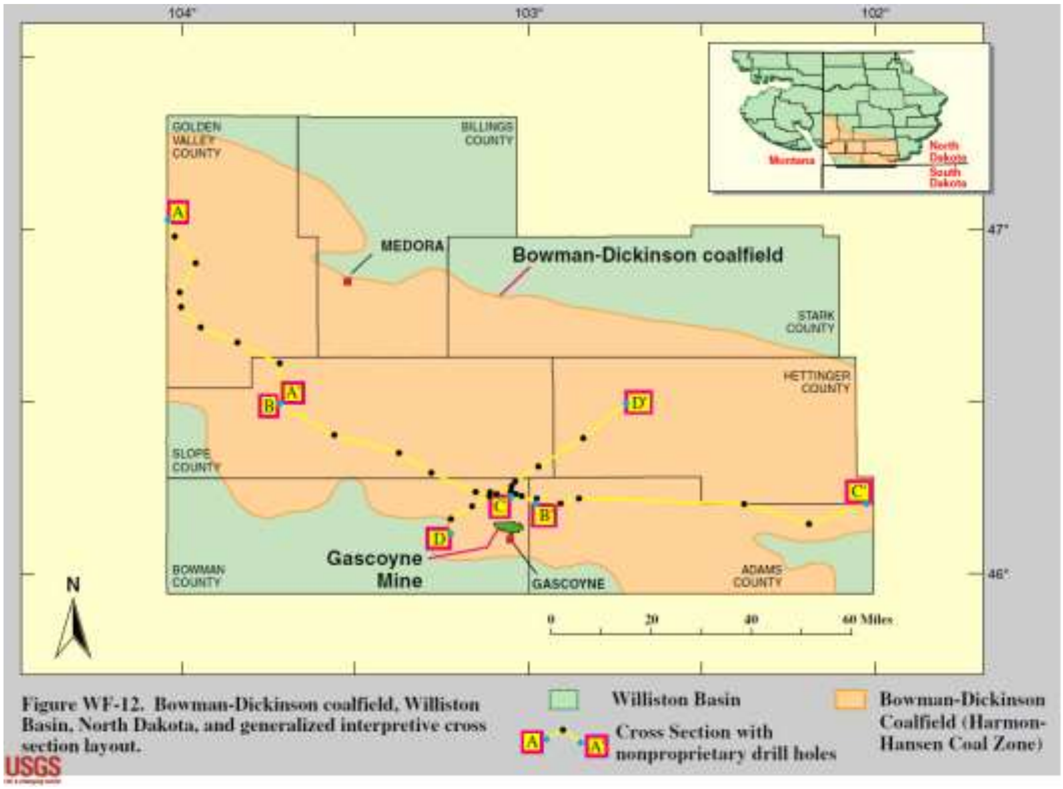

Figure 2-1 Coverage of the Harmon-Hanson Coal Zone in southwestern ND[2]

Additional unpublished sampling/analysis work by the North Dakota Geological Survey (NDGS) (personal communication, Ned Kruger, 2017) has identified multiple other coal resources in the state with REE content approaching that of the H Bed coal. Although complete results are currently not publicly available, a summary of the NDGS sampling work and results to date is available from the North Dakota Department of Mineral Resources website.[3] The USGS CoalQual Database,[4] also shows notable REE content for several samples throughout the state, as well as multiple other samples with incomplete REE analysis, but high levels of individual REEs analyzed. The project team believes the Harmon-Hanson coal zone to be a commercially feasible source of REE-rich coal and expect several other REE-rich resources in the state can be produced as well.

2.2 Concentrating Methods

Figure 2-2 displays a simplified block flow diagram of the concentration process. Due to unique association of REEs with ND lignite coals, a mild leaching process has been developed that extracts REEs directly from

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[2] Flores, R.M., Keighin, C.W., Ochs, A.M., Warwick, P.D., Bader, L.R., Murphy, E.C. "Framework Geology of Fort Union Coal in the Williston Basin." Chapter WF in U.S. Geological Survey Professional Paper 1625-A. 1999 Resource Assessment of Selected Teriary Coal Beds and Zones in the Northern Rocky Mountains and Great Plans Region.

[3] https://www.dmr.nd.gov/ndgs/documents/newsletter/2017Winter/Rare%20Earths%20in%20Coal.pdf

[4] USGS CoalQual Database. Available From: https://ncrdspublic.er.usgs.gov/coalqual/

the raw coal with recovery efficiencies of about 35 to 50% for the REE and Y and about 28% for Sc. The overall process is summarized as follows:

- Selectively mined coal is sourced from the H Bed in North Dakota (650 ppm REE+Y and Sc, whole coal dry basis)
- Spirals are used to remove the mineral fraction from the coal
- The coal is then slurried with dilute mineral acid while maintaining pH to extract REEs
- The coal is washed to remove residual acid
- The final residual coal (with reduced inorganic content) can be dewatered and utilized as fuel or feedstock
- The pregnant leach solution (PLS) containing the REEs is purified to remove iron via sodium carbonate addition to adjust the pH
- REE extracted from solution by mixing the PLS with oxalic acid and sodium carbonate
- In an optional final step, base is added to the remaining solution to increase the pH to extract an aluminum byproduct
- The final REE concentrates are sent for separation at an offsite refinery

Mass balances used in this evaluation are based on bench-scale testing performed at UND with the following set of conditions:

- Coal is from the H Bed seam with known REE and moisture content
- Liquid to dry coal ratio of 2:1 for leaching with dilute mineral acid
- Coal/leaching solution stirred with residence time of 1 hour while maintaining the pH through addition of acid
- After filtering coal from the PLS, coal is washed with water in a 2:1 liquid to solid ratio
- Amount of sodium carbonate added for all steps based on maintenance of a specific pH value
- A 90-minute residence time during impurities removal step, to maximize precipitation of iron
- REE precipitation performed by adding oxalic acid in a specific ratio before sodium carbonate addition to increase pH
- Residence time of 2 hours for REE precipitation
- Aluminum recovery performed with sodium carbonate addition up to a pH of 6, then sodium hydroxide used for remainder of pH adjustment
- All solids filtered, washed, dried, and analyzed for REE, other target elements and impurities content
- All liquids filtered and analyzed for REE, other target elements and impurities content
- Mass balances determined based on analysis results from liquid streams and solid products

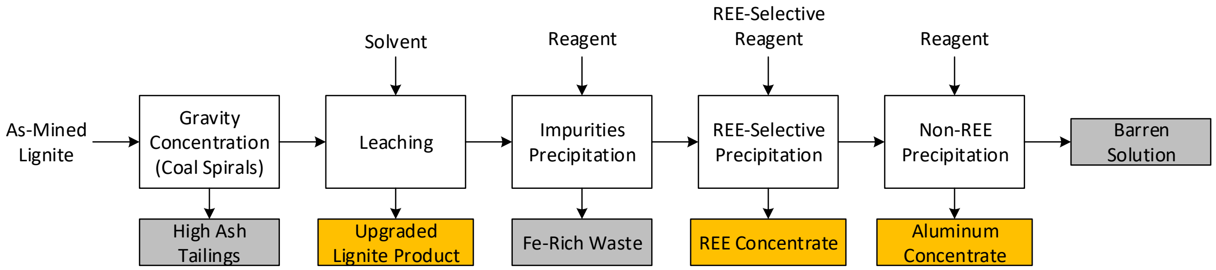

Figure 2-2 **Simplified diagram of the REE concentrating process**

Figure 2-2 includes the simplified diagram of the REE concentrating process evaluated in the TEA. **NOTE**: The concentrated REE product is sent for final separation and could be located off-site or co-located. For this study, it was assumed a commercial buyer would purchase the concentrated REE product.

