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Evaluation Of Rare Earth Element Extraction From North Dakota Coal-Related Feed Stocks

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EVALUATION OF RARE EARTH ELEMENT EXTRACTION FROM NORTH DAKOTA COAL-RELATED FEED STOCKS

By

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Bachelor of Science in Chemical Engineering, University of North Dakota, 2006

A Dissertation

Submitted to the Graduate Faculty

of the

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for the degree of

Doctor of Philosophy in Chemical Engineering

Grand Forks, North Dakota

May

2017

This dissertation, submitted by Daniel A. Laudal in partial fulfillment of the requirements for the Degree of Doctor of Philosophy in Chemical Engineering from the University of North Dakota, has been read by the Faculty Advisory Committee under whom the work has been done and is hereby approved.

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Dean of the School of Graduate Studies

April 19, 2017

Date

PERMISSION

Title	Evaluation of Rare Earth Element Extraction from North Dakota Coal-Related Feed Stocks
Department	Chemical Engineering
Degree	Doctor of Philosophy

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Daniel A. Laudal
April 25, 2017

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you for everything you’ve done for me, for instilling in me the importance of academics and self-motivation and for always believing in me.

This dissertation is dedicated to my three girls

ABSTRACT

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 dissertation details a study on 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 the agency who funded this research 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, and to prove or disprove the research hypotheses, 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, 174 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 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 an outcropping of the Harmon-Hansen coal zone in southwestern North Dakota that contained 2300 ppm on an ash 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 dilute acid leaching process to 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 0.5M sulfuric acid at 40°C, 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. This represents a concentration factor of 24 over the feed coal. The target of two weight percent rare earths could be achieved by a number of secondary processing methods, such as pH modification or forced air oxidation to selectively precipitate impurities from the rare earths-containing solution.

The process developed in this study is simple, highly effective, low cost and novel, with several differentiating benefits compared to methods being developed in the literature. These are made possible by the unique properties of North Dakota lignite coals and the weakly-bonded organic association of the rare earth elements. Key differentiators include the use of the raw coal as the feedstock, the ability to use a mild leaching process, and not needing extensive physical beneficiation processes prior to rare earths extraction. The process is environmentally benign and was demonstrated to be economically viable at the current market conditions. Due to the use of the raw coal as the feedstock, the process can be advantageously integrated with any number of coal utilization processes to augment economics, lower costs and maximize efficiency and synergies. This study 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.

1 INTRODUCTION

This chapter provides background information on rare earth elements and explains what they are, how they are used and how they are produced. Additional details are located in Appendix A.

1.1 Rare Earth Elements Background

Rare earth elements (REE) include a group of elements with atomic numbers from 57-71, making up the lanthanide series of elements consisting of lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), promethium (Pm), samarium (Sm), europium (Eu), gadolinium (Gd), terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), thulium (Tm), ytterbium (Yb), and lutetium (Lu). Yttrium (Y) and Scandium (Sc) are often included in the group because of their similar properties, depending on the author. This document includes both Y and Sc in the list of REEs. Figure 1 shows these elements in the periodic table.

Groupings into light REE (LREE) and heavy REE (HREE) are generally accepted according to the molecular weight, with LREE including La through Sm and HREE including Eu through Lu as well as Sc and Y. The elements can further be grouped according to their criticality arising from a combination of supply scarcity and end-use importance into categories of critical, non-critical and excessive. These groupings will be further discussed in Chapter 2 of this dissertation. Pm is the only naturally radioactive REE, with a half-life of about 20 years, and essentially all Pm in the earth's crust has decayed into other elements, resulting in no known natural sources. The only sources today are artificially created.

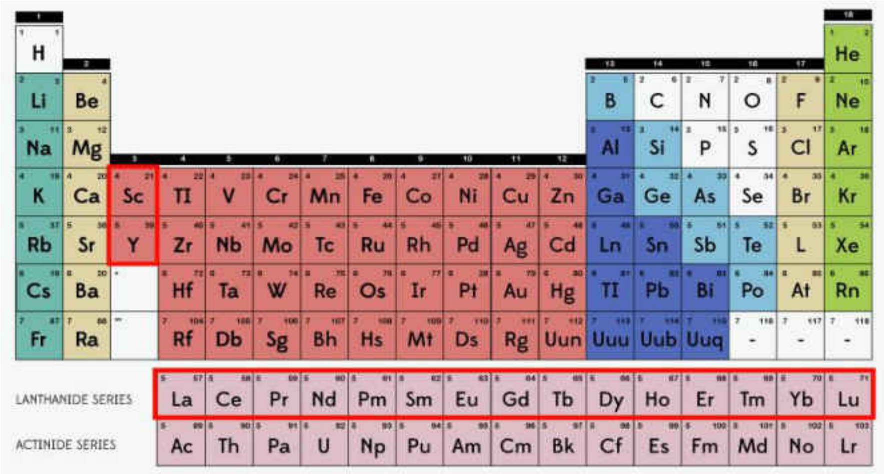


Figure 1. Rare earth elements on the periodic table as denoted by dark red boxes

The term ‘rare earth elements’ is actually a misnomer. REEs are quite abundant within the earth’s crust, falling in approximately the 50th percentile of elemental abundances [1], and in fact are about 200 times more abundant than gold [2]. The name originated from their discovery in the 18th century, where at the time they were discovered with a class of oxides called ‘earths’ and the elements were presumed to be quite scarce. Table 1 displays the estimated concentration of the REEs in the upper continental crust, as determined by multiple investigators [3, 4, 5, 6, 7, 8]. Besides the radioactive Pm, the rarest of the REEs is Tm, with Ce being the most prevalent. With the exception of the non-lanthanides (Y and Sc) the HREE are scarcer than the LREE. The average of the datasets shown in Table 1 is provided in Figure 2 for the lanthanide elements to show the general decreasing abundance as molecular weight increases. The figure also shows clearly that the elements with even atomic numbers are more abundant than odd number elements. This is because odd number elements have only one or two stable isotopes, while the even numbers have from four to seven.

Table 1. Concentration of rare earth elements in the earth's crust – units are parts per million by weight (ppmw)

Element	**Mason and Moore (1982)**	**Jackson and Christiansen (1993)**	**Sabot and Maestro (1995)**	**Wedephol (1995)**	**Lide (1997)**	**McGill (1997)**
La	30	29	18	30	39	5 to 18
Ce	60	70	46	60	66.5	20 to 46
Pr	8.2	9	5.5	6.7	9.2	3.5 to 5.5
Nd	28	37	24	27	41.5	12 to 24
Sm	6	8	6.5	5.3	7.05	4.5 to 7
Eu	1.2	1.3	0.5	1.3	2	0.14 to 1.1
Gd	5.4	8	6.4	4	6.2	4.5 to 6.4
Tb	0.9	2.5	0.9	0.65	1.2	0.7 to 1
Dy	3	5	5	3.8	5.2	4.5 to 7.5
Ho	1.2	1.7	1.2	0.8	1.3	0.7 to 1.2
Er	2.8	3.3	4	2.1	3.5	2.5 to 6.5
Tm	0.5	0.27	0.4	0.3	0.52	0.2 to 1
Yb	3.4	0.33	2.7	2	3.2	2.7 to 8
Lu	0.5	0.8	0.8	0.35	0.8	0.8 to 1.7
Y	33	29	28	24	33	28 to 70
Sc	22	N/A	10	16	22	5 to 10
Total	206.1	205.2	159.9	184.3	242.17	

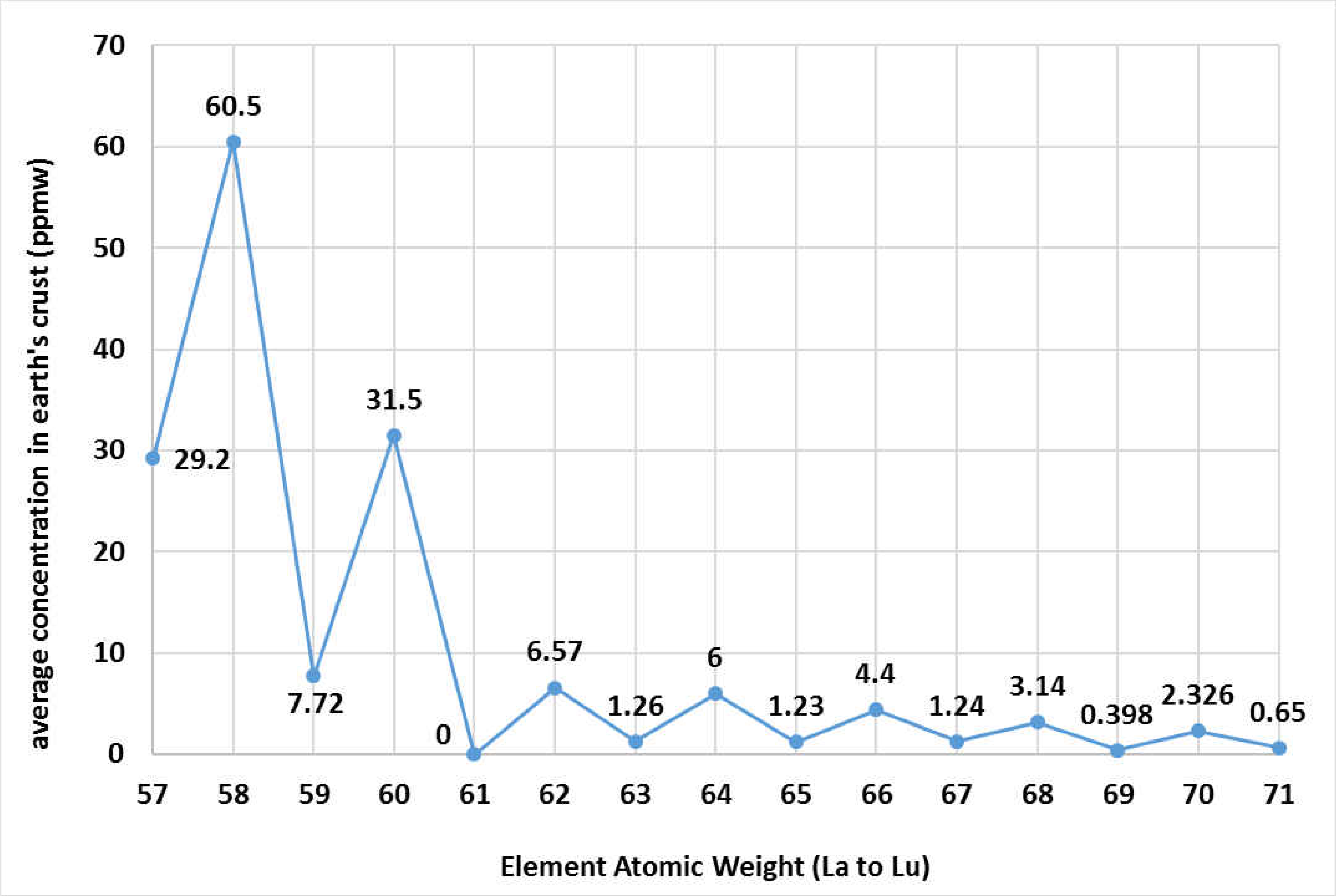


Figure 2. Average of data in **Error! Reference source not found.** for the lanthanide elements - concentration in the e

1.2 Chemistry and Physical Properties of Rare Earth Elements

The electron configuration of the REEs dictates the chemical, metallurgical and physical behaviors of the elements. All REEs have trivalent oxidation states, with Ce, Pr and Tb also capable of tetravalent, and Sm, Eu and Y also capable of divalent oxidation states. The lanthanides are chemically very similar and are difficult to separate from one another, mainly because their 4f electrons are part of the ion core and do not directly participate in bonding with other elements. For the 14 lanthanides, the valence electrons are all the same: $5d6s^2$; for Sc: $3d4s^2$; and for Y: $4d5s^2$.

A unique aspect of the lanthanides is the phenomenon of lanthanide contraction that causes a decrease in ionic radius with increasing molecular weight from La to Lu, as shown in Figure 3 [9] for the trivalent states. Exceptions exist for the divalent and tetravalent states for some of the elements. The contraction is caused by penetration of the 5s and 5p orbitals into the 4f subshell so that the 4f orbital is not shielded from increasing nuclear charge. When the shielding is poor, the positively charged nucleus has a greater attraction to the electrons pulling them, resulting in decreasing ionic radius as the atomic number increases. The contraction is actually what makes separation of the lanthanides reasonably possible, as the density, melting point and hardness generally increase from low to high molecular weight throughout the series, while the basicity decreases. The basicity, in particular, is the foundation for some separation techniques.

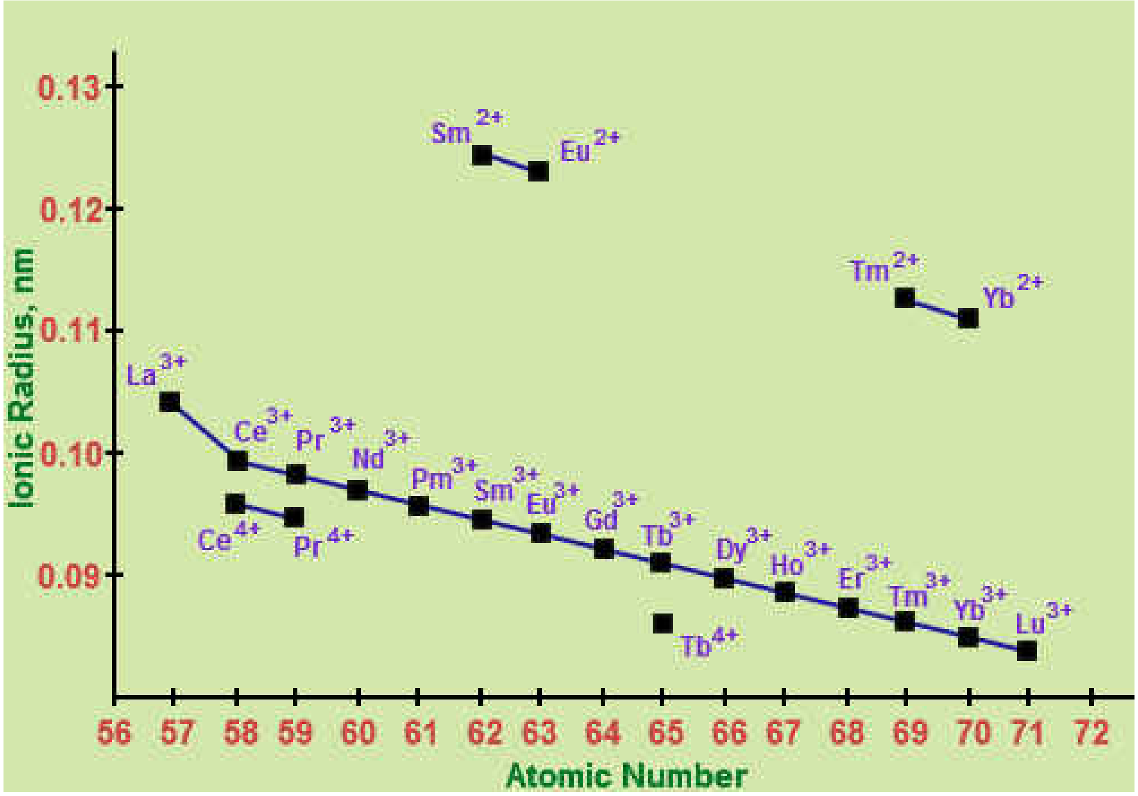


Figure 3. Lanthanide contraction that results in smaller ionic radius for higher molecular weight elements [9]

Although the lanthanides are chemically very similar there are some stark differences in their physical properties. For example, the melting points for the elements plotted against molecular weight are shown in Figure 4 [1]. Here, there are deviations for Eu and Yb that can be attributed to their divalent electron structure capability. Sc and Y exhibit melting temperatures close to that of the heaviest lanthanides. The chart shows that the melting point varies by an approximate factor of two. There are also large deviations in other physical properties such as boiling point and vapor pressure that arise due to differences in electron configuration which impacts magnetic properties and crystal structures.