2.3 Development / Testing

Batch parametric testing was completed on the bench-scale system with the H Bed coal to optimize the process conditions prior to the continuous production testing. Each of the process unit operations were evaluated over a range of conditions to optimize performance. This testing was completed sequentially such that the first unit operation was optimized prior to testing of the next. Process conditions used during production testing were chosen based on the following:

- The pH for leaching chosen to achieve maximum REE extraction from the coal with the least amount of acid to minimize processing costs
- Leaching residence time based on laboratory kinetics testing results which showed majority of REE extraction from the coal occurred in within the first 30 to 40 minutes
- The pH for the impurity removal step was chosen to maximize iron removal and minimize REE loss
- Oxalic acid concentrations chosen to maximize purity of REE in the primary product and maximize recovery of REE in the secondary product
- The pH for aluminum precipitation chosen to maximize aluminum recovery with the least amount of base to minimize processing costs

Assumptions for the TEA

- Process conditions and residence times will be the same as during bench-scale testing
- Mass balance data used for the TEA is based upon the highest fidelity (least experimental challenges) obtained the week of bench-scale testing. Due to a limited bench-scale testing period and introduction of a recycle stream, extraction efficiencies were seen to be improving from week to week and had not reached an optimized value during production testing. REE extraction improvements and decreasing acid consumption is anticipated with further testing.
- Assume size reduction of coal feedstock for leaching at -4 US mesh particle size; bench-scale tests performed using this size
- Ambient temperature (~25°C or room temperature) operation.

Baseline leaching data for the H Bed feedstock is listed in Table 2-1. This study will focus on the H Bed feedstock with a coal feed rate of 10,000 lb/hr for the activated carbon production. This production rate was based on the sizing for the activated carbon plant in evaluation for installation with the existing steam generation plant at VCSU (work previously conducted by UND under separately funded project; referenced in Section 2.1). For humic acid production, a coal feed rate of 40,000 lb/hr of H Bed coal was used.

Table 2-1 Total Recovery into Product Results of the H Bed Lignite Testing

H Bed Feedstock		
Element	**Initial ppm**	**Percent Recovered**
Sc	25.3	28%
Y	66.4	50%
La	96.6	45%
Ce	229	41%
Pr	28.5	39%
Nd	119	39%
Sm	25.5	38%
Eu	5.71	39%
Gd	22.7	41%
Tb	3.16	44%
Dy	16.8	46%
Ho	2.97	48%
Er	8.01	48%
Tm	1.05	48%
Yb	6.47	48%
Lu	0.88	48%
Co	13.5	35%
Ga	15.3	3%
Ge	15	17%
Th	14.3	19%
U	18.3	13%
Al	20200	0.5%
Fe	25600	3.4%
Ca	2450	0.0%

2.4 Environmental Considerations

The environmental impact was considered during the approach of the system configuration. Many of the gases and byproduct solids are processed to be a saleable product thus reducing waste streams discharging from the plant. The energy footprint was also reduced by recirculating viable sources of waste heat throughout the process. The following considerations are discussed to better understand how the proposed system was designed to optimize waste streams and energy usage to approach an environmentally benign process.

The weak association of REEs in ND lignite coal presents a unique opportunity that, based on a thorough literature review of the modes of occurrence of REEs in coal, is not likely possible for higher rank coal types (i.e., bituminous) or for most coal-related byproducts (i.e., roof/floor sediments or combustion flyash).[5] [6] [7] [8] [9] [10] The process is simple, environmentally benign, and low cost, and is based on industrially proven mineral extraction methods widely utilized (including at the Mountain Pass Mine USA and in China for REE recovery). Some of the advantages of this technology are summarized below:

- Mild leaching of the raw coal at low/ambient temperature – environmentally benign processing
    - ✓ Hard rock ores or coal flyash require highly concentrated (i.e., >80wt% acid) acid baking at high temperatures (200-300°C) to achieve reasonable extraction of the REE. This is expensive and makes environmentally friendly processing challenging.
- Minimal NORM extraction from the coal
    - ✓ Concentration of thorium and uranium in all streams and products in this REE recovery process significantly less than regulations for thorium and uranium in rare earth materials listed in Title 10 Code of Federal Regulations Part 40, Section 40.13 (c) (1) (vi)[11].

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[5] Dai, S., Ren, D., Chou, C.-L., Finkelman, R.B., Seredin, V.V., Zhou, Y., Geochemistry of trace elements in Chinese coals: a review of abundances, genetic types, impacts on human health, and industrial utilization. International Journal of Coal Geology. doi:10.1016/j.coal.2011.02.003, 2011a.

[6] Dai, S., Wang, X., Zhou, Y., Hower, J.C., Li, D., Chen, W., Zhu, X., Chemical and mineralogical compositions of silicic, mafic, and alkali tonsteins in the late Permian coals from the Songzao Coalfield, Chongqing, Southwest China. Chemical Geology, 282, 29–44, 2011b

[7] Bouska, V., and Pesek, J., Quality parameters of lignite of the North Bohemian Basin in the Czech Republic in comparison with the world average lignite, International Journal of Coal Geology 40, 211–235, 1999.

[8] Hower, J.C., Granite, E.J., Mayfield, D.B., Lewis, A.S., and Finkelman, R.B., Notes on Contributions to the Science of Rare Earth Element Enrichment in Coal and Coal Combustion Byproducts, Minerals 2016, 6, 32; doi:10.3390/.

[9] Eskenazy, G.M., Rare earth elements in a sampled coal from the Pirin deposit, Bulgaria. Int. J. Coal Geol. 7, 301–314, 1987.

[10] Seredin, V.V. and Dai, S., Coal Deposits as potential alternative sources for lanthanides and yttrium, International Journal of Coal Geology, 94 (2012)87-93.

[11] Commission, U.S. Nuclear Regulatory. *Title 10 Code of Federal Regulations Part 40.*

- Minimal production of waste

    - ✓ Utilization of the coal through activated carbon or humic acid production reduces the amount of waste streams in the process. Additional payable revenue is also generated through the addition of one of these processes.
    - ✓ Water used to wash coal is recycled within the process and reused in the leaching step. Recycling of the wash water cuts down on acid costs and increases total REE recovery.
    - ✓ Sale of the iron and aluminum concentrates also reduces the waste produced in the process.
    - ✓ The only waste streams produced in this process are the tailings from coal spiraling and the barren solution after the PLS has been processed.

- REEs can be leached directly from the raw coal using simple, highly effective, industrially proven processes – a highly economical approach

    - ✓ The resulting residual coal has decreased ash content, and thus a higher value, and can be utilized in an array of coal conversion processes to augment economics

    - ✓ Other valuable elements, such as germanium, gallium (and others) are extracted with high efficiency along with the REEs, and can be recovered/purified to improve economics

    - ✓ Silica impurity is not extracted with the REEs, a significant benefit because it is known to cause technical issues for purification processes

2.4.1 Acid Gases from Leachate Process

Acid gases from the leaching process are anticipated. A scrubber has been considered in the capital cost that will remove the acid vapors from the gases. Water can scrub the acid gas and form acid that can be reused back into the acid leaching system. No additional environmental equipment is anticipated during the leaching process. To the extent possible, zero acid discharge methodology has been included.

2.4.2 PLS Processing

Addition of sodium carbonate during processing of PLS for impurity removal, REE precipitation, and aluminum recovery is anticipated to off-gas CO_2. The CO_2 can be combined with the gases from the power plant before being sent to the CO_2 capture system.

2.4.3 Activated Carbon and Syngas Production from Coal Byproduct

This design developed the residual coal byproduct into valuable activated carbon through drying, carbonation, and activation of the solids. The gas that is produced from the heating process of the activated carbon development is also a valuable product called Syngas. Both syngas and activated carbon become revenue streams instead of waste streams thus reducing the environmental footprint of the plant.

2.4.3.1 Waste Heat Usage

There is a significant heat input required mainly for the activated carbon and syngas production. Waste heat is available from the flue gas of the indirectly heated natural gas-fired dryers and kilns (in the co-located activated carbon plant). The waste heat is intended to be recirculated back into the system through the heater exhaust gases which use a heat recovery device to transfer the sensible heat to the combustion air to preheat the air during normal operation. This process will also cool the exhaust gases so they can be sent to the existing stack (at VCSU) without high temperatures. Lower-grade heat in the air-cooled heat exchanger at the end of the activated carbon process can also be a viable source, but not considered as a savings in the operating expense parameters during this study.

2.4.4 Humic Acid Production from Coal Byproduct

Acid gases are anticipated in the humic acid production process. A scrubber has been considered in the capital cost that will remove the acid vapors from the gases. Water can scrub the acid gas and form acid that can be reused back into the system. Organic acid effluents produced in the process must also be captured. Additionally, humic acid precipitation is conducted with concentrated acids, with the residual liquid (pH <1) typically disposed. This free acid may also be utilized in the REE plant but is not accounted for in the TEA.

3.0 Process Design

This section presents the process design for achieving the REE concentrate as well as for both the activated carbon and the humic acid product. This design is based on bench-scale testing results and may change as additional testing is completed and evaluated.

3.1 Coal Preparation

It is assumed that the coal as-received is large in size and will require crushing and pulverizing to achieve an acceptable particle size for leaching and further processing. The crusher and pulverizer will reduce the coal to about 4 US mesh (4.76 mm) prior to the spiraling process. The coal will then be sent to the spirals as a density separation process. The high density, high ash material will be separated from the coal and the overall ash content of the coal will be reduced. The following list summarizes the major pieces of equipment:

- Raw Coal Storage
- Primary Crusher & Coal Bin
- Coal Pulverizer & Fine Coal Feed Bin
- Dust Collection Baghouse
- Primary Spirals
- Scavenger Spirals

3.2 Leaching

After spiraling, the coal is conveyed to the acid leaching tank where it is mixed with a dilute mineral acid for a residence time of approximately 1 hour. Additional concentrated acid is added to the tank to maintain the pH of the mixture. The pH value is chosen based on achieving the maximum amount of leaching of the REEs with the least amount of acid to minimize processing cost.

After leaching, the slurry is sent to a filter press where the coal is collected and the PLS is separated from the coal. The coal is washed with water to remove any residual acid from the coal and to collect REE remaining in the pore water of the coal within the prior filter press (without discharging). This water is then recycled into the leaching process to reduce acid consumption and improve REE recovery. The washed coal is dried prior to any additional processing, which is discussed further in Sections 3.4. The following list summarizes the major pieces of equipment:

- Acid leach tank
- Acid scrubber
- Leached coal filter press
- Primary coal wash tank
- Primary coal wash filter press
- Secondary coal wash tank
- Secondary coal wash filter press
- Rotary kiln dryer

3.3 Impurity Removal

After the PLS is separated from the coal, it is sent to the iron precipitation unit where the pH is adjusted using sodium carbonate to precipitate the iron and other impurities. The solution reports to the clarifier to drop out the iron solids. The solids are periodically removed with a sludge pump and sent to a filter dewatering step where the iron is separated, and the filtrate retained for further processing. The following list summarizes the major pieces of equipment:

- Iron precipitation tank
- Clarifier
- Iron byproduct storage bin

3.4 REE Precipitation

The REE PLS is then sent to the REE precipitation unit where oxalic acid is added along with sodium carbonate to adjust the pH and precipitate REE. The solution is pumped to a filter press where the REE solids will be separated from the liquid. This REE precipitation step can be repeated to produce a secondary REE product. The purpose of the primary and secondary REE precipitation step is to produce a primary product, which is higher in purity of REE, and a secondary product, which has slightly lower REE concentration, but which allows for the extraction of nearly all of the REE from the PLS.

From the filter press, the REE solids are roasted to form rare earth oxides before being sent to a tank where they are mixed with water to dissolve calcium and increase the purity of the product. A filter press is used to separate the solids from the water. The REE product will be sent to an offsite refinery for processing and separation. The refinery is not defined as part of this project. The following list summarizes the major pieces of equipment:

- REE precipitation tank
- Precipitated REE filter press
- Indirect rotary kiln
- Ca separation tank
- Purified REE filter press
- Final REE product storage bin

3.5 Aluminum Recovery

As an optional final processing step, an aluminum product can be generated from the remaining PLS. After REE precipitation, the PLS is sent to the aluminum precipitation unit where base is added to increase the pH and precipitate an aluminum concentrate. Sodium carbonate is added to the solution up to a pH of 6, and then sodium hydroxide is added to finish adjusting the pH. The aluminum solids are collected in a filter press. The following list summarizes the major pieces of equipment:

- Aluminum precipitation tank
- Precipitated aluminum filter
- Al byproduct storage bin
- Barren liquor solution tank

3.6 Carbonization and Activation

The carbon plant is being evaluated for integration with the new VCSU steam plant as part of a separately funded project (referenced previously in Section 2.1). The design of the carbon plant has been taken from this previous work, and the REE extraction components have been added to evaluate the overall economics. The following equipment is included in the carbonization and activation processes:

- Indirect Fired Rotary Kiln (Carbonation)
- Indirect Fired Rotary Kiln (Activation)
- Rotary Air Cooler
- High Temperature Fans (Syngas Capture and Transfer)
- Waste Heat Recovery Units

The washed dewatered coal is transferred to the carbonization and activation steps through a series of natural gas-fired rotary kilns. Pyrolysis of the coal occurs at about 600°C in the carbonization kiln to produce a solid char and a combustible product gas stream (syngas). Pyrolysis is a thermochemical decomposition of organic materials in the absence of oxygen while using elevated temperatures that releases volatiles from the coal. In the activation step, the char from the carbonization kiln is contacted with sub stoichiometric quantity of steam at about 900°C to partially gasify the char (i.e., $H_2O_{(g)} + C_{(s)} \rightarrow CO_{(g)} + H_{2(g)}$). The activation step produces the final solid activated carbon product and syngas consisting primarily of hydrogen and carbon monoxide. The syngas produced from these steps is sent to the existing VCSU steam plant to be used as fuel to produce steam. The high temperature flue gas streams from the indirectly-fired kilns can be used to preheat combustion air. Figure 3-1 shows the basic steps to produce the activated carbon. Streams Q1, Q2 and Q3 represent heat either being added or removed as part of the carbonization and activation process. Streams 3 and 8 represent syngas leaving the process that can be used as a fuel. The final cooled product represented as stream 11 is the saleable activated carbon. More details are provided in the mass balance in Section 4.5.

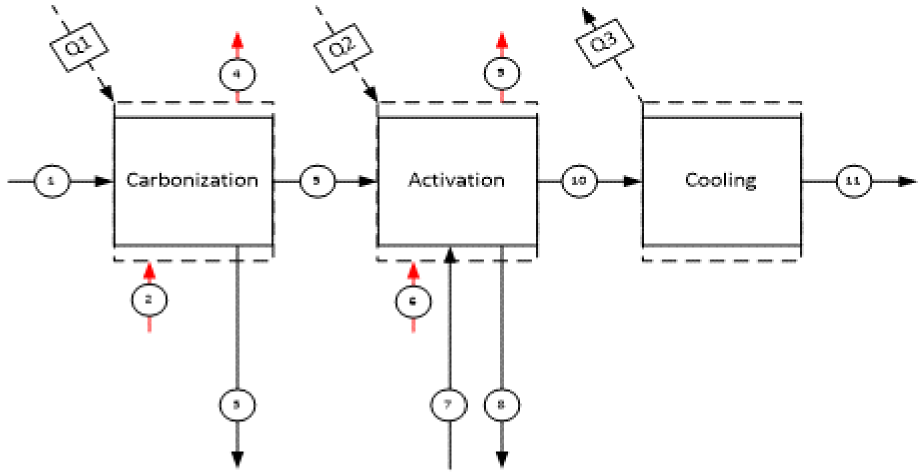

Figure 3-1 Simplified Flow Diagram of Carbonization and Activation

3.7 Humic Acid Production

Humic acid production is also being considered as an option of a value-added process to be integrated with the REE extraction process. The overall economics are being evaluated based on the design of this process. The following equipment is included in the Humic Acid Production processes:

- Acid Leach Tanks
- Acid Leach Tank Mixers
- Acid Leach Tank Pumps
- Acid Scrubbers
- Filter Presses

The washed dewatered coal is transferred to a tank where it is mixed with NaOH to dissolve the humic acid from the coal with a liquid to solid ratio of 10:1. The residual coal is separated from the solution using a filter press. The humic acid solution is then sent to another tank where acid is added to drop the pH and precipitate humic acid before being filtered in a filter press.

4.0 Mass and Energy Balances

Mass and energy balances in this section are based on the size of the activated carbon production plant. Values for the humic acid option are in parenthesis following the activated carbon plant size based values.