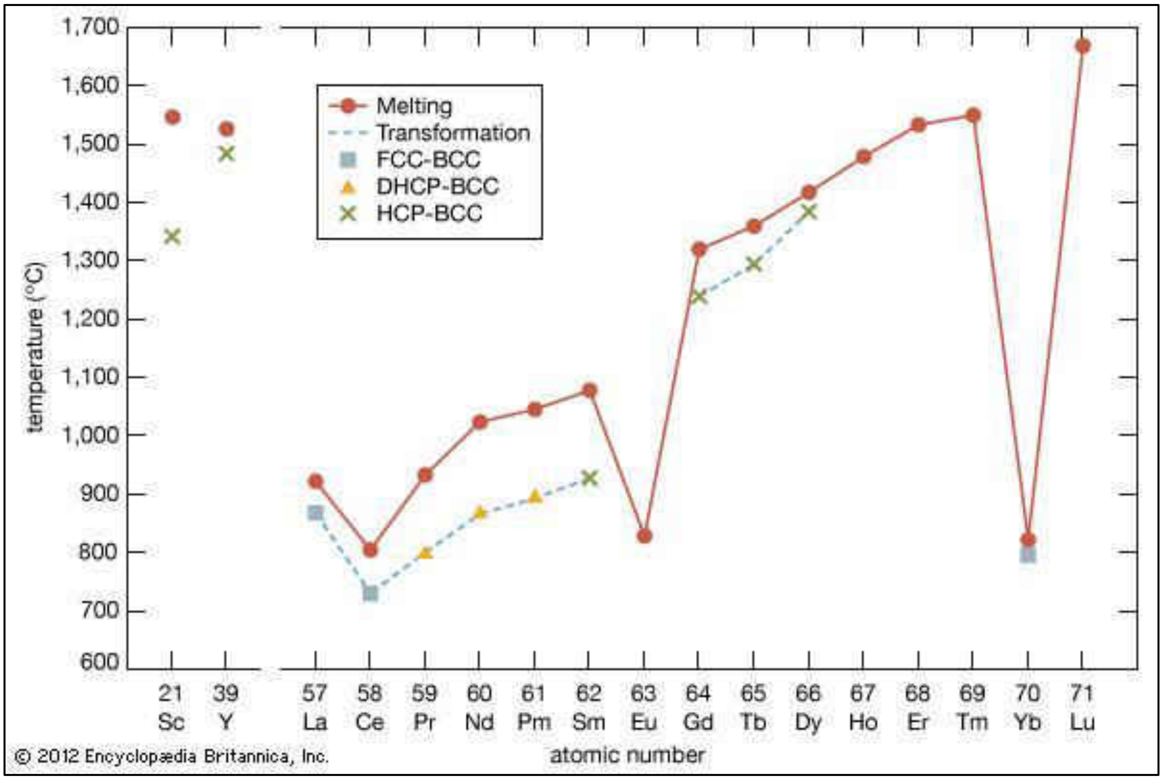


Figure 4. Melting points and transition temperatures for the REEs [1]

All of the REEs except Eu crystallize into one of four close-packed structures, shown in Figure 5 [1]. Two of these are the common hexagonal close-packed (hcp) and face-centered cubic (fcc), but two are intermediates that are unique to the lanthanides among all metals – the double hexagonal (dhcp) and the Sm-type, both of which are combinations of hcp and fcc. Some of the REEs can exist in multiple structures (La, Ce, Sm, Y) depending on temperature. Most of the REEs also have a high-temperature body-centered cubic (bcc) structure. The transition temperatures are shown in the previous Figure 4. Eu is unique, which has a bcc structure throughout its solid phase temperature range.

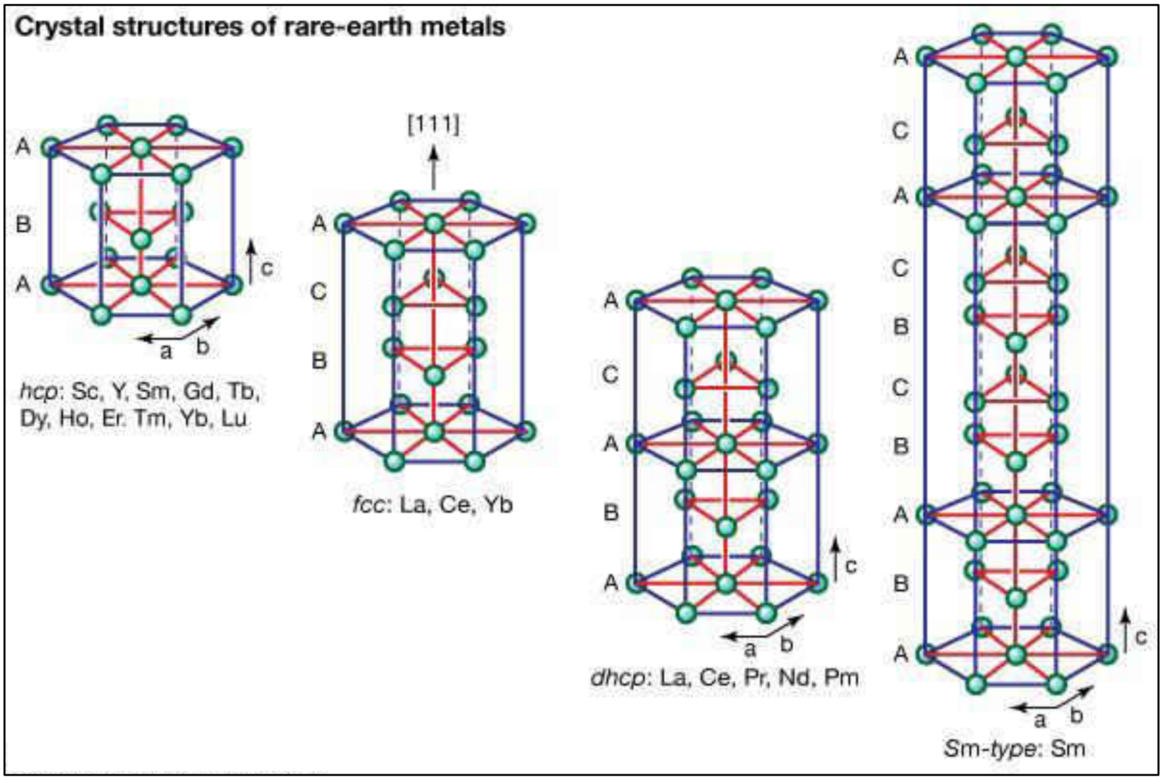


Figure 5. Crystal structures of the rare earth elements [1]

Magnetic properties of the lanthanides are also dictated by the electron configuration. The magnetic properties of the elements result from the number of unpaired 4f electrons. When moving across the lanthanide series, one 4f electron is added, each of which has a magnetic moment due to the electron's spin. The additional electrons all align parallel until half (total of 14) of the 4f level is filled, which occurs at Gd with seven 4f electrons. Past Gd, the new electrons align antiparallel, adding paired 4f electrons up until Lu, where no magnetic moment exists because all 4f electrons are paired. The REEs without unpaired electrons (Sc, Y, La, Lu, and divalent Yb) are all weakly magnetic. However those elements with unpaired 4f electrons are highly magnetic and form the largest group of magnetic metals in the periodic table. Gd, with the maximum of seven unpaired electrons exhibits the highest magnetic moment, and orders ferromagnetically at room temperature, making it the only other element besides the 3d electron elements (Fe, Co, Ni) to do so. Their unique magnetic properties make some of the lanthanides valuable for permanent magnet formulations, of which rare earth magnets make up the strongest produced today.

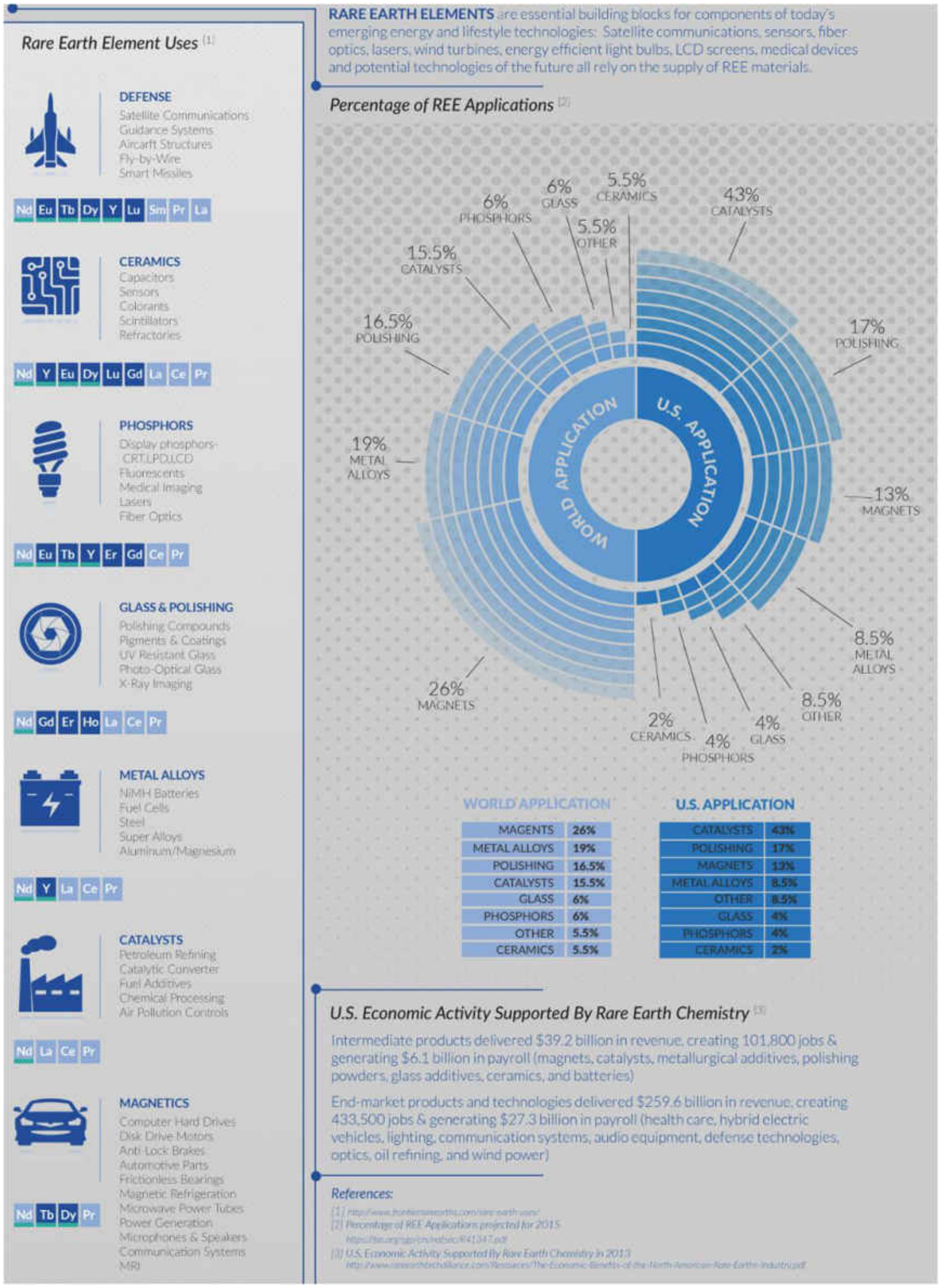
The LREE and HREE exhibit very different oxidation rates in air, which is mainly due to the formation of different oxide product variations. La through Nd form the hexagonal A-type structure; Sm through Gd form the monoclinic B-type structure; Tb through Lu, Sc, and Y form the cubic C-type structure. Oxidation rates are affected by the different oxidation coating for each structure, with the C-type forming a very tight coating that prevents further oxidation, while the A-type allows continued exposure of fresh metal surface through reaction with water vapor in the air that results in progressive oxidation. The B-type also forms a coating, but not as coherent as the C-type, resulting in slightly faster oxidation. Eu, due to its bcc structure oxidizes the fastest of any of the REEs, which actually forms a hydrate hydroxide in moist air, and must always be kept in an inert atmosphere during handling, as should the A-type forming REEs. The HREEs, however, can be exposed to air for very long periods with very little oxidation.

The metals react very strongly will all acids, with the exception of hydrofluoric acid, releasing hydrogen gas. They also easily react with H_2 to form RH_2 and under strong hydriding conditions RH_3 (with the exception of Sc). The lanthanides also react directly with water to liberate hydrogen gas, with rate depending on temperature. They are strong reducing agents, and their compounds are typically ionic in nature. REEs are able to form compounds with all of the elements to the right of and including the group 7 metals (manganese, technetium and rhenium) in the periodic table, and also with beryllium and magnesium. Some of the important or the most studied categories of REE compounds are oxides, sesquioxides, hydrides and halides. REEs can also react with organic molecules and form complexes, with evidence suggesting that the organic complexes of HREE elements are stronger than LREE [10].

The luminescent properties of rare earth elements are another unique feature. In luminescence, electrons in the atoms absorb energy and move from their lower ground states to higher, excited states. When the excited electrons release energy by returning to their lower ground states, the energy produced can be in the form of visible light. For instance red light can be produced with Eu and Y, blue light with Eu, green or blue light with Tb and a brilliant white light with Tb and Eu.

1.3 Uses of Rare Earth Elements

REEs have sometimes been known as “chemical vitamins” because combining very small amounts with other materials can result in vastly different properties. According to the 2014 American Chemistry Council REE Report [11], despite the small volume of REE used in industry, literally hundreds of billions of products are made possible by rare earths, which are a critical and essential element in many advanced technologies. According to the U.S. Department of Energy National Energy Technology Laboratory (DOE NETL) [12], the REEs provide significant value to our national security, energy independence, environmental future, and economic growth. Due to their unique properties that include magnetic, luminescent and electrochemical properties, the REEs make technologies perform with reduced weight, emissions and energy consumption; or give them greater efficiency, performance, miniaturization, speed, durability, and thermal stability [11]. The U.S. DOE NETL [12] has prepared an infographic detailing the applications and markets for REEs, as shown in Figure 6. According to the NETL data, catalysts represent the largest volume application in the United States, with magnets being the largest application globally. Major market segments that rely on REE-based products or technologies include: health care, transportation and vehicles, lighting, communications systems, audio equipment, military defense technologies, and modern electronics. For example, the REEs are used for numerous military defense products such as in engines, night-vision devices, radar systems, missile weapons guidance systems and communication systems. The new U.S. F-35 aircraft contains over half a ton of REEs that are distributed in minute amounts throughout the aircraft. Navy ships use about two tons of REEs and submarines use about four tons [13]. Lynas Corporation has estimated the percentage of REEs used in a range of applications, as shown in Table 2 [14]. Data from 2010 and 2015 is presented in Figure 7 [15] that shows how REE uses have changed in recent years. The figure shows that the primary growth sectors appear to be magnets and polishing, with decrease in catalyst market share. A discussion on each of the major market sectors for REE is provided in Appendix A.



Rare Earth Element Uses [1]

DEFENSE
Satellite Communications
Guidance Systems
Aircarft Structures
Fly-by-Wire
Smart Missiles

Nd Eu Tb Dy Y Lu Sm Pr La

CERAMICS
Capacitors
Sensors
Colorants
Scintillators
Refractories

Nd Y Eu Dy Lu Gd La Ce Pr

PHOSPHORS
Display phosphors-
CRT,LPD,LCD
Fluorescents
Medical Imaging
Lasers
Fiber Optics

Nd Eu Tb Y Er Gd Ce Pr

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

Nd Gd Er Ho La Ce Pr

METAL ALLOYS
NiMH Batteries
Fuel Cells
Steel
Super Alloys
Aluminum/Magnesium

Nd Y La Ce Pr

CATALYSTS
Petroleum Refining
Catalytic Converter
Fuel Additives
Chemical Processing
Air Pollution Controls

Nd La Ce Pr

MAGNETICS
Computer Hard Drives
Disk Drive Motors
Anti-Lock Brakes
Automotive Parts
Frictionless Bearings
Magnetic Refrigeration
Microwave Power Tubes
Power Generation
Microphones & Speakers
Communication Systems
MRI

Nd Tb Dy Pr

RARE EARTH ELEMENTS are essential building blocks for components of today's emerging energy and lifestyle technologies: Satellite communications, sensors, fiber optics, lasers, wind turbines, energy efficient light bulbs, LCD screens, medical devices and potential technologies of the future all rely on the supply of REE materials.