4.1 Leaching Requirements

As discussed in Section 2.0 Design Basis/Approach, a dilute mineral acid was selected for this process. The TEA focuses on the H Bed feedstock with a feed rate of 10,000 lb/hr, which is based on the sizing for the activated carbon plant in evaluation for installation with the existing steam generation plant at VCSU (Humic Acid – 40,000 lb/hr).

- Using 10,000 lb/hr of coal calls for approximately 7.4 ft^3/hr of concentrated mineral acid, which will be used to make the dilute acid based on scaled bench system results (Humic Acid – 29.5 ft^3/hr of acid). This may vary slightly as this step is pH controlled, and acid consumption may vary with changes in coal composition.

4.2 Iron Precipitation

As discussed in Section 2.0 Design Basis/Approach, iron is the major impurity causing the REE concentration of the leachate to be reduced. From bench-scale testing results, it has been found that nearly 80% Fe removal from the PLS can be achieved, with a loss of only 0 to 2% REE in the solution through pH adjustment by sodium carbonate addition.

- Based on scaling of bench system testing results, sodium carbonate will be fed at a rate of 270 kg/hr for the activated carbon process (Humic Acid – 1,090 kg/hr). This may vary slightly with potential changes in PLS composition.

4.3 REE Concentration

REE concentration, both in the feedstock and in the final product, is a major factor in measuring the success and viability of the proposed system, as a higher concentration will decrease costs of downstream separation. According to DOE guidelines for this program, the REE concentrations in the feed need to exceed 300 ppm (whole sample basis) for feasible commercial deployment whether in ash or raw coal feed. H Bed coal used in this study has an REE+Y and Sc concentration of about 650 ppm on a whole coal basis. As discussed in Section 2.0 Design Basis/Approach, oxalic acid and sodium carbonate are used to precipitate REE from solution.

- Oxalic acid will be added at a rate of 215 kg/hr (Humic Acid – 860 kg/hr)

- The feed rate for sodium carbonate will be approximately 190 kg/hr (Humic Acid – 780 kg/hr). This rate may vary slightly with changes in PLS composition.

4.4 Aluminum Precipitation

As discussed in Section 3.5, aluminum precipitation is an optional step in this process. If aluminum recovery is included in the process, bench-scale testing has shown that over 70% of the aluminum extracted from the coal can be recovered in the aluminum concentrate product using sodium carbonate and sodium hydroxide to adjust the pH. Some variation may be seen in the feed rates for both sodium carbonate and sodium hydroxide as the composition of the PLS may have some variation with changes in coal composition.

- Sodium carbonate is fed at a rate of 79 kg/hr (Humic Acid – 320 kg/hr)

- Sodium hydroxide feed rate is 156 kg/hr (Humic Acid – 620 kg/hr)

4.5 Production of Syngas and Activated Carbon

The hydrogen in the syngas as well as some of the carbon-containing compounds have an estimated heating value of about 10,000 BTU/lb. Assuming 50% of the fixed carbon is recoverable as activated carbon, the process yields 2,010 lb/hr of activated carbon and over 7,200 lb/hr of syngas. The payback of selling both activated carbon and syngas has been included in this study. It is assumed the syngas would be sent directly to VCSU steam plant as fuel to replace natural gas and activated carbon sold wholesale to a distributor.

4.6 Heating Requirements & Waste Heat Recovery

The following gives the baseline information for the carbon plant as designed in UND's separately funded project (referenced in Section 2.1). Ash is completely inert throughout the process and remains with the final activated carbon product.

Energy Balance Assumptions:

- Utilize sensible heat available in the indirect heating flue gas from the multiple hearth furnace(s)
- Preheating combustion air—send cooled flue gas to VCSU facility for exhaust via existing stack
- Chemcad used to evaluate energy balance reusing waste heat in countercurrent heat exchangers
- Waste heat exhaust temperature was high enough to maintain gaseous state while maintaining above heat exchanger pinchpoint
- Dryer exhaust is combined with heater exhaust for waste heat recovery in the drying process
- Heating process uses 0.049 ratio of fuel/air in combustion process
- Combustion air, fuel, and coal feed is fed to system at 70°F atmospheric conditions
- Natural gas composition is based on typical pipeline natural gas
- The process to make steam used in activation is not considered in the energy balance
- Used 0.3 Btu/lb-°F as the heat capacity for the solids

The drying, carbonation, activation, and cooling phases were simulated in ASPEN Plus® and checked with Chemcad to determine the amount of heat input required for the processes. The utilization of waste heat was then reused in the processes to show how optimized scenarios could save energy and reduce waste streams. Three heat recovery exchangers have been considered in the capital cost in this study. There is also energy from the cooling process that is viable to be recirculated, but has not been evaluated to show a savings in energy.

4.7 Production of Humic Acid

Humic acid production for the process was calculated by assuming 25% of the leached coal could be recovered as humic acid. This yields a production rate of 8,000 lb/hr humic acid. The payback of selling humic acid has been included in this study. It is assumed the humic acid would be sold for pharmaceutical or fertilization purposes. Acid and base requirements for this process include:

- Sodium hydroxide feed rate of 12,800 lbs/hr
- Acid requirements for this process are approximately 170 ft^3/hr

5.0 Technical and Economic Analysis

A Technical and Economic Analysis (TEA) for this phase was prepared and is described in the following sections. The main components include capital expenses, operating expenses, payable revenue, and the payback analysis.

5.1 Technical and Economic Analysis Background

The TEA focuses on evaluating the cost of leaching, impurity removal steps, and extraction and concentration of REEs and other target elements from coal in conjunction with either activated carbon production or humic acid production. In conducting the TEA, the principal process drivers considered include: material price, resource composition/ concentration, leaching efficiency, and operating and maintenance expenses.

The TEA accounts for the major variables affecting both capital (CAPEX) and operating (OPEX) expenses for mineral recovery and processing in conjunction with an offsite refinery to further process and separate the REE concentrate into the respective rare earth oxides and other target element products. Since there are no published data for polymetallic concentrates (as would be produced by our process), we evaluated the process on an end-to-end basis that accounted for all of the costs to achieve saleable REE/element oxide products, including an offsite refinery. By modeling the all-in costs to achieve saleable products, we do not need to know the sales price of the REE concentrate, which is the product of our processing plant. Instead, that value is wrapped into the larger calculation of net profit. We address the cost of the offsite refinery by assigning a processing cost per ton of element produced which includes the refiner's operating cost plus profit. Since the refiner would process our concentrate on a contract basis, we have not included any capital expense for the refinery – it is assumed to be built and available for contract processing. This approach allows us to use published market prices for the REE/element oxide products to calculate gross revenue for the project, subtract refinery costs, and estimate the net profit of the recovery effort that is within our scope. This provides a net revenue stream (after accounting for internal OPEX) that can be used, along with the estimated extraction plant CAPEX to determine IRR, ROI, or other relevant economic parameters.

5.1.1 Market Impacts

The following section briefly discusses the market implications of introducing new sources of domestic production of REE+Y and Sc, as well as other metals that have a large impact on the economics of the proposed plant. Data is obtained from the 2020 USGS Mineral Commodities Report[12]. It is important to note that these discussions are based on production rates from the proposed plants. With installations at additional and larger facilities, impacts are likely to be different.

According to the USGS Mineral Commodities Report, total estimated consumption of REE+Y in the United States has increased from 9,550 to 13,000 metric tons from 2015 to 2019. The U.S. is a net importer with

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[12] Gambogi, J. "Rare Earths – Mineral Commodity Summary". USGS Mineral Commodity Summaries, 2020.

about 14,900 metric tons imported in 2019. Mountain Pass Mine produced 26,000 metric tons of REE mineral concentrate in 2019, which was all exported to China. Total domestic consumption of Yttrium was about 600 metric tons in 2019, all of which was imported. Approximately 14 tons per year of REE oxides are produced from the activated carbon plant evaluated in this study after final purification (the humic acid plant would produce 57 tons per year). Due to the very small fraction of overall domestic consumption, besides reducing reliance on imports, it is not expected that any significant impact would result from introduction of this new domestic production source of REE.

Production of approximately 0.5 ton/year of scandium oxide for the activated carbon plant or 1.8 ton/year for the humic acid plant, on the other hand, is likely to have an impact on the market, as according to the USGS Mineral Commodities Report, total *global* consumption of scandium was approximately 15 to 20 tons in 2019. Because the current market price of Scandium is very high, while the market consumption is very small, introduction of new resources for scandium, such as coal, is likely to impact the market price. However, upon increase of the supply, additional interest may be garnered from the auto and aerospace industries (for aluminum-scandium alloys) to expand the market utilization.

Another major contributor to sales from the proposed plant is germanium oxide, with a production rate of about 0.25 ton/year from the proposed activated carbon plant. The proposed humic acid plant would produce about 0.75 ton/year. According to the USGS Mineral Commodities Report, total domestic consumption of germanium was about 30 metric tons in 2019, down from 34 metric tons in 2015. The U.S. is a net importer of germanium, with total imports of about 27 metric tons in 2019. Although not to the same extent as scandium, it is expected that germanium production from new coal resources would have an impact on the market. Currently used primarily in fiber and infrared optics (~50%), germanium also has use in solar cells, which may be a growth market in the event of larger domestic supply.

5.2 TEA Assumptions & Conditions

Our (preliminary) TEA makes the following assumptions/conditions:

1. The processing facility that receives the REE concentrate is located nearby to minimize shipping costs and/or the cost of shipping is built into the refiner's processing costs.
2. CAPEX for the finishing refinery facility is not considered, since it will be utilized on a contract basis that accounts for refinery costs and refiner's profit
3. The REE and other target elements are obtained from the coal at combined recoveries calculated from Phase 2 testing, depending on the element
4. REE and other target element separation costs, including 20% refiner's profit for toll refiner, are estimated at present prices to be:
    a. $500 per dry ton of contained REE oxide (per element) – includes REE, Y, Sc, Ga, Ge
        i. Based on industry experience and considered conservative to reduce risk
        ii. Accounts for shipping cost assuming the refiner is not co-located
    b. $500 per dry ton of contained base metal (per element) – includes Co, Cu, Zn, Mn
        i. Based on industry experience and considered conservative to reduce risk
        ii. Accounts for shipping cost assuming the refiner is not co-located

5. All of the REE/target element products are saleable at their currently published market value
6. REE/target element/impurity concentrations are from UND laboratory testing data
7. Activated carbon is produced as a saleable product at 8,454 tons/yr
    a. Under the alternate scenario of humic acid production, humic acid is produced at 33,600 tons/year based on a 40,000 lb/hr coal feed rate
8. Capital cost was calculated using cost estimate resources, equipment vendor quotes, and engineering judgement based on industry experience
9. Leaching/processing cost factors were estimated at:
    a. Raw coal cost = $25 per ton
        i. Includes mining of coal and shipping to facility via truck
    b. Electricity cost = $0.0813 per kWh
        i. Provided by Valley City, ND Public Works
    c. Natural gas cost = $3.50 per MMBtu
        i. Based on similar projects completed by Barr and typical natural gas cost in industry
    d. Water cost = $3 per 1000 gallons
        i. Provided by Valley City, ND Public Works
    e. Steam cost = $8 per 1000 lbs
        i. Based on similar projects completed by Barr
    f. Mineral acid cost = $0.10 per lb (assumed 100% makeup rate)
        i. Quote from Hawkins Chemical
    g. Yearly operator cost = $1,620,000
        i. Based on assuming 5 operators at $54,000 salary per shift
        ii. 50% fringe & overhead rate
        iii. Four shifts (24/7 operation)
    h. 15% added to overall process cost for miscellaneous items
        i. Typical factor for cost estimates at this level of detail – engineering judgement
10. The estimated cost for the proposed process is considered to be a Class 5 estimate, as described by AACE International, Cost Estimate Classification System with an expected accuracy range of -20% to -50% (low) and +30% to +100% (high) (AACE, 2005).[13]

The opinion of probable cost provided in this report is made on the basis of Barr's experience and qualifications and represents our best judgment as experienced and qualified professionals familiar with the project. The cost opinion is based on project-related information available to Barr at this time and includes a conceptual design of the project. The opinion of cost may change as more information becomes available, further design is completed, etc. In addition, since we have no control over the cost of labor, materials, equipment, or services furnished by others, or over the contractor's methods of determining prices, or over competitive bidding or market conditions, Barr cannot and does not guarantee that proposals, bids, or actual costs will not vary from the opinion of probable cost prepared by Barr. If greater assurance as to probable cost is required, Barr recommends to collect further information including pilot-

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[13] AACE International, 2005. Cost Estimate Classification System – As Applied in Engineering, Procurement, and Construction for the Process Industries, 2005, p. 1 – 9. http://www.aacei.org/toc/toc_18R-97.pdf

scale testing results and complete further design to provide a higher accuracy cost estimate. Table 5-1 below shows the AACE Class 5 accuracy range and level of project to further clarify the boundaries of the cost estimate provided in this report.

Table 5-1 Description of Classification Values and Methods for Generic Cost Estimate

	Primary Characteristic	Secondary Characteristics			
	Level of Project Definition	End Usage	Methodology	Accuracy Range	Preparation Effort
Estimate Class	Expressed as % of complete project definition	Typical purpose of estimate	Typical estimating method	Typical +/- range relative to best range index of 1[a]	Typical degree of effort relative to least cost index of 1[b]
Class 5	0% to 2%	Screening or feasibility	Stochastic or judgment	10 to 20	1
Class 4	1% to 5%	Concept study or feasibility	Primarily stochastic	5 to 10	2 to 4
Class 3	10% to 40%	Budget, authorization or control	Mixed but primarily stochastic	3 to 6	3 to 10
Class 2	30% to 60%	Preliminary estimate	Primarily deterministic	2 to 3	5 to 20
Class 1	50% to 100%	Check estimate or engineer's estimate	Deterministic	1	10 to 100

Notes:

[a] If the range index value of "1" represents +10/-5%, then an index value of 10 represents +100/-50%.

[b] If the cost index value of "1" represents 0.005% of project cost, then an index value of 100 represents 0.5% of project cost.

Because the technology is still at an early phase, some of the assumptions and numbers listed above will require refinement as the process matures through additional testing. However, where possible, we have incorporated cost data from similar processing systems in order to estimate the system CAPEX and some of the system OPEX.

5.3 Base Case TEA

The Base Case TEA (activated carbon production) includes the following process steps:

1. Coal crushing
2. Acid leaching

3. Leached coal filtering
4. Coal washing
5. Washed coal dewatering
    a. Filter Press
    b. Drying
6. Impurity removal (iron)
7. Iron filtering
8. REE precipitation
9. REE filtering
10. Aluminum byproduct removal
11. Aluminum filtering
12. Carbonization
13. Activation

As an alternative to activated carbon production, a scenario based on humic acid production was also completed at a material feed flow rate of 40,000 lb/hr. In this scenario, process steps 12 and 13 are changes to 'Alkaline Extraction' and 'Acidification', with additional tanks, agitators, pumps, and filters required for the humic acid processing.

The Base Case CAPEX was generated using preliminary process flow diagrams. The OPEX was generated assuming operating and maintenance rates for each equipment item and using the H Bed bench-scale testing results and a dry coal mass flow rate of 10,000 lb/hr for activated carbon or 40,000 lb/hr for humic acid.

The Base Case TEA uses the results of the H Bed coal bench-scale testing as discussed in Section 2.3. Using those results, a payable revenue for the REE oxides and select target elements was estimated using published market values.[14] Additional payable revenue is generated from the sale of activated carbon and a fuel source of syngas produced from the carbonation and activation process that displaces the use of natural gas for the VCSU steam plant. The sale of humic acid would also provide additional payable revenue. The payback analysis uses each of these components to estimate a simple payback and an IRR, ROI and NPV over 10 and 20 years. These are all further discussed in the following sections.

5.3.1 Capital Expenses

The capital expense (CAPEX) for the proposed process is considered a Class 5 estimate, as described by the AACE International, Cost Estimate Classification System with an expected accuracy range of -20% to -50% (low) and +30% to +100% (high) (AACE, 2005).[15] The equipment was sized assuming a leaching processing rate of 10,000 dry lb/hr of coal (40,000 dry lb/hr of coal for humic acid).