Percentage of REE Applications [2]

WORLD APPLICATION

MAGENTS	26%
METAL ALLOYS	19%
POLISHING	16.5%
CATALYSTS	15.5%
GLASS	6%
PHOSPHORS	6%
OTHER	5.5%
CERAMICS	5.5%

U.S. APPLICATION

CATALYSTS	43%
POLISHING	17%
MAGNETS	13%
METAL ALLOYS	8.5%
OTHER	8.5%
GLASS	4%
PHOSPHORS	4%
CERAMICS	2%

U.S. Economic Activity Supported By Rare Earth Chemistry [3]

Intermediate products delivered $39.2 billion in revenue, creating 101,800 jobs & generating $6.1 billion in payroll (magnets, catalysts, metallurgical additives, polishing powders, glass additives, ceramics, and batteries)

End-market products and technologies delivered $259.6 billion in revenue, creating 433,500 jobs & generating $27.3 billion in payroll (health care, hybrid electric vehicles, lighting, communication systems, audio equipment, defense technologies, optics, oil refining, and wind power)

References:

[2] *Percentage of REE Applications projected for 2015*

[3] *U.S. Economic Activity Supported By Rare Earth Chemistry in 2013*

Figure 6. U.S. DOE NETL REE applications and markets infographic [12]

Table 2. Applications for rare earth elements (% by mass) [13]

Application	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Y	Other
Magnets	--	--	23.4	69.4	--	--	2	0.2	5	--	--
Battery alloys	50	33.4	3.3	10	3.3	--	--	--	--	--	--
Metal alloys	26	52	5.5	16.5	--	--	--	--	--	--	--
Auto catalysts	5	90	2	3	--	--	--	--	--	--	--
Petroleum refining	90	10	--	--	--	--	--	--	--	--	--
Polishing compounds	31.5	65	3.5	--	--	--	--	--	--	--	--
Glass additives	24	66	1	3	--	--	--	--	--	2	4
Phosphors	8.5	11	--	--	--	4.9	1.8	4.6	--	69.2	--
Ceramics	17	12	6	12	--	--	--	--	--	53	--
Other	19	39	4	15	2	--	1	--	--	19	--

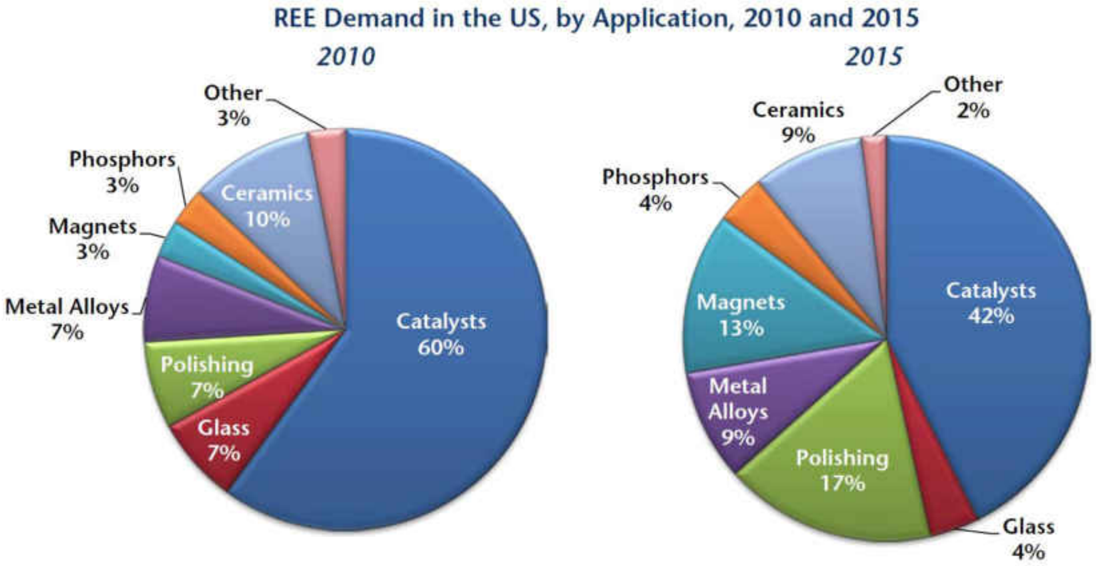


Figure 7. Comparison of rare earth elements usage by application from 2010 to 2015 [15]

1.4 Geology of Rare Earth Elements

According to the Geological Society of London [16], the REEs have long been recognized as useful because of their unusual chemical and physical properties, but their natural occurrence is strongly dependent on geological circumstances, and only in a few locations are they found in sufficient quantity and concentration, and in a suitable form and setting, to make their extraction and exploitation economically viable. As described previously in Section 1.2, due to their chemical similarity, REEs are very difficult to separate from one another, and hence they are also often found together in nature in a range of mineral forms. The REEs are less abundant than the common rock-forming elements, more abundant that the precious metals and similarly abundant to base metals and metalloids, as shown in Figure 8 [17].

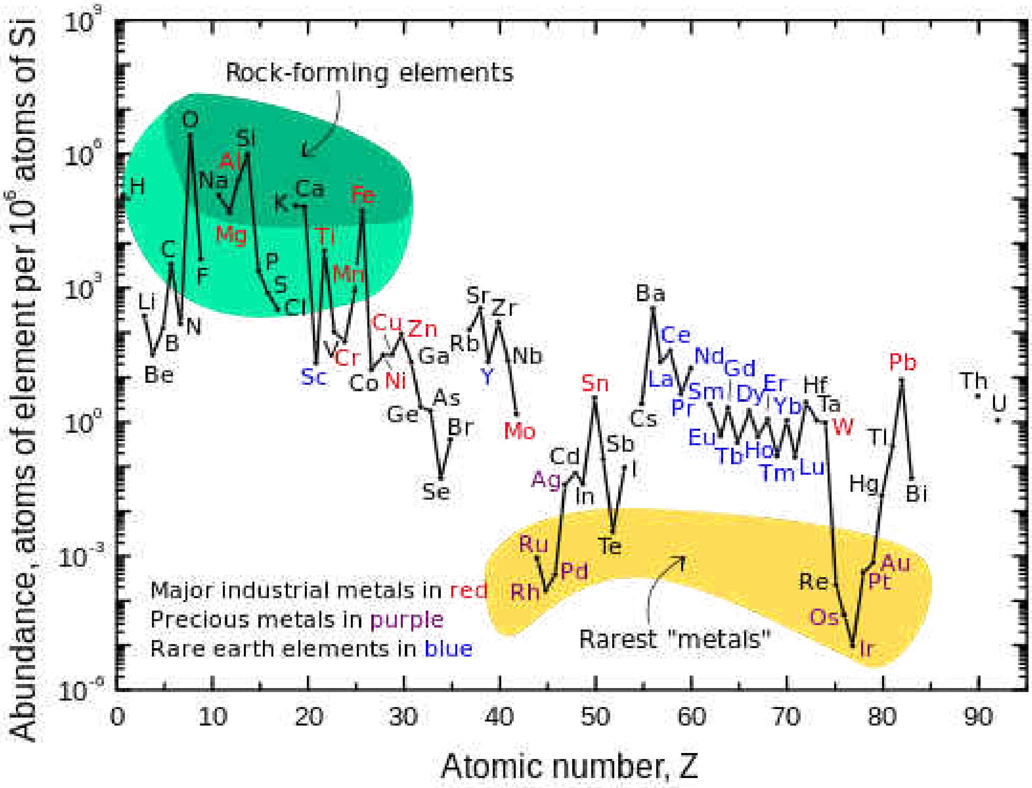


Figure 8. Relative abundance of elements in earth's crust compared to Silicon [17]

However, one particular challenge is that REE are rarely found in high concentrations in abundant minerals because of their coordination number, ionic radius and charge. The most abundant mineral forms on earth are silicates, and REE usually don't fit in these minerals because of their large radii, high charge and high coordination numbers [2]. The coordination number is defined as the number of nearest neighbor anions around a cation in a mineral structure. While the coordination number of some common crustal minerals (quartz and garnet) are 4, the coordination numbers of LREE are > 9 and HREE are 6 to 9. Due to their high valence (mainly 3+) combined with moderately high ionic radii (between 64 and 125 pm) and very high coordination number, REE have high ionic potentials – also called field strengths – and therefore are referred to as high field strength elements (HFSE). The differences in charge and size between the HFSE and the common rock-forming elements (Si, Al, K, Na…etc) mean they do not readily substitute into the structures of the common rock-forming minerals and thus behave ‘incompatibly’ [18]. Figure 9 [19] displays coordination numbers for the REEs and their relative abundance in various mineral classes as a function of the coordination number. These authors conclude that due to coordination number, the LREE concentrate mainly in carbonates and phosphates, while the HREE are found mainly in oxides and some phosphates.

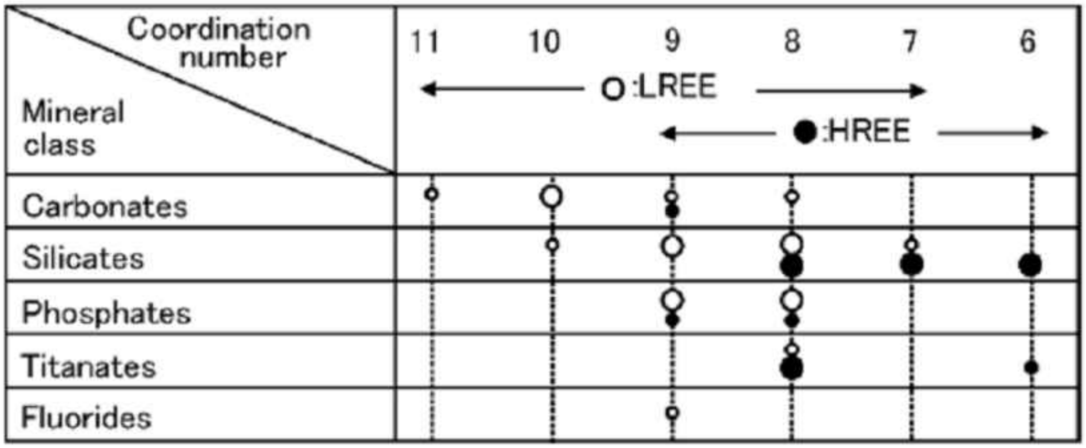


Figure 9. The coordination numbers and abundance of LREEs and HREEs in the structural sites for rare earth mineral classes. Open circles designate LREEs. Shaded circles represent HREEs. The size of the circles represents relative abundance for each mineral class [19]

Rare earth ores are the result of the concentration of REEs either in igneous rocks or in sediments such as sand or clay. Primary rare earth ores contain REEs concentrated in minerals through magmatic processing such as partial melting, fractional crystallization and metasomatism, while secondary rare earth ores are formed from weathering and transportation sedimentary processes [20]. There are about 200 known minerals containing REEs [19], however, commercial production of rare earths is primarily from six sources, as identified below [21]:

- Bastnasite [(Ce,La)(CO_3)F],
- Monazite [(Ce,La)PO_4)],
- Xenotime (YPO_4),
- Loparite [(Ce,Na,Ca)(Ti,Nb)O_3]
- Apatite [(Ca,REE,Sr,Na,K)$_3$Ca$_2$(PO_4)$_3$(F,OH)],
- Ion-adsorption clays

Of these, the first three – bastnasite, monazite, and xenotime – are the most important sources [22], making up about 95% of the world's known reserves for REEs [23]. The U.S. Geological Survey (USGS) has compiled and classified REE-bearing mineral deposits, as shown in Table 3 [20] and Table 4 [17] . Bank and others (2016) [2] have broken down the various REE mineral deposits into two general groupings as summarized below:

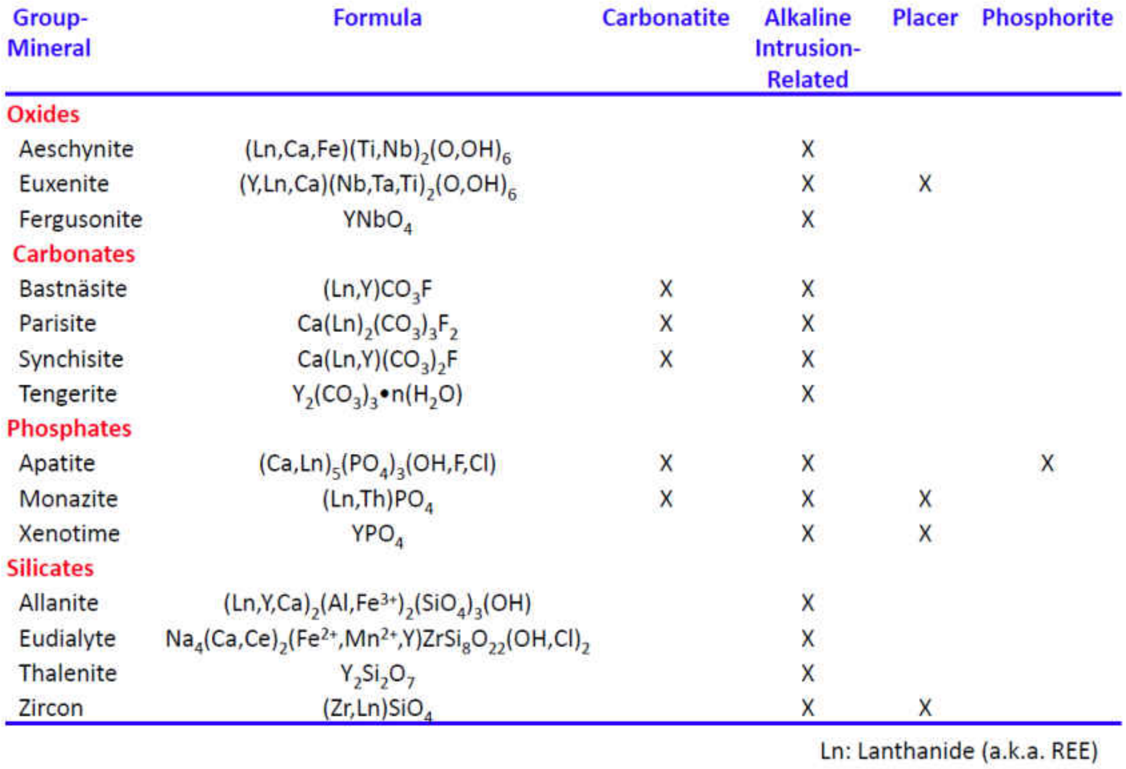
1. Magmatic Deposits
    a. Carbonatite deposits
    b. Peralkaline deposits
    c. Pegmatitic apatite
2. Sedimentary Deposits
    a. Residual/placer deposits
    b. Phosphorite deposits or phosphates
    c. Ion-adsorption clays
    d. Coal and associated sediments

With the exception of coal, which is discussed in detail in Chapter 3, Appendix A contains a discussion of each of the above mineral classifications.

Table 3. Classification of rare earth elements-bearing mineral deposits [20]

Association	**Type**	**Example**
Peralkaline igneous rocks	Magmatic (alkali-ultrabasic)	Lovozero, Russia
	Pegmatite dikes (alkali-ultrabasic)	Khibina Massif, Russia
	Pegmatite dikes (peralkaline)	Motzfeldt, Greenland
	Hydrothermal veins and stockworks	Lemhi Pass, Idaho
	Volcanic	Brockman, Western Australia
	Metasomatic-albitite	Miask, Russia
Carbonatites	Magmatic	Mountain Pass, California
	Dikes and dialational veins	Kangakunde Hill, Malawi
	Hydrothermal veins and stockworks	Gallinas Mtns., New Mexico
	Skam	Saima, China
	Carbonate rock replacement	Bayan Obo, China
	Metasomatic-fenite	Magnet Cove, Arkansas
Iron oxide copper-gold	Magnetite-apatite replacement	Eagle Mountain, California
	Hematite-magmetite breccia	Olympic Dam, South Australia
Pegmatites	Abyssal (heavy rare earth elements)	Aldan, Russia
	Abyssal (light rare earth elements)	Five Mile, Ontario
	Muscovite (rare earth elements)	Spruce Pine, North Carolina
	Rare earth elements-allanite-monazite	South Platte, Colorado
	Rare earth elements-euxenite	Topsham, Maine
	Rare earth elements-gadolinite	Ytterby, Sweden
	Miarolitic-rare earth elements-topaz-beryl	Mount Antero, Colorado
	Miarolitic-rare earth elements-gadolinite-fergusonite	Wasau complex, Wisconsin
Porphyry molybdenum	Climax-type	Climax, Colorado
Metamorphic	Migmatized gneiss	Music Valley, California
	Uranium-rare earth elements skarn	Mary Kathleen, Queensland
Stratifom phosphate residual	Platform phosphorite	Souteast Idaho
	Carbonatite-associated	Mount Weld, Western Australia
	Granite-associated laterite	South China
	Baddeleyite bauxite	Pocos de Caldas, Brazil
	Karst bauxite	Montenegro
Paleoplacer	Uraniferous pyritic quartz pebble conglomerate	Elliot Lake, Ontario
	Auriferous pyritic quartz pebble conglomerate	Witwatersrand, South Africa
Placer	Shoreline Ti-heavy mineral placer	Cooljarloo, Western Australia
	Tin stream placer	Malaysia

Table 4. Classification of REE-bearing mineral deposits [17]



Group-Mineral	Formula	Carbonatite	Alkaline Intrusion-Related	Placer	Phosphorite
Oxides					
Aeschynite	$(Ln,Ca,Fe)(Ti,Nb)_2(O,OH)_6$		X		
Euxenite	$(Y,Ln,Ca)(Nb,Ta,Ti)_2(O,OH)_6$		X	X	
Fergusonite	$YNbO_4$		X		
Carbonates					
Bastnäsite	$(Ln,Y)CO_3F$	X	X		
Parisite	$Ca(Ln)_2(CO_3)_3F_2$	X	X		
Synchisite	$Ca(Ln,Y)(CO_3)_2F$	X	X		
Tengerite	$Y_2(CO_3)_3 \bullet n(H_2O)$		X		
Phosphates					
Apatite	$(Ca,Ln)_5(PO_4)_3(OH,F,Cl)$	X	X		X
Monazite	$(Ln,Th)PO_4$	X	X	X	
Xenotime	YPO_4		X	X	
Silicates					
Allanite	$(Ln,Y,Ca)_2(Al,Fe^{3+})_2(SiO_4)_3(OH)$		X		
Eudialyte	$Na_4(Ca,Ce)_2(Fe^{2+},Mn^{2+},Y)ZrSi_8O_{22}(OH,Cl)_2$		X		
Thalenite	$Y_2Si_2O_7$		X		
Zircon	$(Zr,Ln)SiO_4$		X	X	

Ln: Lanthanide (a.k.a. REE)

1.5 Rare Earth Elements Mineral Processing, Purification and Refining

To produce pure REE metals or REE-compounds suitable for manufacturing of products, such as those described previously in Section 1.3, an extremely complex set of steps is required, and each type of ore or mineral deposit requires a unique set of processes. Appendix A contains a detailed discussion. However, in general, rare earth elements production can generally be divided in five stages/processes, as shown below [24]:

1. **Extraction** of REE-containing material such as an ore or a specific waste fraction
2. **Concentration** of the material (increasing the % content of REE from a very low level to about 60-70%)
3. **Purification** to produce a REE-containing mixture (usually an acidic solution) pure enough for separation

4. **Separation** of different REE or REE fractions present
5. **Refining** into a sellable product (REE compounds or metals, either pure or in defined mixtures)

A simplified flow diagram, shown in Figure 10, is broken down into three phases to achieve individual pure rare earth oxides (REO): i) physical beneficiation, ii) chemical beneficiation, iii) separation & purification. An example of the flowsheet for the Mountain Pass Mine (California, USA) bastnasite ore is provided in Figure 11, and gives an indication of the extreme complexity of the mineral processing steps that must be completed to achieve individual pure REOs (i.e. Steps 1-4 above), even before refining into the REE products. Figure 12 breaks down the processing steps for hard rock-type deposits and ion-adsorbed clay-type deposits required to arrive at a mixed REO product (i.e. Steps 1-3 above).

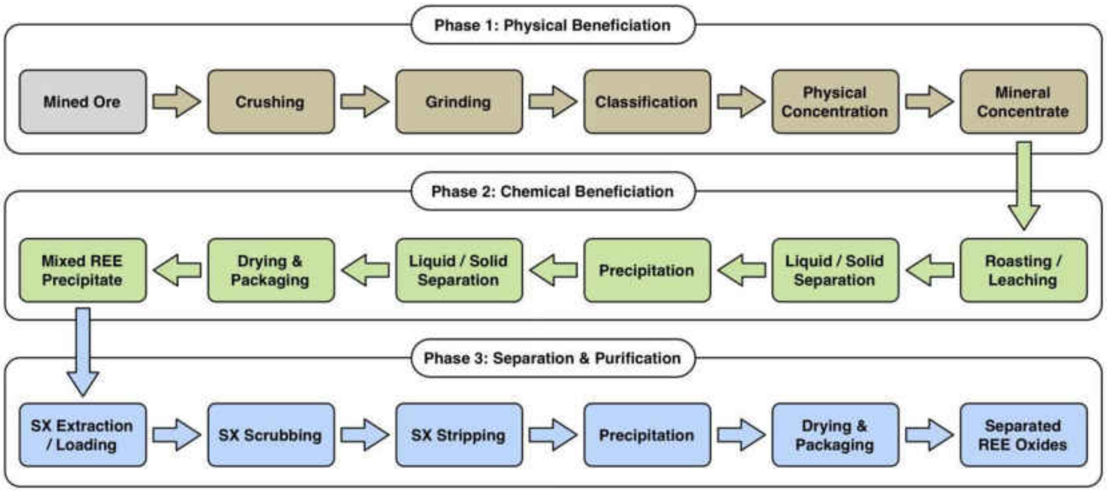


Figure 10. Rare earth elements productions broken down into phases of processing [25]

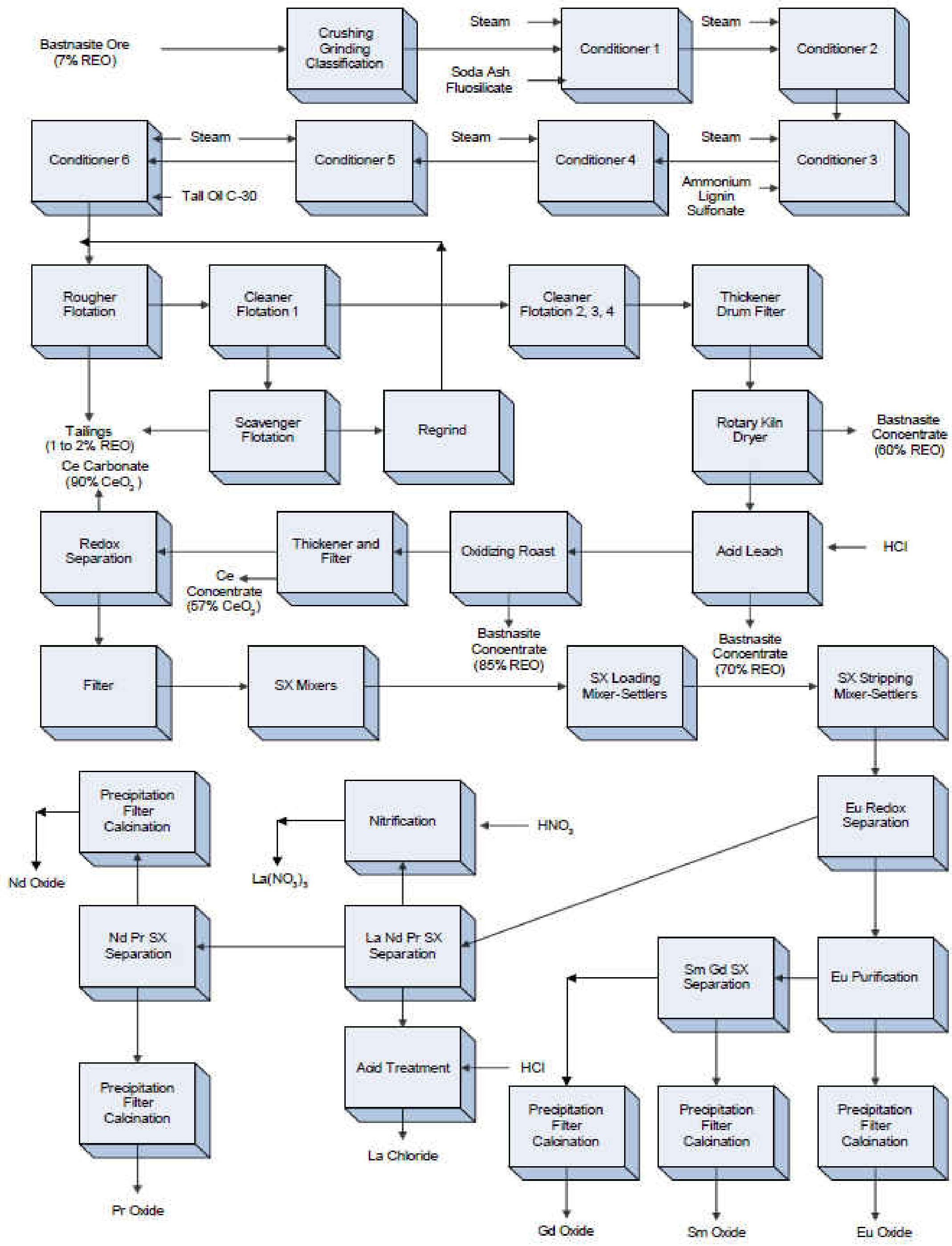


Figure 11. REE mineral processing flow sheet for the Mountain Pass Mine [26]

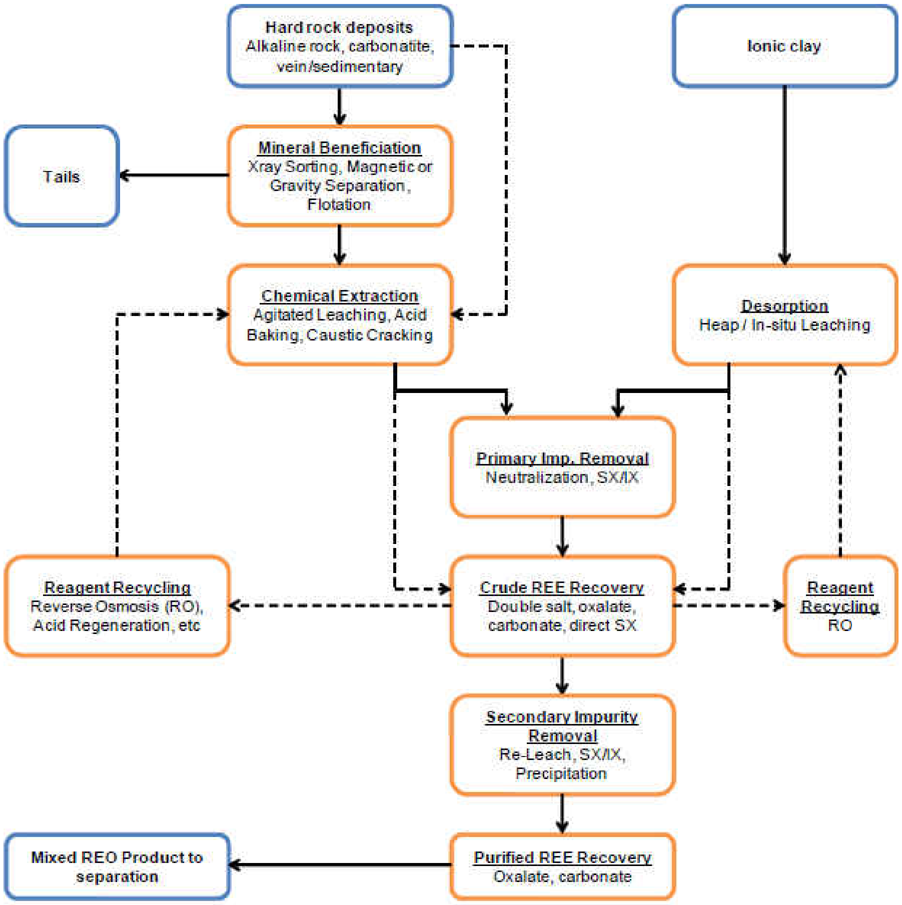


Figure 12. Generic mineral processing scheme to achieve mixed rare earth oxides for two general ore types [27]

1.6 Dissertation Outline

This dissertation contains seven chapters. Following this introductory chapter, Chapter 2 presents the research undertaken in this study. The motivation and rationale for the research, as well as the approach and scope are detailed in this chapter.

Chapter 3 contains background information on rare earth elements in coal and coal byproducts, including theory on deposition and modes of accumulation, the associations of rare earths in coal, the classification of rare earth distributions in coal and finally a preliminary assessment of the prospects of coal and coal byproducts as resources for rare earths.

Chapter 4 contains a description of the results of sampling and characterization of North Dakota lignite coal-related feedstocks in this study. This chapter details the research methods, the results obtained and presents conclusions based on the results.

Chapter 5 contains a description of the results of laboratory-scale rare earth extraction and concentration testing. Details of the experimental methods, results and conclusions drawn are presented.

Chapter 6 contains details of a technical and economic feasibility assessment performed in this study. The overall process design will be described as conceptualized based on results of laboratory testing, including its novel contributions. A summary of an economic assessment performed by Barr Engineering is also included along with discussions of market impacts.

Chapter 7 presents the overall summary of this study, including key conclusions as related to project objectives and novel contributions with a tie-back to the initial hypotheses. This chapter also details the personal opinions of this author regarding recommendations for future research.

2 PROPOSED RESEARCH

This chapter presents the proposed research work. The first sections outline the motivation for the research and its importance (i.e. the research problem). The remaining sections outline the work performed which includes the statements of the research hypotheses, a summary of the research approach, the project goals and the overall significance of the research.

2.1 The Research Problem

In brief, the research problem can be summarized as: *Is recovery of rare earth elements from North Dakota coal-related feedstocks technically and economically feasible?*

Investigations into coal and coal byproducts as potential alternative resources for rare earth elements have only recently been initiated. The background on the motivation for these investigations and the work described in this dissertation is provided in the following sections.

2.1.1 Criticality of Rare Earth Elements

The REEs, as well as other important mineral commodities, have recently been categorized based on their criticality. The criticality is typically represented as a combination of the supply risk and impact of supply restriction or importance to a particular set of applications/technologies. An older example (2008) by the National Resource Council [28] for a range of mineral commodities is presented as Figure 13. In 2008, the REEs were classified as one of the more critical commodities, along with other elements such as platinum group metals, manganese and indium. In a more recent study (2011) by the U.S. DOE [29], a critical materials assessment was completed that included REEs broken out into individual elements and evaluated in both a 5 year and 15 year outlook, as shown in Figure 14. The DOE criticality of the elements was judged according to the following factors and weighting:

- Importance to Clean Energy
    - Clean Energy Demand (75%): magnets, batteries, photovoltaic films and phosphors used in clean energy technologies
    - Substitutability Limitations (25%): assessment of the practicality of substituting with less critical materials
- Supply Risk
    - Basic Availability (40%): assessment of current supply versus current demand. Short term accounts for current mine product and mid-term accounts for future mine production as well as projections in future demand
    - Competing Technology Demand (10%): assessment of the constraint in supply for clean energy demand based on increased energy demand in other technology sectors

  - Political, Regulatory and Social Factors (20%): assessment of stability in major producing countries that may affect supply, such as import/export quotas or restrictions on new mining projects
  - Codependence on Other Markets (10%): assessment evaluating risk based target mineral as primary product or byproduct. Codependence may be an advantage or disadvantage depending on the mineral that drives the production levels from an economic standpoint.
  - Producer Diversity (20%): assessment of risk regarding lack of diversity in producing country or company (i.e. monopoly or oligopoly)

From the DOE analysis, the REEs Dy, Nd, Tb, Y and Eu are considered the most critical, and in fact are the most critical of all the elements evaluated in the DOE study. The less critical REEs include La, Ce, Sm and Pr, as well as all of the other REEs (elements not shown were classified as not critical in this study). In both the short and mid-term cases, Dy is considered the most critical. Another way to look at this type of analysis is to simply evaluate projections of supply shortfalls for specific elements. In their 2015 study, the U.S. Department of Defense [30] identified six REEs that are expected to have significant supply shortfalls for defense applications, as shown in Figure 15. Based on market evaluation by IMCOA [31], Seredin (2010) [32] has further broken down the criticality of the REEs into the following groups:

- Critical: Nd, Eu, Tb, Dy, Y, Er
- Uncritical: La, Pr, Sm, Gd
- Excessive: Ce, Ho, Tm, Yb, Lu

It is clear from each of these analyses that REEs represent among the most critical of current mineral commodities both domestically and globally. These classifications have generally remained the same since the above studies, as the U.S. DOE NETL website currently lists Nd, Eu, Tb, Dy and Y as the critical elements [12]. However, for the purposes of consistency, the Seredin (2010) definitions will be used for the remainder of this document.