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[15] AACE International, 2005. Cost Estimate Classification System – As Applied in Engineering, Procurement, and Construction for the Process Industries, 2005, p. 1 – 9. http://www.aacei.org/toc/toc_18R-97.pdf

The CAPEX estimate includes the following items:

- Raw Coal Storage Bin
- Belt Conveyors
- Primary Crusher
- Crushed Coal Storage Bin
- Coal Pulverizer
- Fine Coal Bin
- Dust Collection Baghouse
- Deslime Screen
- Primary, Scavenger Spirals
- Coal Feed Belt
- Acid Leach Tank, Mixer, Pump
- Acid Scrubber
- Filter Press (Leached Coal Dewatering)
- Primary Coal Wash Tank and Pump
- Filter Press (Primary Coal Wash Dewatering)
- Wash Water Recycling Storage Tank and Pump
- Secondary Coal Wash Tank and Pump
- Leached Coal Dryer
- Upgraded Coal Storage Bin
- Iron Precipitation Tank, Mixer, Pump, Feeder
- Iron Clarifier and Pump
- Iron Product Storage Bin
- REE Precipitation Tank, Mixer, Pump, Feeders
- Filter Press (REE Solids Dewatering)
- Aluminum Precipitation Tank, Mixer, Pump, Feeders
- Filter Press (Aluminum Solids Dewatering)
- Aluminum Product Storage Bin
- Barren Liquor Solution Tank, Mixer, Pump
- Indirect Fired Rotary Kiln (REE Solids Roasting)
- Calcium Dissolution Tank, Mixer, Pump
- Final REE Product Storage Bin
- Indirect Fired Rotary Kiln (Carbonation)
- Indirect Fired Rotary Kiln (Activation)
- Tank Heaters
- Rotary Air Cooler
- High Temperature Fans (Syngas Capture and Transfer)
- Air Compressor
- Waste Heat Recovery Unit
- Building
- Ductwork and Piping

The total estimated project cost for the base case plant is $36.8 million. This includes additional cost for installation, site work, and site electrical and controls as a percentage of the total equipment cost. Also, an engineering, legal, and administrative amount is included as a percentage of the total construction cost.

The humic acid production case removes the line items between “Indirect Fired Rotary Kiln (Carbonation)” and “Air Compressor” and adds the following items, in addition to a scale-up of the REE plant, for an overall total estimated project cost of $50.7 million.

- Acid Leach Tanks
- Acid Leach Tank Mixers
- Acid Leach Tank Pumps
- Acid Scrubbers
- Filter Presses

5.3.2 Operating Expenses

Operating Expenses (OPEX) include power, fuel, maintenance, raw material cost, and operator cost. The total power cost was estimated using an assumed power requirement for the equipment. The fuel requirements for carbonation and activation were estimated using the process modeling software Chemcad® (produced by Chemstations™). The OPEX includes the following items:

- Coal Cost = $25 per ton, delivered cost
- Electricity, Natural Gas, and Maintenance Expense
- Steam Cost
- Water Cost
- Operator Cost
- Acid Cost
- REE Processing Cost
- Base Processing Cost
- Adder of 15% of total processing cost to account for miscellaneous items

Sewer, waste disposal, precipitation, additional unknown items

The total estimated operating cost is $9.98 million per year with the production of activated carbon. The total estimated operating cost is $69.1 million per year with the production of humic acid.

5.3.3 CAPEX, OPEX & Maintenance Expense Assumptions

Listed below are the assumptions specific to the CAPEX, OPEX, and Maintenance Expense portions of the TEA:

- Sources for capital equipment cost data:

Mine and Mill Equipment Costs, An Estimator's Guide", InfoMine USA Inc., 2016

Quotes for similar pieces of equipment obtained by Barr for other projects in the recent past (and updated to 2016 USD)

These were escalated or de-escalated using the 6/10 rule for different equipment sizes:

$$Final\ Cost = Cost\ from\ Quote * \left(\frac{Equipment\ Size\ from\ Quote}{Equipment\ Size\ for\ Final\ Cost}\right)^{0.6}$$

This method was used for the pulverizer cost

New budgetary quotes for certain pieces of equipment requested from vendors

- Operating and Maintenance costs for equipment were taken for similar pieces of equipment from Mine and Mill Equipment Costs, An Estimator's Guide", InfoMine USA Inc., 2016

Repair Labor $41.30 per hour
Lubricants $28.39 per gallon
Natural Gas $3.50 per MMBTU
20,000 Btu/lb

- Electric Power $0.0813 per kWh provided by Valley City, ND Public Works
- Natural gas consumption rate for kilns is process maximum assuming no credit for recycled waste heat
- Tank sizing calculated based on residence times and flow rates
- All conveyors were assumed to be 100 feet in length, since there is no general arrangement for a study at this level of detail
- Dust collection requirements were assumed to be 10,900 cfm for fine coal dust

Based on available historical quote

- Primary Crusher is assumed to be a hammer mill type crusher
- Fine Coal Feed Bin assumed to be 30-ton capacity
- Raw Coal Storage assumed to be 200-ton capacity
- Process flows based on mass balance based on Phase 2 testing recoveries at 10,000 lb/hr feed.
- Flows scaled linearly for 40,000 lb/hr feed case for humic acid production.

5.3.4 Payable Revenue

For the Base Case process three payable revenue streams have been identified:

1. REEs and Base Metals
2. Activated Carbon
3. Syngas

Humic acid has also been identified as an alternative to activated carbon and syngas as a payable revenue stream.

REE and Base Metals

The market prices used assume the final sale product to be REE/target element oxides. The lab results are elements and not the oxides. To account for the total mass of oxides as the final product the molar mass of the oxide and the element was used to calculate the total pounds of each element. This calculation was completed within the detailed economic analysis and accounted for in the total lb/yr calculation and total payable revenue for the product oxides.

This study has evaluated the economics of producing/purifying all of the REEs, plus Y, Sc, Ga, Ge and select base metals (Co, Cu, Mn, Zn). However, in an actual application, it may be beneficial to target only specific REEs or base metals, namely the higher price/ critical REEs that provide highest incremental value above the refiner's processing cost.

The H Bed coal projects a total of 28,700 lb/yr of REE/target element oxides and about 400 lb/yr of base metals assuming 100% recovery during the refiner processing (i.e., overall recovery on dry whole coal basis is: leaching extraction recovery X recovery from PLS X refining recovery). For the humic acid production case, approximately 115,000 lb/yr of REE/target element oxides and 1,600 lb/yr would be produced.

The calculated value of the finished REE and other element oxides products produced at the refinery is deduced by assuming a refining cost per ton of REE/target element and base metal produced. These were set at $500 per ton of REE, Y, Sc, Ga, Ge (as oxide) and $500 per ton of base metal (Co, Cu, Mn, Zn). These costs are on a per element basis.

Aluminum Sales (Bauxite)

The bauxite-equivalent solid generated during the final unit operation acts as yet another potential source of revenue. This price is assumed at $32/ton[16]. However, this potential revenue stream was deemed as non-profitable, as the low price is unexpected to generate revenue over the additional costs of atypical wastewater treatment bases (sodium hydroxide as compared with lime), and this step (equipment, OPEX and CAPEX) were not included within the TEA values found in Tables 1-1, 5-3,4.)

Activated Carbon

After the REE and base metal leaching, the carbonation and activation process produces activated carbon at a rate of 8,454 tons/yr. The Base Case assumes a sale price of $1,500 per ton (wholesale price based on UND discussions with potential distributors) of activated carbon, totaling $12,680,000 per year in sales.

Fuel Credits (Syngas & Humic Acid-Depleted Lignite)

Syngas is a byproduct of the carbonation and activation process that can be used as a combustion fuel. From the UND data, the syngas generation rate is about 7,200 lb/hr with a heating value of approximately 10,000 BTU/hr. It is assumed that this will be sent to the VCSU Steam Plant. Using a gas price of $3.50 per MMBtu (i.e., same as natural gas), the total revenue from selling the syngas is about $2,100,000 per year.

The total sales (REE, base metals, activated carbon and syngas) per year assuming Base Case operation is $17.2 million before operating expenses.