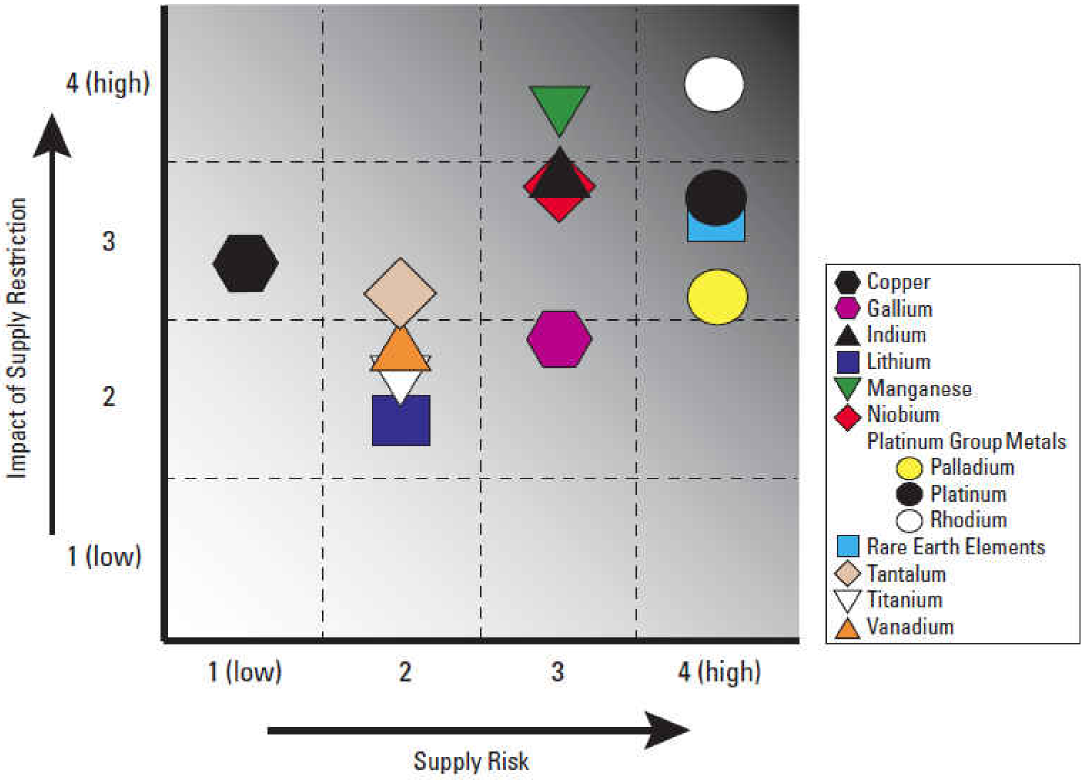
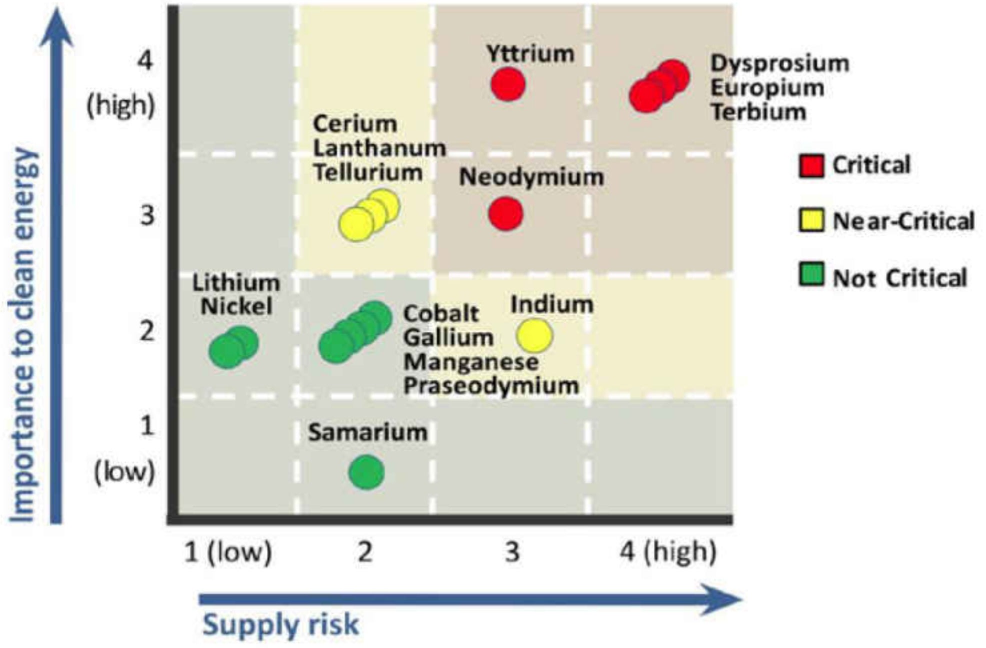
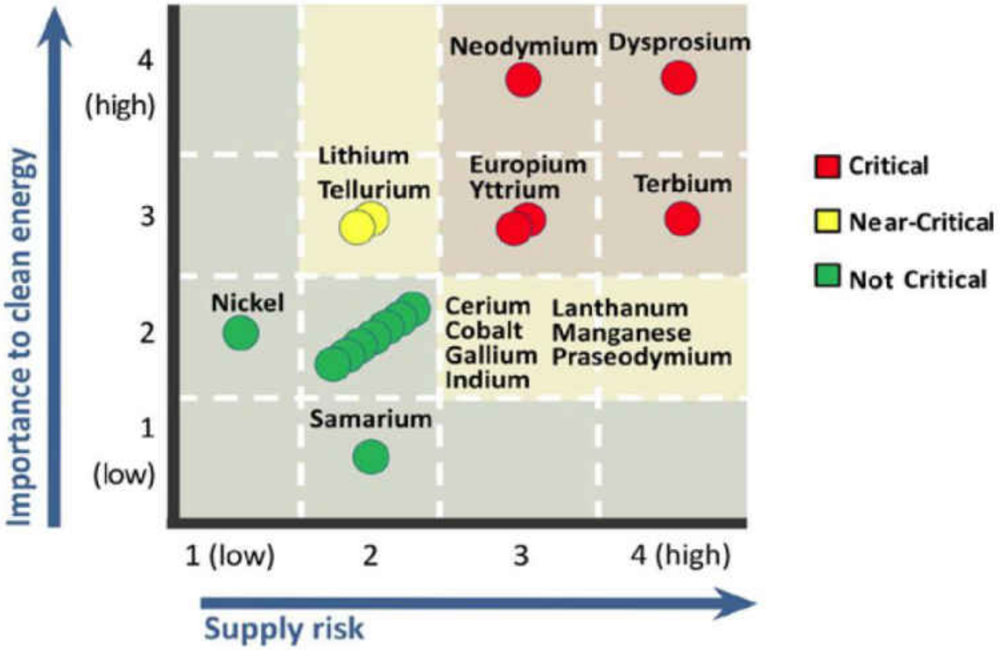


Figure 13. 2008 National Resource Council evaluation of critical materials [28]



Short-Term (0–5 years) Criticality Matrix



Medium-Term (5–15 years) Criticality Matrix

Figure 14. U.S. Department of Energy 2011 critical materials assessment for clean energy [29]

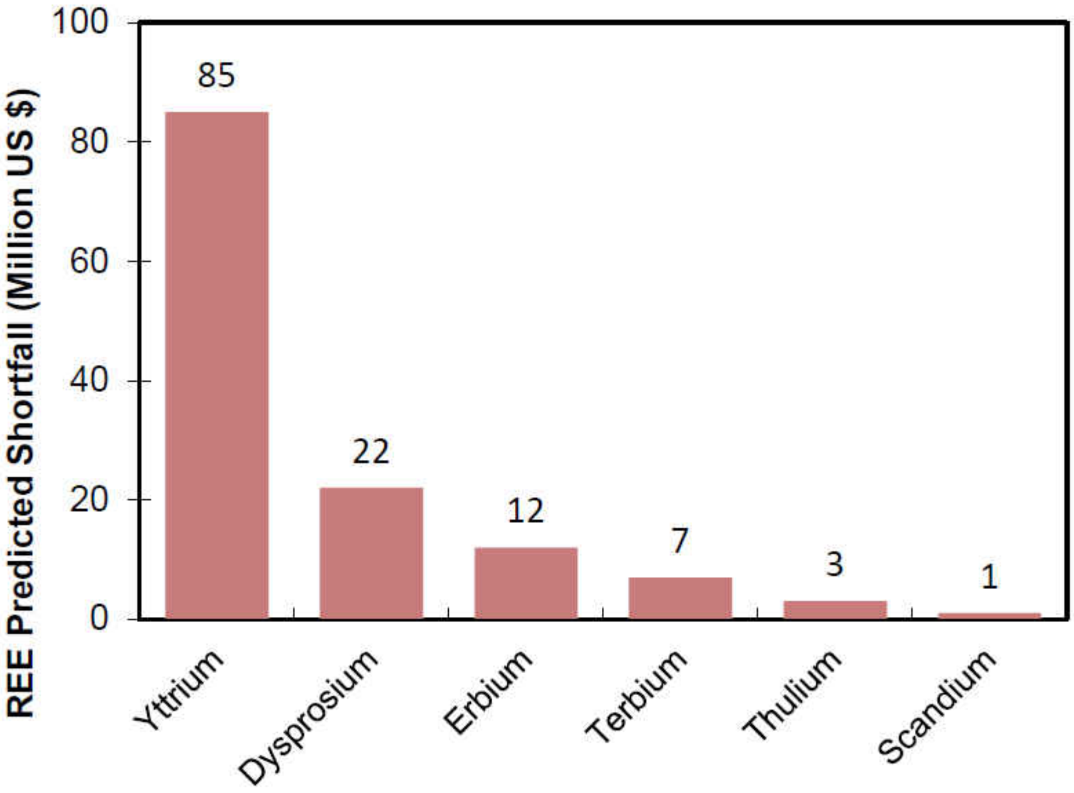


Figure 15. 2015 U.S. Department of Defense projected materials shortfalls for defense applications [30]

2.1.2 Rare Earth Global Outlook

China dominates the REE global market, with estimated total reserves of about 30-50% of the global reserves [33, 34], while controlling the supply over the last decade plus, with a total production of about 83% of the global market in 2016, which is actually down from about 95% prior to 2010 [33]. Figure 16 displays the REE production trends by country for the last several decades. The U.S. controlled the market for most of the back half of the twentieth century, especially starting in the mid-1960s with the introduction of the color television. However, beginning in the 1980s, Chinese production ramped up, and U.S. production could not compete economically for a number of reasons including lower cost Chinese production and comparatively lax environmental regulations. The last remaining U.S. REE mine (Mountain Pass Mine, CA) closed in 2002.

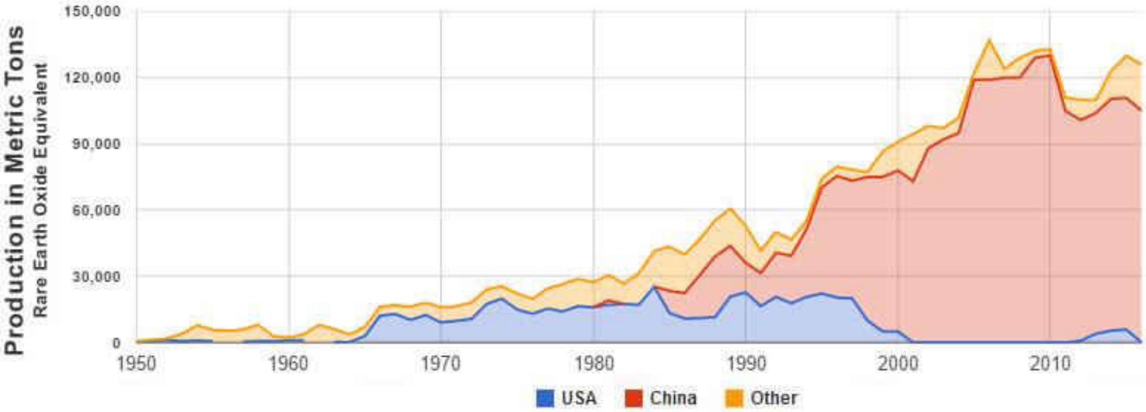


Figure 16. Rare earth element production through 2016 [35]

In recent years, the Chinese government has been attempting to consolidate its massive REE production into six large government-owned companies and eliminate much of the illegal/unregulated mining that was occurring, which as of 2015 accounted for an estimated 30-40 thousand tons of REO [36], or about $^1/_3$ of the total regulated Chinese production from that year. Also, recognizing that their production rates were unsustainable long-term (Figure 17), beginning in 2005, China established export quotas on REEs, both to ensure sufficient supply for its own industries and to gain control over the global market. Sparked by a Chinese REE export embargo against Japan in 2010, supply crisis fears from the Western world caused massive price increases across the board for the REEs. For example, the price of Dy and Nd are shown in Figure 18 from 2008 to 2014. According to Barakos and others, China had successfully demonstrated the power that comes with monopolistic control of an import raw material class. The Chinese Government issued export quotas for both local-owned and foreign-owned REE exporting companies. A dispute was settled in the World Trade Organisation (WTO) from the European Union, Japan and the U.S. against China, who was forced to compromise and change its export policies. The current situation could be described as temporarily stable, yet opaque and fragile [37].

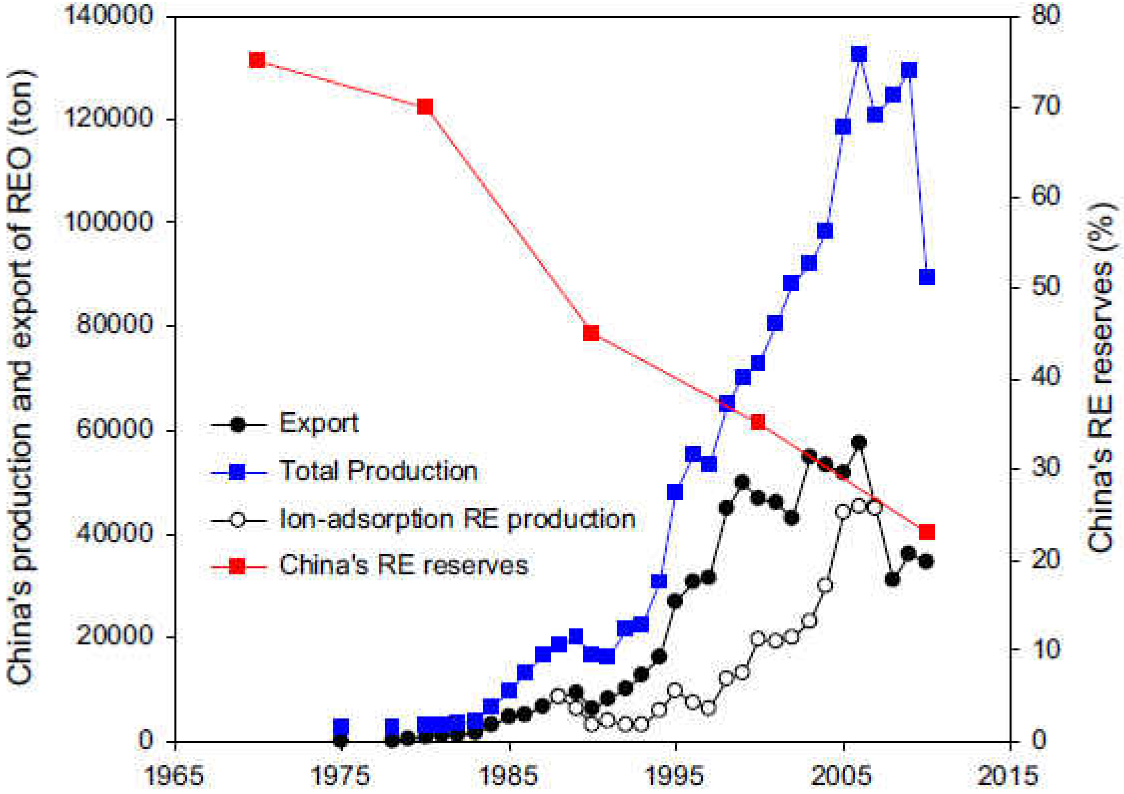


Figure 17. Chinese REE production and exports since 1965 [38]

Due to the supply fears, as well as new-found high prices, many new REE exploration or mining projects were initiated globally in this period, including re-opening of the Mountain Pass Mine in the U.S. under new ownership (Molycorp Minerals LLC). However, since the price surges, a steady decline has been observed, to the point where prices are only slightly higher than the pre-surge levels. Due to low prices, the Mountain Pass Mine has once again been de-commissioned as of the last quarter 2015, and Molycorp has filed for bankruptcy, leaving the U.S. currently 100% import reliant for

REEs [33]. According to the most recent USGS Mineral Commodities Report (2017) [33], global production by country in 2015 and 2016 is shown in Table 5.

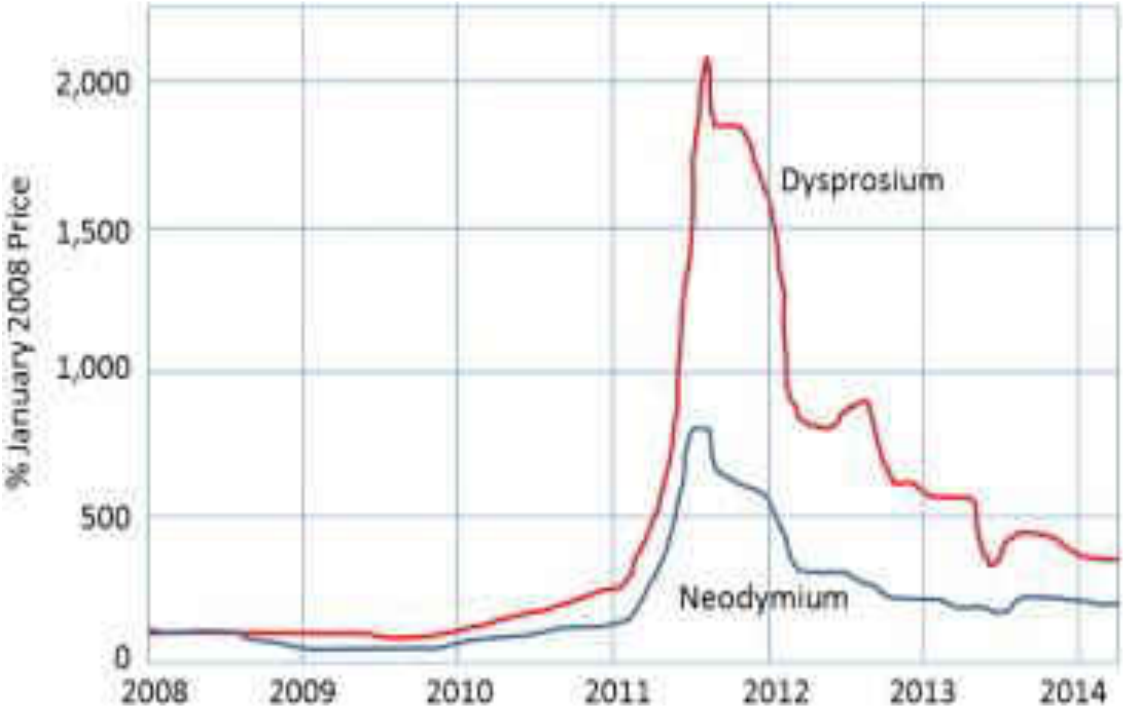


Figure 18. Price of dysprosium and neodymium (% of 2008 price) from 2008 to 2014 [39]

Table 5.Global REE production (metric tons) in 2015 and 2016 [33]

Country	2015	2016
United States	5,900	0
Australia	12,000	14,000
Brazil	880	1,100
China	105,000	105,000
India	1,700	1,700
Malaysia	500	300
Russia	2,800	3,000
Thailand	760	800
Vietnam	250	300
World Total	**130,000**	**126,000**

As of 2015, the active mines and significant exploration projects targeting REEs globally are shown in Table 6 [33], and the geographical location of these project and other resources being investigated are shown in Figure 19. The three major mining provinces in China are Baotou, Sichuan and Jiangxi, which together host about 88% of the Chinese REE resources. Located in Baotou, Bayan Obo is a giant Fe-REE-Nb deposit, where 83% of the Chinese REE reserves are concentrated, mainly as LREE, and the REE are produced as a byproduct from iron ore mining. The Bayan Obo is the world's largest REE resource. The ion-adsorbed clay deposit at Longnan in Jiangxi province makes up about 30% of the Chinese LREE supply, but more importantly nearly exclusively supplies the global HREE market [40]. However, by several estimates, these HREE rich deposits are not long-term sustainable, with depletion expected by 2025 or even earlier [41].

Table 6. Active REE mines and significant exploration projects as of 2015 [33]

Country	Active mines	Significant projects
Australia	Mount Weld	Nolans Bore
Canada		Hoidas Lake
China	Bayan Obo, Weishan Lake, Maoniuping,	
Greenland		Kvanefjeld, Motzfeldt
India	Odisha, Chavara, Manavalakurichi	
Namibia		Lofdal
Russia	Khibiny, Lovozero	
South Africa		Zandkopsdrift
Sweden		Nora Karr
USA	Mountain Pass (Until mid-2015)	Bear Lodge, Bokan-Dotson Ridge

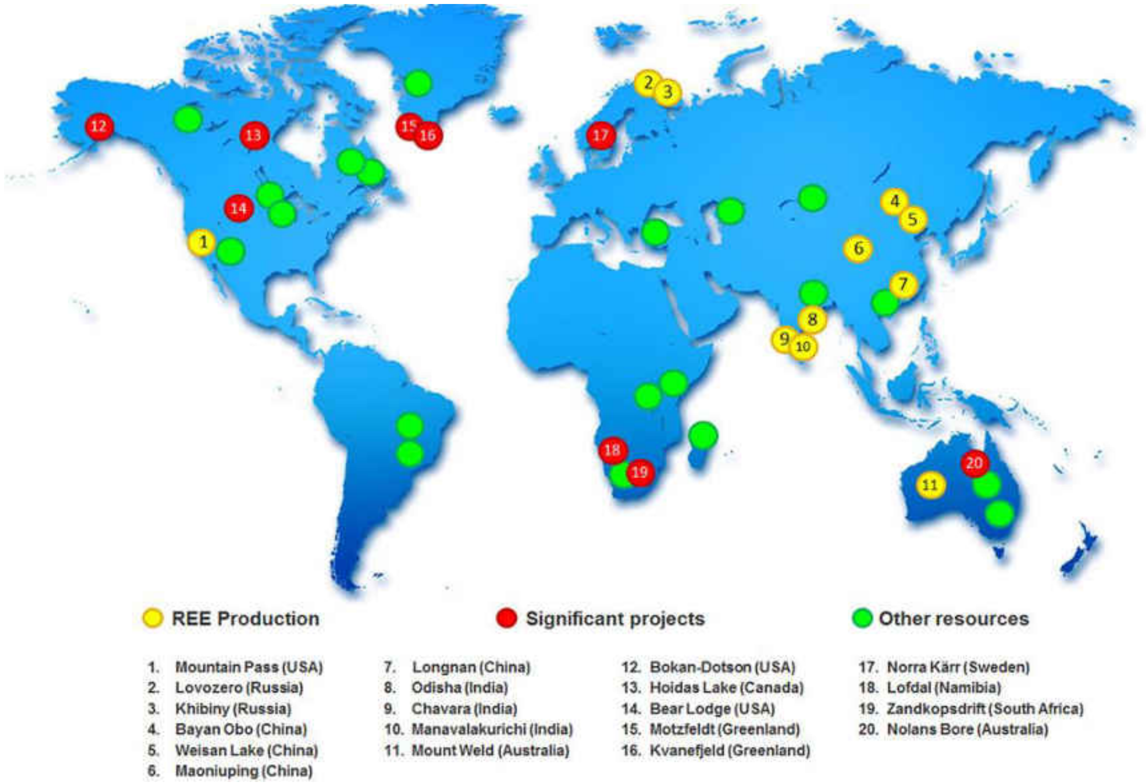


Figure 19. Global REE mines, exploration projects and other resources [37]

Some of the main REE producers outside of China are Australia, Russia and India. Indian REE are produced mainly from extensive heavy mineral sand placer deposits and are extracted by three government-owned companies. Russia has several large REE deposits (fourth largest reserves by country [33]), mainly in the form of magmatic derived alkaline igneous deposits. Australian production is mainly from the Mount Weld mine, a large carbonatite intrusion containing mainly bastnasite mineral.

Some of the notable exploration projects in the U.S. include Bear Lodge (Wyoming) and Bokan Mountain (Alaska). The HREE-rich Bear Lodge deposit is an alkaline igneous rock deposit and is being developed by Rare Element Resources, which prepared an Environmental Impact Statement in 2016, but is now on hold [42]. The largest HREE deposit known in the U.S. is the Bokan Mountain deposit in Alaska, which contains about 40 wt% HREE. UCORE Rare Metals is evaluating the resource [43]. Of the other exploratory projects highlighted in Table 6, none are expected to commence mining operations in the near future [37].

2.1.3 Summary of Research Motivation

The previous two sections have described the criticality of rare earth elements as well as the current global outlook. Combined with information previously provided in Chapter 1, the below summarizes the motivation for this research.

- Due to their unique chemical and physical properties, rare earth elements are crucial materials for today's modern economy and are used in a host of technologies/products that are essential for the economic well-being and security of the United States. Emerging and critical applications include permanent magnets for wind turbines and motors in hybrid/electric vehicles and numerous REE-based products used in military defense applications.
- China completely dominates the rare earth element value chain from mining, to beneficiation, to extraction, to separation and to refining and component product manufacturing. The lack of developed mining projects and intellectual know-how in the rest of the world has resulted in monopolistic control of the markets by China. China has previously exercised the impact of this control, as seen by export limitations and massive price increases observed in 2011. Refining plants are almost exclusively found in China, meaning that even if other parts of the value chain are present elsewhere, that China still controls the end-use markets, and ultimately the pricing.

- Market usage of rare earth elements is shifting from the mature applications for LREEs (i.e. catalysts, polishing) to new high-tech applications mainly for the HREE (i.e. permanent magnets). The HREE are much less common in nature and are only known to exist in a few economically mineable locations in the world.
- Analysis by multiple groups has identified the most critical REEs based on a combination of their supply scarcity and end-use importance. These are typically accepted to include Nd, Eu, Tb, Dy, Y and Er, and are considered among the most critical of all mineral commodity elements.
- China essentially produces 100% of the global supply of the HREE, including many of the critical REE identified above. However, the source of the HREE is the ion-adsorbed clays mined in South China, which is not a long-term sustainable resource. Estimates have placed depletion of this resource by as soon as 2025. China also understands this, and has begun to tighten its grip on the rare earths market by consolidating all of its mining into six state-owned companies and cracking down on extensive illegal mining practices.
- The United States is currently 100% import reliant for REEs and REE-based products, with its last mine having closed in 2015. Even when open, the concentrate from the Mountain Pass mine was exported to China for processing/refining and component product manufacturing. Further, the Mountain Pass mine is deficient in the critical REEs, making it unable to satisfy the growing market demand even if it were to be re-opened.

- Other HREE-rich deposits have been identified, including in the U.S., but projects are at early stages of development and environmental issues dealing with disposal of radioactive wastes (Th, U) carry a large public stigma.

With the above, it is clear that new domestic resources for REEs, in particular the HREE and critical REE be identified and processes developed to produce them in the U.S. To that end, Representative Duncan Hunter (R-CA) in March 2017 introduced the Materials Essential to American Leadership and Security (METALS) Act which would create loan facilities aimed at encouraging U.S.-based companies to get back into mining REEs and producing REE-based products. In his address to congress, Rep. Hunter stated:

> The U.S. must no longer be wholly dependent on foreign sources of strategic and critical materials. The risk of this dependence on national security is too great, and it urgently demands that we re-establish our depleted domestic industrial base.

Additionally, the U.S. DOE NETL [12] has recently launched a research program aimed at development of the nation's coal resources as one of these new REE supply resources. As will be discussed in detail in Chapter 3 of this dissertation, coal is known to be enriched in REEs above crustal averages and can have a favorable distribution of HREE and critical REE. Additionally, since the mining, beneficiation and utilization infrastructure for coal is already well developed at large scales, opportunities may exist for value-added extraction of REEs from already concentrated sources along the coal-use value chain.

2.2 Research Approach and Scope of Work

To determine the feasibility of rare earth elements recovery from North Dakota coal-related feedstocks, the following approach was adopted for this study:

- Perform sampling and analysis to identify North Dakota lignite coal or lignite coal-related materials with total REE content greater than 300 ppm (whole sample or ash basis), a threshold deemed by others [44] as the minimum for economic viability. This work is presented in detail in Chapter 4.
- Determine the geochemistry of the potential feedstocks and understand the forms and modes of occurrence of the REEs, which is information needed to inform the development of extraction and concentration methods. This work is presented in detail in Chapter 4.
- Investigate and test environmentally benign methods to separate, extract or concentrate the REEs to a target of two percent by weight of REEs on a dry pure elemental basis, a level that would make it a viable synthetic replacement for traditional mineral ores, allowing existing processing/refining methods to be leveraged. This work is presented in detail in Chapter 5.
- Perform a technical and economic analysis of a commercial concentrating facility based on the concentration methods identified to demonstrate economic viability given both the current market and potential future market scenarios. This work is presented in detail in Chapter 6.

The sampling and analysis work in this project mainly focused on the Falkirk Mine and the Coal Creek Station power plant, both near Underwood, North Dakota. Samples were collected from the mine that included the coal seams, as well as the mineral-rich sediments associated with the coal seams as roof, floor and partings materials. Samples collected from the power plant included streams associated with the Great River Energy DryFining™ lignite drying process as well as combustion ashes.

The extraction/concentration testing initially focused on physical beneficiation processes to target concentration of the REEs in mineral-rich materials, such as the associated sediments and the reject streams from the DryFining™ process. The testing was subsequently expanded into methods for extraction/concentration of REEs from the coals.

The technical and economic feasibility study included investigation of the economics of REE extraction combined with an activated carbon production plant co-located with a combined heat and power facility, as well as a stand-alone REE extraction facility.

2.3 Research Hypotheses

To determine the feasibility of recovering rare earth elements from North Dakota coal-related feedstocks, the content and modes of occurrence of the REEs in the materials needed to be elucidated. Based on previous research regarding REE content in North Dakota lignite and associated sediments [45, 46], as well as initial analysis of samples from the DryFining™ process, the following research hypotheses were established prior to commencement of this study.

- The REEs would be concentrated in the mineral-rich materials associated with coal seams – the roof/floor/partings

- The REEs would be concentrated into the mineral-rich reject stream from the DryFining™ process
- The REEs would be present mainly as ultra-fine mineral grains of size < 10 microns and associated with clay, phosphate and carbonate minerals
- The REEs would be depleted or absent in the organic matter of the coals
- Physical beneficiation processes could be used to concentrate REE-bearing minerals to the target of two percent by weight. Processes could include gravity concentration, magnetic separation, flotation, elutriation and fine particle separations. The target of two percent by weight of REEs would be achievable using a combination of these.

The work performed in this study was structured to prove or disprove the above hypotheses, which combined, allowed determination of the technical and economic feasibility of rare earth element recovery from North Dakota coal-related materials.

2.4 Research Significance

North Dakota is host to the world's largest lignite coal deposit [47] and its economy and energy portfolio is heavily invested in lignite mining and utilization. This study provides the foundation for a potential completely new industry focused on lignite use. As mentioned previously, evaluation of coal and coal byproducts as alternative resources for rare earth elements is a newly established research area. Some earlier and ongoing work by others on evaluating the content and form of REEs in North Dakota coal-related materials has been completed [45, 46, 48, 49], but this study undertakes a completely new task of developing methods and technologies to extract and concentrate the REEs. In addition, new fundamental understanding of the geochemistry of REEs in lignite and lignite-related materials will be revealed. The ultimate significance of this research is development of a high performance, environmentally benign and economically viable technology for REE production from an alternative resource that will limit dependence on foreign supplies and strengthen the economic and national security of the U.S.

3 RARE EARTH ELEMENTS IN COAL AND COAL BYPRODUCTS

This chapter provides background on rare earth elements in coal and coal byproducts. Theories on the deposition and accumulation mechanisms are discussed, as well as modes of occurrence and distribution characteristics. Finally, a discussion on the prospects of coal and coal byproducts as alternative resources for REE production is provided, with a highlight to a preliminary assessment for North Dakota coals.

3.1 Origin, Classification and Modes of Occurrence

As mentioned previously in Chapter 2, the concentration of rare earth elements in some coals and surrounding sediments can be enriched beyond that found in the earth's crust. For example, high total REE content (i.e. > 0.1%) has been found in coal seams, as well as in the host and basement rocks of some coal basins globally. However, up until recently, these coal resources were not widely evaluated or considered as possible sources for REEs, as the mining industry focusing on traditional mineral ore deposits was thriving and deemed sufficient to supply world demand indefinitely. Obviously, however, things have changed in the last decade, with the REE value-chain dominance by China, as well as dwindling supplies of the particular REEs that make up the most important growing market sectors (heavy/critical REEs). The following sections are meant to provide a brief overview of the literature available detailing some early work in the latter part of the twentieth century, mainly focused on understanding the geochemistry of trace elements in coal, and also some more recent work that has more comprehensively investigated REEs, in particular their genetic origins in coal, their modes of occurrence and overall content. Chapter 4 of this dissertation contains detailed results of sampling and characterization of the REEs in North Dakota lignite coal-related materials. Many of the conclusions from various literature sources discussed below are substantiated by the findings of this research.