During humic acid extraction, a portion of the resultant coal remains (approximately 75%), leaving a higher BTU/lb fuel source (due to the extraction of oxygen-containing humic substances). This material is produced

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[16] Bray, E. Lee. "Bauxite and Alumina - Mineral Commodity Summary" (2020). USGS Mineral Commodity Summaries.

at a rate of 240 MMBTU/hr, with an expected price near the coal of $1.25/MMBTU, resulting in an annual revenue of about $2,500,000. Capture of this revenue would require a nearby user of this material, with an equivalent burn rate of ~70 MW_{th}, capable of use in industrial and/or electric utility systems.

Humic Acid

After the REE and base metal leaching, the humic acid extraction is calculated to yield 33,600 tons/year of humic acid. The base case assumes a sale price of $2,000 per ton (based on UND discussions,[17]), totaling $67,200,000 per year. The total sales (REE, base metals, and humic acid) per year is $79.3 million before operating expenses.

5.3.5 Payback Analysis

Each cost and revenue component discussed in the previous sections is used to estimate ROI, IRR, and simple payback. Table 5-2 provides the analysis.

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[17] Billingham, K. "Humic Products: Potential or presumption for agriculture". Department of Primary Industries, NSW, 2012.

Table 5-2 Payback Analysis Summary

Item	Activated Carbon	Humic Acid
CAPEX	($36,800,000)	($50,700,000)
OPEX	($9,980,000)	($69,100,000)
REE and Base Metal Payable Amount per year	$2,500,000	$9,600,000
Upgraded Coal Payable Amount	$12,700,000	$67,200,000
Fuel Credit	$2,100,000	$2,500,000
Net Annual Revenue per year	$5,100,000	$10,400,000
Simple Payback (years)	5.1	4.9
IRR (10 years)	15%	16%
ROI (10 years)	10%	11%
NPV (10 years) @12% discount rate	$4,200,000	$8,200,000
IRR (20 years)	19%	20%
ROI (20 years)	15%	16%
NPV (20 years) @12% discount rate	$17,400,000	$27,200,000
CAPEX/annual dry ton feed	$900	$300
OPEX/annual dry ton feed	$240	$410
Net Revenue/annual dry ton feed	$173	$62

5.4 Sensitivity Analysis

Sensitivity Analysis above and below the Base Case was completed for the following cases for each co-product case (humic acid and activated carbon):

- Base Case CAPEX increased by 25%
    - Overall CAPEX increased by 25% for all equipment

- Base Case CAPEX decreased by 25%
    - Overall CAPEX decreased by 25% for all equipment

- Upgraded Coal Price increased by 10%
    - Increased price of humic acid and activated carbon production by 10%

- Upgraded Coal Price decreased by 10%
    - Decreased price of humic acid and activated carbon production by 10%

- Increased REE and CM recovery by 10%
    - Improvement in recovery of REE/target metals by 10% based upon improving dewatering efficiency of coal

- Decreased REE and CM recovery by 10%
    - Loss in REE/target metal by 10% based upon reducing NORM content below hazardous thresholds in applicable coals

- REE Price increased by 10%
    - Overall REE price increase by 10% from utilized values

- REE Price decreased by 10%
    - Overall REE price decreased by 10% from utilized values

- Increased REE-processing OPEX cost by 25%
    - Processing costs for REE extraction and concentrate production increased by 25% (not associated activated carbon & REE refining costs)

- Decreased REE-Processing OPEX cost by 25%
    - Processing costs for REE extraction and concentrate production decreased by 25% (not associated activated carbon & REE refining costs)

The results of the sensitivity analysis are presented in Table 5-4.

Table 5-3 Sensitivity Analysis Summary – Activated Carbon

Economic Parameter	Net Annual Revenue	Simple Payback (years)	IRR (10 years)	ROI (10 years)	NPV (10 years) @12% DR	IRR (20 years)	ROI (20 years)	NPV (20 years) @12% DR
Base Case	$7,300,000	5.1	15%	10%	$4,200,000	19%	15%	$17,400,000
CAPEX +25%	$7,300,000	6.3	9%	6%	($5,000,000)	15%	11%	$8,200,000
CAPEX -25%	$7,300,000	3.8	23%	16%	$13,400,000	26%	21%	$26,600,000
AC Price +25%	$10,400,000	3.5	25%	18%	$22,100,000	28%	23%	$41,000,000
AC Price -25%	$4,100,000	9.0	2%	1%	($13,700,000)	9%	6%	($6,300,000)
REE/CM Recovery +10%	$8,100,000	4.5	18%	12%	$9,200,000	22%	17%	$24,000,000
REE/CM Recovery -10%	$6,500,000	5.7	12%	8%%	($300,000)	17%	13%	$11,500,000
REE/CM Price +25%	$7,800,000	4.7	17%	11%	$7,000,000	21%	16%	$21,200,000

Economic Parameter	Net Annual Revenue	Simple Payback (years)	IRR (10 years)	ROI (10 years)	NPV (10 years) @12% DR	IRR (20 years)	ROI (20 years)	NPV (20 years) @12% DR
REE/CM Price -25%	$6,700,000	5.5	13%	8%	$1,300,000	18%	13%	$13,500,000
REE OPEX +25%	$4,900,000	7.6	5%	3%	($9,400,000)	12%	8%	($600,000)
REE OPEX -25%	$9,700,000	3.8	23%	16%	$17,700,000	26%	21%	$35,300,000

Table 5-4 Sensitivity Analysis Summary – Humic Acid

Economic Parameter	Net Annual Revenue	Simple Payback (years)	IRR (10 years)	ROI (10 years)	NPV (10 years) @12% DR	IRR (20 years)	ROI (20 years)	NPV (20 years) @12% DR
Base Case	$10,400,000	4.9	16%	11%	$8,200,000	20%	16%	$27,200,000
CAPEX +25%	$10,400,000	6.1	10%	6%	($4,400,000)	16%	11%	$14,500,000
CAPEX -25%	$10,400,000	3.5	24%	17%	$20,900,000	27%	22%	$39,900,000
HA Price +25%	$27,200,000	1.9	53%	44%	$103,200,000	54%	49%	$152,700,000
HA Price -25%	($6,400,000)	N/A	N/A	N/A	N/A	N/A	N/A	N/A
REE/CM Recovery +10%	$13,800,000	3.7	24%	17%	$27,200,000	27%	22%	$52,200,000
REE/CM Recovery -10%	$7,000,000	7.3	6%	4%	($11,300,000)	12%	9%	$1,400,000
REE/CM Price +25%	$12,500,000	4.1	21%	15%	$19,800,000	24%	20%	$42,500,000
REE/CM Price -25%	$8,400,000	6.0	16%	12%	($3,300,000)	18%	14%	$21,100,000
REE OPEX +25%	$7,000,000	7.2	6%	4%	($11,000,000)	16%	12%	$12,000,000
REE OPEX -25%	$15,300,000	3.3	28%	20%	$35,900,000	30%	25%	$63,800,000

The economic/sensitivity analysis indicates that the two most impactful metrics for profitability of the combined REE/carbon processing plant include the price of the upgraded carbon product (Activated carbon/humic acid), and the OPEX of the REE processing facility. The sensitivity shows that increasing/decreasing the sale price of the activated carbon has a 20-year NPV differential (between the plus and minus cases) of ~$47 million, compared with the difference in profitability vs >$100 million NPV with the humic acid facility, clearly highlighting the importance of the secondary product. However, as these markets are perceived to more stable as compared with the REE, these fluctuations are deemed unlikely. Further, REE OPEX changes have a 20-year NPV differential of $36 million for the AC, and $62 million for the humic acid case. Further, these differences may be compared with REE price differences (NPV diff. of $8 million and $21 million for AC and HA, respectively), showing the relative stability of the process towards fluctuations within the REE markets. More so, the net revenue of the combined plant is greater than the potential revenue associated with the REE/target metal sale, allowing the plant to avoid operating at a loss even with no REE revenue, but will significantly hamper/prevent payback of the capital equipment.

6.0 Summary & Conclusions

According to this TEA the project is profitable. The following summarize the main conclusions from the TEA:

- The lab results indicate that a 54% REE concentrate (oxide basis) is achievable using a dilute mineral acid leach, but requires additional impurity removal (i.e., iron removal via pH adjustment)
- Profitability risk and market risk is minimized with the sale of activated carbon or humic acid

Approximately \$12.7 million in sales for activated carbon (10,000 lb/hr feed basis)
Approximately \$67.2 million in sales for humic acid (40,000 lb/hr feed basis)

- REE/target element oxides and base metals also contribute a good portion in sales; approximately \$2.4 million (\$9.6 million for humic acid)

Assumes the final product is REE/target element oxides

- The 10-year and 20-year NPV is

-\$8.1 million and \$1.1 million respectively assuming 12% discount rate (activated carbon)
-\$7.1 million and \$6.9 million respectively assuming 12% discount rate (humic acid)

- The H Bed coal or similar coal is the preferred feedstock

Additional discussion regarding different scenarios and next phases of study are provided in the last few sections.

6.1 Discussion of Worst, Likely and Best-Case Scenarios

The technical and economic data presented in this report are developed based upon the bench-scale data and quoted/discovered pricing for all elements and reagents, and are purposefully conservative, with the economics tending towards the 'low REE recovery' scenarios. However, additional 'likely' scenarios will be discussed below from a technical and economic standpoint to give insight into possible outcomes.

The technical and economic data presented in this report are purposefully conservative, and thus the economics are likely to be more towards the 'worst-case' scenario. However, based on the request from DOE, below we discuss these three scenarios both from a technical and economic standpoint to give indication of the spectrum of possible outcomes.

Technical Scenarios

The primary technical drivers dictating the success of the technology are: i) overall REE/valuable element recovery, ii) REE content and distribution of elements in the feedstock, and iii) complexity/number of processing steps. Each of these categories are discussed below.

REE Recovery Efficiency: Since the REE recovery efficiency presented in this study is based on bench-scale testing data performed by UND, we classify these results as 'likely'. As additional process optimization is accomplished in subsequent testing, there may be some tradeoffs between overall recovery and process simplicity. For instance, it may be economically beneficial to reduce leaching contact time to reduce equipment sizes or increase throughput, at the same time potentially reducing REE recovery. On the other hand, improvement of the leaching processes via a better understanding of the modes of occurrence of the REE in the feedstocks may improve overall REE recovery. It is also possible that the extraction could be optimized to best accommodate downstream separation processes (i.e., increase recovery efficiency from selective extraction steps). Increased recovery is also expected as dewatering efficiency is increased. REE recovery efficiency also depends on the feedstock chemistry. Extraction efficiencies of elements such as Scandium and Germanium have a large impact on overall economics as well because of their high market prices. We would classify the best and worst-case scenarios at ±10% recovery in the leaching step, making the worst-case scenario 10-40% recovery and the best-case scenario 30-60% recovery (variation of Table 2-1).

Increased Operating Costs: We have evaluated one coal type, with its impurity and REE distribution. Some lignites previously identified with REE > 300 ppm on a whole coal basis also contain significantly higher organic-based impurities (such as Fe and Al) which are anticipated to significantly increase operating costs of the REE plant (with the upgraded carbon plant buffered against these adjustments). The operating costs anticipated to increase include the acid costs (due to higher acid consumption), general base costs (higher precipitating material concentrations, such as Fe), and higher oxalic acid costs (due to increased aluminum complexation). Further, higher potential labor costs may be assumed in such a case, likely due to potential variability and control of the feedstock (requirement of higher-skilled labor). Additionally, this scenario may be used to define a lower REE-bearing coal (by 25%), with all costs reflected of this.

Complexity/Number of Processing Steps: This study has presented 13 main processing steps as outlined in Section 4.3 including the production of either activated carbon or humic acid byproducts. The processing steps involved in this REE extraction process are all simple, highly effective, and industrially proven. However, if higher purities/more impure feedstock are utilized, the complexity of generating higher-purity materials, including the addition of hydrometallurgical cleaning steps (such as solvent extraction or ion-exchange), would increase both capital and operating costs.

Economic Scenarios

The primary economic drivers are: (i) CAPEX/OPEX, (ii) upgraded carbon sales price, and (iii) REE/target element price. Each are discussed briefly below.

CAPEX/OPEX: This study has made conservative assumptions for capital and operating expenses to account for the early stage of technical development, and thus we believe the data presented to be the likely case, but erring slightly towards the worst-case. The main driver dictating capital and operating expenses is process complexity. Our sensitivity analyses have evaluated a ±25% change in both the CAPEX and OPEX. This includes evaluation of a more complex plant, lower REE purity, and/or additional extractable impurities feedstocks.

Upgraded Carbon Sales Prices: The sale price for activated carbon used in this study is based on wholesale prices derived from discussions of the UND team with potential distributors. Because the price of activated carbon has a dramatic impact on plant profitability, it is important to understand the impact of its salability.

By most projections, the market for activated carbon products is expected to increase significantly in the coming years, due mainly to two new environmental regulations for drinking water standards (Disinfectants and Disinfection Byproducts rule) and for control of mercury emissions from industrial sources (Mercury and Air Toxics Standards). This study has evaluated production of a powdered activated carbon product that would be suitable for application to mercury control. A single large-scale power plant may consume as much as two million pounds of activated carbon annually, and thus the production from this plant is not expected to impact market demand, and could conceivably offer a price (shipping) advantage to North Dakota-based facilities. The sensitivity analysis evaluates a ±25% change in activated carbon prices.

The sale price for humic acid used in this study is based on current market prices for humic acid used for fertilization purposes. New markets for this material, which particularly will demand higher-quality, lower-ash feedstocks of humic acid, are specialty carbon, additional pharmaceutical uses, and lithium-ion battery material. With these increased market potentials demanding of high-purity products, we would anticipate the price to slightly rise above the current fertilizer demand. As a result, the 'base-case' would be anticipated to be more conservative, leaning towards the 'worse-case' scenario. The sensitivity analysis for humic acid pricing was completed evaluating a ±25% change in price.

REE/Target Metal Sales Volatility: Sales prices for the REE/target elements are based on current market prices, and thus are considered the likely case. However, REEs have experienced a huge price range in recent years, with spikes from 2010 to 2011. Our sensitivity analyses have evaluated a ±25% fluctuation in the current prices to understand the impact. While we do not believe 2011 prices to be realistic in the near-term, we also do not foresee a major decline in prices.

Additionally, evaluation of the extreme worst-case scenario was envisioned, particularly with a 100% price reduction in REE prices (no salable value), with each proposed plant remaining in a positive net revenue option, permitting resilience against potential market perturbations, even while maintain all OPEX associated with the REE plant. However, the NPV/IRR on these cases is very poor, indicative of the requirement to sell REE to payoff capital assets.

Results

The data presented in this document can reasonably be assumed as the likely or average scenario, accounting for conservative assumptions. REE-specific best-case scenarios would involve: (i) improvement in REE recovery from the feedstock, (ii) increases in REE/target element sales prices, (iii) reduced process complexity through beneficial leaching, and (iv) increased upgraded carbon price. Worst-case scenarios would include: (i) reduction in REE/target element content in feedstocks, (ii) reductions in REE/target element recovery from the feedstock, (iii) increased process complexity, and (iv) reductions in overall REE/target element/upgraded carbon sales prices.

The worst-case scenario could be estimated as the following combined sensitivity case:

- Increase in OPEX by 25%
- Reduction in REE Recovery by 5%
- Decrease in REE/target element sales price by 10%
- Decrease in upgraded carbon sales price by 10%

When combining the above, worst-case economic metrics for the activated carbon plant are as follows:

- 20-year IRR: 5%
- 20-year ROI: 3%
- Simple Payback: 12.5 years
- 20-year NPV (12% discount rate): ($14,800,000)

Whereas the humic acid plant under the worst-case scenario is not profitable (no net revenue), primarily as a result of the decreased carbon price and the increased OPEX of the REE plant.

The best-case scenario could be estimated as the following combined sensitivity case:

- Increase in REE recovery from feedstock by 5%
- Increase in REE/target element sales price by 10%
- Decrease in CAPEX/OPEX by 10%
- Increase in upgraded carbon sales price by 10%

When combining the above, best-case economic metrics for the activated carbon plant are as follows:

- 20-year IRR: 31%
- 20-year ROI: 26%
- Simple Payback: 3.2 years
- 20-year NPV (12% discount rate): $43,400,000

The humic acid best-case economic metrics (from above) are:

- 20-year IRR: 48%
- 20-year ROI: 43%
- Simple Payback: 2.1 years
- 20-year NPV (12% discount rate): $118,500,000