3.1.1 Genetic Origin of REEs in Coal Basins

According to a review of metalliferous coals by Seredin and Finkelman (2008) [50], metals, including REE can be accumulated in the coals at various stages during and after its formation, from the earliest at peat-accumulation to the latest anthracite stage. Thus, the processes in coals can be subdivided into syngenetic, diagenetic and epigenetic; syngenetic being during peat accumulation, diagenetic being after peat burial and during the coalification processes, and epigenetic being after the coal compaction and solidification. The epigenetic stage can further be divided based on the age or type of coal (i.e. lignite, subbituminous, bituminous, anthracite stages and intermediates). The key modes of metal (REE) input into the coals are [50]:

- Wind: Impacts the transport of particulate associated with volcanic or cosmic impact events that geographically distribute metal/REE source materials
- Water: The primary input source for metal enrichments in coals, which can be transported either by surface or ground waters. Examples of surface water transport include leaching of ore deposits containing trace elements found in water-soluble minerals, and leaching of volcanic ash/magma materials that

contain soluble trace element forms. Ground waters of coal basins are commonly highly mineralized or contain large concentrations of dissolved trace element ions. Groundwater circulation is prevalent through the more porous materials in the early stages of coalification (i.e. lignite is very porous, whereas higher rank coals are less permeable). In later stages, groundwater circulation occurs through faults and permeable sediments surrounding the coal seams.

- Multistage or polygenetic: These typically result in abnormal metal accumulations and are the result of an array of ore-forming processes that occur during various stages of coalification.

REE-enriched coals are primarily formed under three geological conditions at various stages in the evolution of the coal basins, as described below [50]:

- Tuffaceous type: Volcanic activity is known to be the source of many REE-enriched coals throughout the world, including Western coals of the United States [51]. REE-bearing coals originating by the precipitation of acid and alkaline pyroclastics into basins are known. Tuffaceous type REE enrichments also typically include elevated levels of zirconium (Zr) and hafnium (Hf), and are usually accompanied by a Eu minima (i.e. less Eu enrichment than would be expected when normalized to crustal averages). There are numerous mineral forms that hold the REEs in tuffaceous type coals, examples of which include phosphates (monazite, apatite), aluminophosphates (crandallite) and zircon.
- Infiltration type: Epigenetic leaching of various source materials can result in solubilized REE ions being transported into the coal basins with subsequent

adsorption onto the organic matter. Accumulation of REEs in this manner typically results in enrichment in the upper portions of coals and overlying sediments.

- Exfiltration type: These REE-enriched coals occurred due to discharge of hydrothermal solutions from the sedimentary basin, and subsequent adsorption/deposit during peat accumulation or during early coalification stages where organic matter has a high affinity for metal ions and is highly permeable. Eu minima in these coals are associated with basins that hold granitic basement rocks or are framed by acidic volcanic tuffs. These deposits typically show a "C" shaped stratigraphic REE distribution pattern, with highest concentration at the lower and upper margins of the seams. These types of coals will also be enriched in a number of other trace elements, depending on the chemistry of the source fluids.

In summary, the major sources and modes of REE-enrichment in coal basins are from volcanic deposition, surface water leaching/transport of REE-containing source materials, and ascending flows of mineralized hydrothermal/deep waters. In each case, the content and form of the REE in the coals depends on numerous factors such as the stage of coalification and the chemistry of the source materials or the hydrothermal fluids.

3.1.2 Rare Earth Element Distribution Patterns in Coal

In their evaluation of coal deposits as potential alternative sources for REEs, Seredin and Dai (2012) [52] have compiled data from a large database of REE analysis of coals globally, most of which were from Russia and China. Their study grouped REE distribution patterns based on their relative enrichment compared to the earth's upper continental crust, and have proposed genetic sources based on the type of distribution and anomalies present. They have grouped REE distributions in coals into three main patterns based on molecular weight: i) Light (L-type), ii) medium (M-type), and iii) heavy (H-type). Anomalies in the distribution typically come from negative or positive Ce, Eu or Y. Their method involved a data normalization approach that takes the ratio of the concentration of REE in the coal (ash basis) to the concentration in the earth's upper continental crust (data previously provided in Chapter 1).

The L-type distribution is a similar distribution to many traditional ore types. An example of an L-type is provided in Figure 20. In this figure, there are clear dips and spikes associated with Ce, Eu and Y, which represent distribution anomalies. The authors have concluded that coals with L-type REE distribution are of tuffaceous or infiltrational origin and contain a high proportion of REE-bearing minerals.

The M-type distribution is provided as an example in Figure 21. Three subgroups have been identified: A) strong pronounced Eu-minimum, B) strong pronounced Eu-maximum, and C) swell-like without Eu-anomalies. The M-type distribution is typical for any acidic natural waters that may circulate in coal basins [53]. The M-type distribution is quite common for coals due to the higher sorption capacity of the medium molecular weight REEs by organic matter compared to the light and heavy REE [54]. It will be shown in Chapter 4 of this dissertation that the North Dakota lignite coals analyzed in this work primarily fit into the M-type pattern, with the highest REE content samples analyzed fitting the C subgroup above and exhibiting the swell-like pattern centered around Eu.

The H-type distribution is provided as an example in Figure 22. The H-type distribution in coals is explained by wide spread of natural waters that are enriched in HREE that circulate in coal basins [55]. The source waters can be a wide variety of chemistries, with some examples including marine waters, alkaline terrestrial waters and high temperature volcanogenic fluids. As such, the REE distribution in these coals is highly variable, depending on the source of the enrichment.

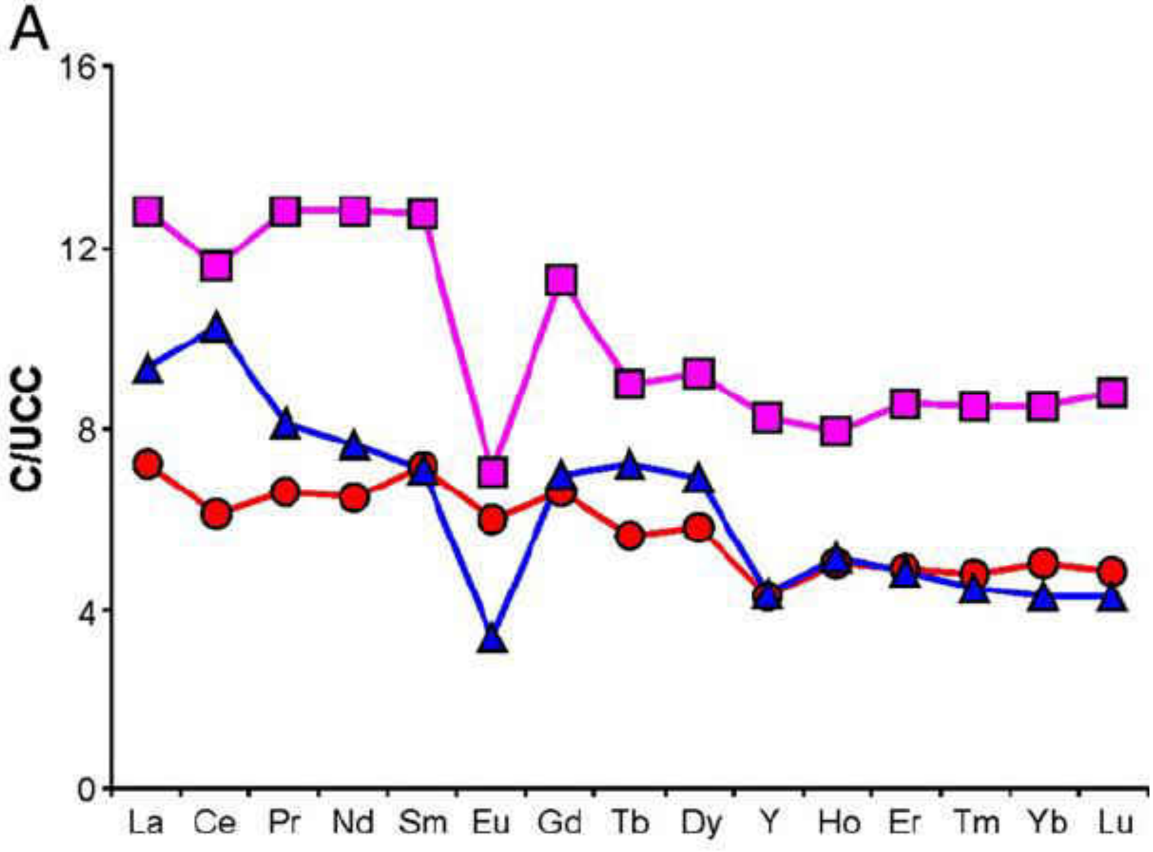


Figure 20. L-type REE distribution from Seredin and Dai (2012) [52]

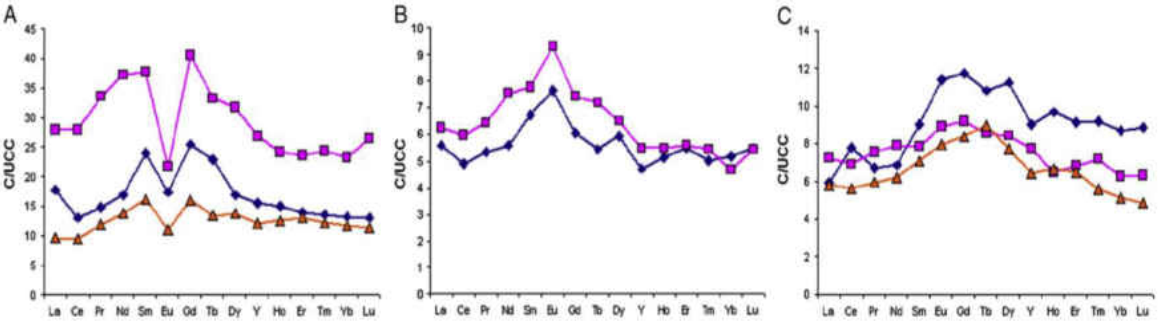


Figure 21. Examples of M-type REE distribution from Seredin and Dai (2012) [52]

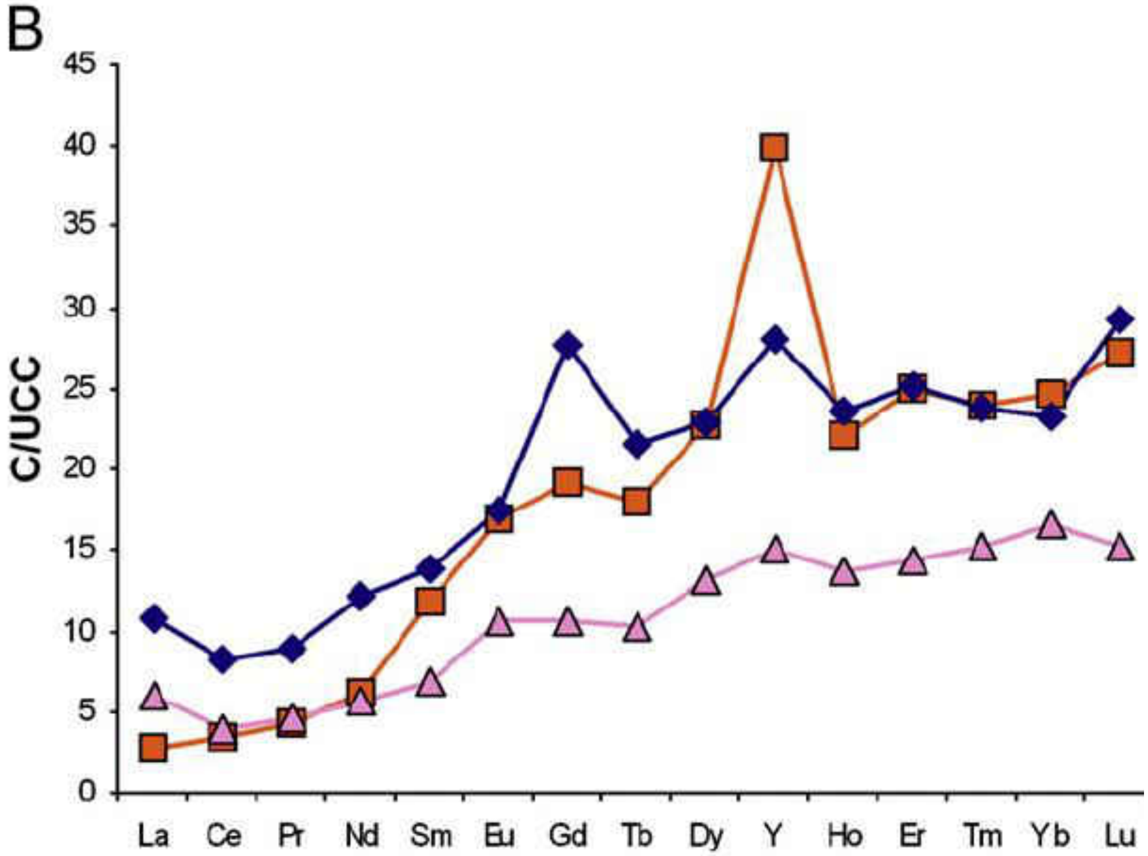


Figure 22. H-type REE distribution example from Seredin and Dai (2012) [52]

Based on their approach of REE-distribution classification, Seredin and Dai (2012) have also proposed a method of resource assessment for evaluating the suitability of coal (or coal ash) as a resource for REE recovery. They have established a total REE cutoff of between 800-1000 ppm REO content in the coal ash, depending on seam thickness as well as the parameters shown below:

- Outlook Coefficient (Coutl): Ratio of critical REE (Nd, Eu, Tb, Dy, Er, Y) to excessive REE (Ce, Ho, Tm, Yb, Lu), as calculated by Equation 1
- Percentage of Critical Elements in total REE (REYdef,rel%), as calculated by Equation 2

$$\mathrm{Coutl} = [(\mathrm{Nd}+\mathrm{Eu}+\mathrm{Tb}+\mathrm{Dy}+\mathrm{Er}+\mathrm{Y})/(\Sigma\mathrm{REE})]/[(\mathrm{Ce}+\mathrm{Ho}+\mathrm{Tm}+\mathrm{Yb}+\mathrm{Lu})/(\Sigma\mathrm{REE})] \qquad (1)$$

$$\mathrm{REYdef,rel\%} = (\mathrm{Nd}+\mathrm{Eu}+\mathrm{Tb}+\mathrm{Dy}+\mathrm{Er}+\mathrm{Y})/\Sigma\mathrm{REE} * 100 \qquad (2)$$

Based on their extensive database, Seredin and Dai (2012) created the plot shown in Figure 23 which compares various global coal ashes (black diamonds) to some traditional mineral deposits using the above parameters. From the data, they have prepared three clusters of groupings that represent ‘unpromising’, ‘promising’ and ‘highly promising’ REE content distributions. Moving up and right on the plot skews the distribution more towards the critical REE, and would indicate a more promising resource. The first cluster contains the most well-known carbonatite-type mineral ore deposits that contain almost exclusively the LREE, and together produce the large majority of global REE supply. These are considered unpromising according to this method. The second and third clusters contain many coals worldwide, and as will be shown in Chapter 4 of this dissertation, also include coals from North Dakota. The most promising resource identified here is the Longnan ion-adsorbed clay deposit in Southern China, which is currently almost the exclusive global supplier for HREE and most of the critical REE.

Seredin and Dai (2012) have concluded that coal, and in particular coal ashes, represent more promising resources for REE than most existing mineral ore deposits. In fact, they state that mining of the Mountain Pass and similar resources will neither mitigate the crisis in REE resources nor eliminate the shortage of the most critical REE, but will only result in overproduction of excessive Ce [52].

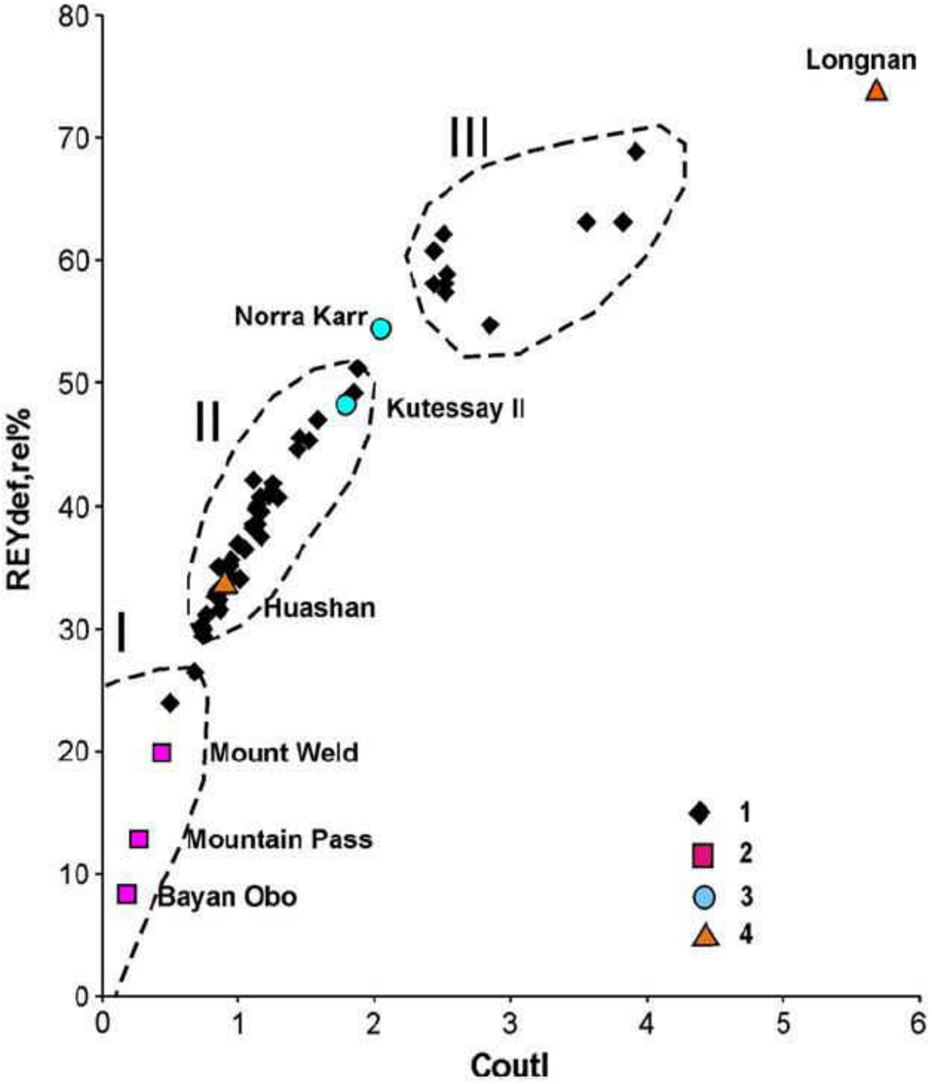


Figure 23. Classification of REE-rich coal by outlook for individual REE distribution in comparison with selected deposits of conventional types. X-axis: Coutl is the ratio of critical to excessive REEs. Y-axis: REYdef,rel% is the percentage of critical REE in the total REE. 1 - REE-rich coals; 2 - carbonatite deposits; 3 - hydrothermal deposits; 4 - weathered crust elution-deposited (ion-adsorbed) deposits. Clusters of REE-rich coal distinguished by outlook for REE distribution (numerals in figure): I – unpromising, II – promising, and III – highly promising [52].

3.1.3 Modes of Occurrence of Rare Earth Elements in Coal

A number of studies [56, 57, 58, 59, 60, 61, 62, 63, 64, 65], [66, 67, 68, 69, 70, 71] have shown that REEs in coal can be present in the following generalized groupings:

- Syngenetic clastic and pyroclastic minerals (mainly monazite, xenotime) or minerals of terrigenous (derived from erosion of rocks on land) and tuffaceous origin (i.e. zircon, apatite)
- Diagenetic and epigenetic minerals of authigenic origin. These can include aluminophosphates, sulfates of the alunite supergroup, water-bearing phosphates, oxides and carbonates or fluorocarbonates
- Organic compounds.

Overall, studies have suggested that both mineral and organic REE modes of occurrence are present in most coals [52], with the relative proportions and forms being highly variable depending on a number of factors such as the coal rank and depositional environment. A brief review of REE minerals and REE organic associations in coal are provided in the following sections.

3.1.3.1 Rare Earth Element Minerals in Coal

Seredin and Dai (2012) [52] have also complied a review of the REE minerals that are commonly found in coals globally. Fine-grained detrital (broken pieces of rocks/ minerals) REE-bearing minerals derived both from clastic and pyroclastic sources have been found in many coals [56, 65]. However, authigenic minerals represent the large majority of REE-bearing minerals found in coals. Impregnations of very fine-grained

REE minerals are common in coals, which are predominantly phosphates such as monazite. LREE-bearing minerals are the dominant form of REE minerals in coal, despite the fact that many coals are M-type or H-type. The minerals can often primarily be in the clay matter of the coal or in the partings or margins of the seams, with the organic matter free of the minerals. Other forms of REE minerals are carbonates and fluorocarbonates that are typical of REE-rich coals that were subjected to input by hydrothermal fluids. The coals that can be described as having a polygenetic input source (described previously in Section 3.1.1), can often have a wide array of REE-bearing minerals and can occur both in the clay and organic matter of the coals [67].

3.1.3.2 Rare Earth Element Organic Associations in Coal

Again, Seredin and Dai (2012) have compiled a review of the various forms of organic REE associations in coals [52]. Many REE-rich coals can contain a significant proportion of their total REE as organically associated, particularly in coal with low ash and low-rank (lignite, subbituminous). A number of inferred organic associations have been indirectly measured by methods such as negative correlation of REE content with ash yield and enrichment of REEs in the light specific gravity fractions [56, 57, 58, 62, 63, 67, 68, 71]. These types of indirect methods are validated by experimental work evaluating the sorption characteristics of REE by peat, coals and humic acids [72, 73]. Further evidence of organic associations can be inferred by the presence of mainly L-type REE-bearing minerals in coals with M-type or H-type distributions, suggesting that the medium and heavy REE are enriched in the organic matter.

Direct evidence of REE association with the organic matter in coal has been established as well. For example, Seredin and Shpirt (1999) [54] have shown that about 50% of the REE content of two Russian coals were contained within the humic matter, and were easily extracted by dilute caustic leaching. Their testing also showed that the humic matter is slightly enriched in the medium weight REEs, compared to the light and heavy REEs. Sequential extraction methods have also been used to determine REE modes of occurrence. For example, organically-bound REE were observed in a bituminous coal using a step-by-step acid leaching technique [56]. In general, there appears to be three types of REE organic associations: i) cations attached to organic acid groups, ii), REEs in organic complexes (chelate groups), and iii) adsorbed or weakly bound REEs on the organic matter. For example, Eskenazy [72] found that Na^+, K^+, $Ca^{2+,}$ and Mg^{2+} bound to –COOH and –OH were replaced by REE cations. Aide [74] showed that HREE-organic complexes are more stable than LREE-organic complexes, and that a decrease in pH causes a decrease in the stability of the complexes [75, 76]. Finkelman also found that the HREE preferentially complexed over the LREE with the organic matter [77]. Loosely bound REE can also be found adsorbed to clay matter within the organic matrix or onto the humic matter [63, 78].

It will be shown in Chapter 4 of this dissertation that the primary modes of occurrence of REEs in North Dakota lignite coal are organically associated either as ion-exchangeable cations on carboxylic acid groups or as complexes, loosely adsorbed on the clay minerals or organic matter, or present as REE-minerals.

3.2 Prospects of Coal as Alternative Resources for REE – U.S. Analysis

The major U.S. coal producing regions and coal ranks are shown in Figure 24. The U.S. has significant deposits of lignite, subbituminous, bituminous and some anthracite coals. According to the Energy Information Administration data [79], the U.S. ranks only behind China in total coal production, at about 900,000 thousand short tons in 2015 (Figure 25), with a large majority of that being bituminous and subbituminous coals, as shown in Figure 26. In terms of total reserves, the U.S. leads the world by a significant margin, with over one quarter of the world's proven reserves [80]. North Dakota by itself hosts the single largest deposit of lignite known in the world at an estimated 351 billion tons, with about 25 billion tons of that being economically mineable [47].

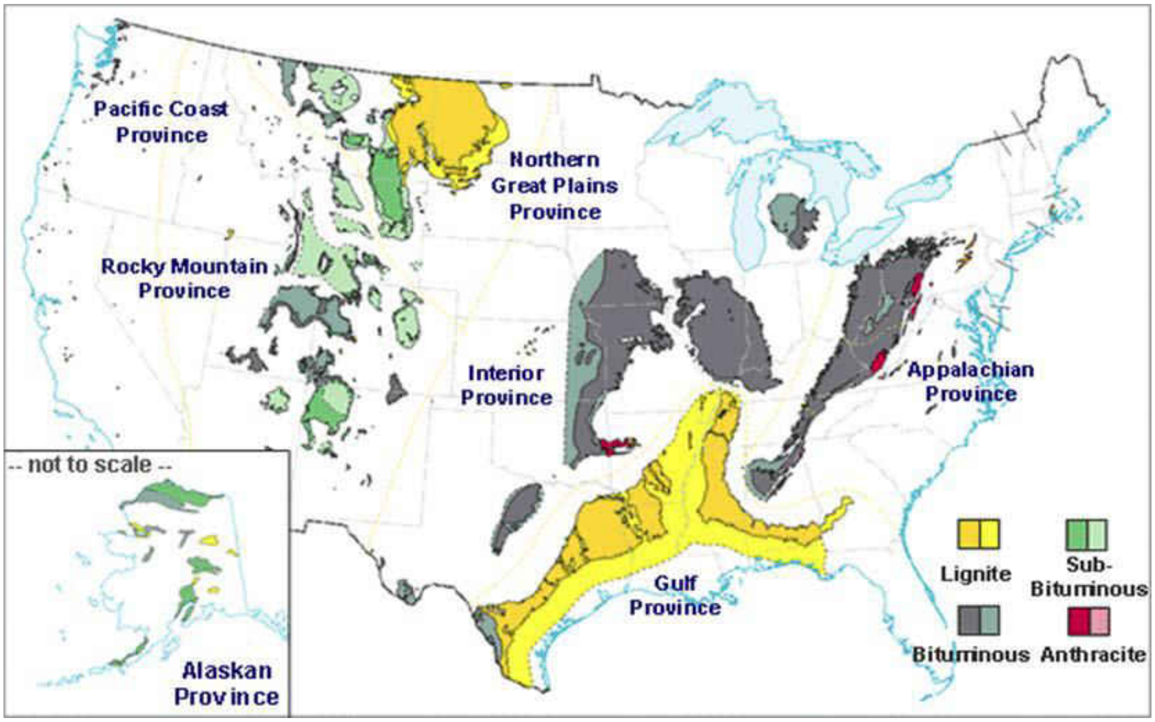


Figure 24. Major U.S. coal producing regions and coal ranks [81].

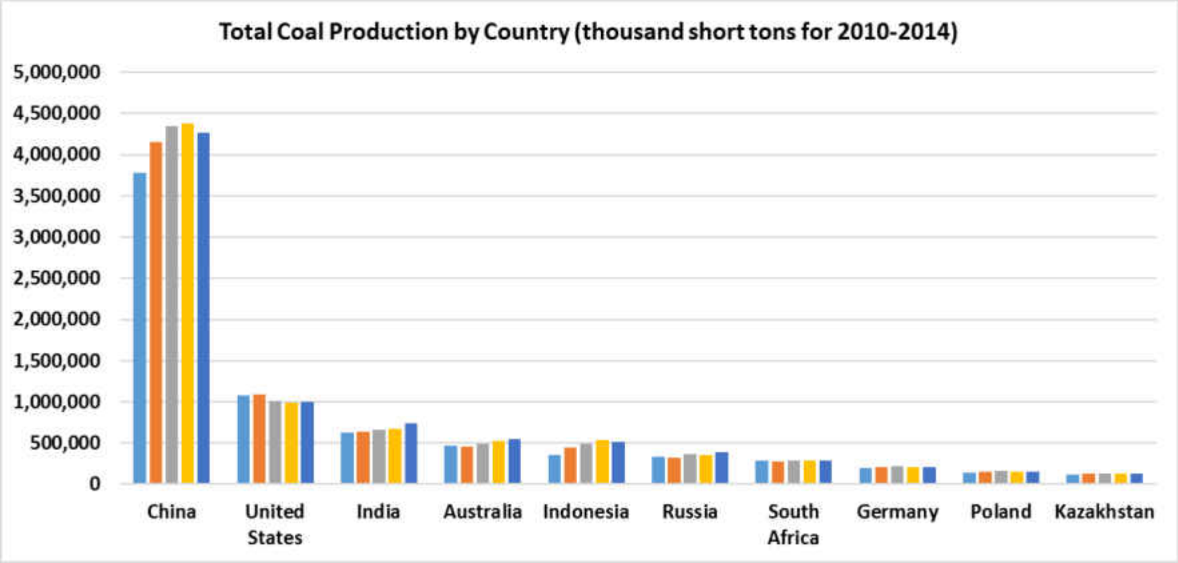


Figure 25. Total coal production by country. Bars represent individual years from 2010 to 2014 [79]

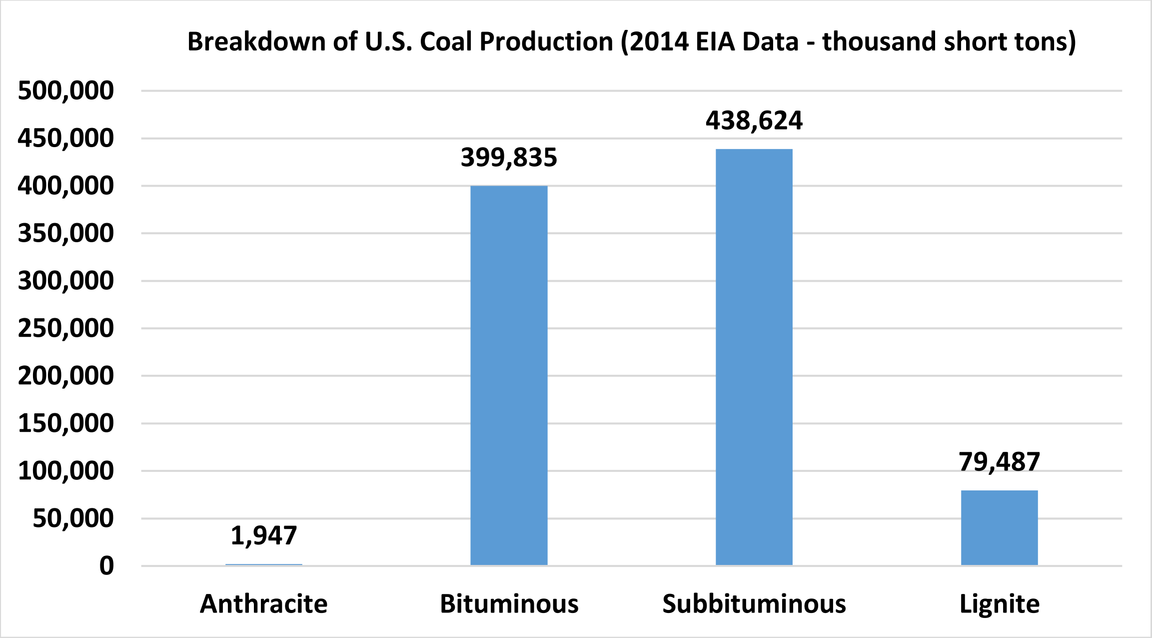


Figure 26. Breakdown of U.S. coal production by coal rank (2014) [79]

Ackman and others (2012) [81] performed a detailed assessment of the prospects of coal and coal byproducts as alternative resources for REE in the U.S. and found that "unintended production" of REE associated with coal mining potentially exceeds 40,000 tons annually, of that the HREE may exceed 10,000 tons annually. They estimated that total recoverable reserves of REE in coal may exceed 2 million tons for the major coalbeds and formations in the U.S. In addition to this, the existing coal mines have already absorbed the cost of mining and in many cases also the cost of transportation, crushing, grinding and coal cleaning. Therefore, there may be opportunities for value-added recovery of REEs in several locations throughout the coal utilization value chain, as summarized in Figure 27. For example, waste streams produced during the coal preparation/cleaning processes may be enriched in REEs or other valuable metals as compared to the as-mined coal and would be attractive targets. Further, in many cases, the fine coal tailings streams have considerable 'good coal' remaining, but that cannot be recovered economically due to their fine particle size. However, by recovering REEs from these wasted streams, it may provide the economic incentive to recover the coal particles, not only resulting in a new revenue stream in the REEs, but also improved efficiency of the coal preparation plant.

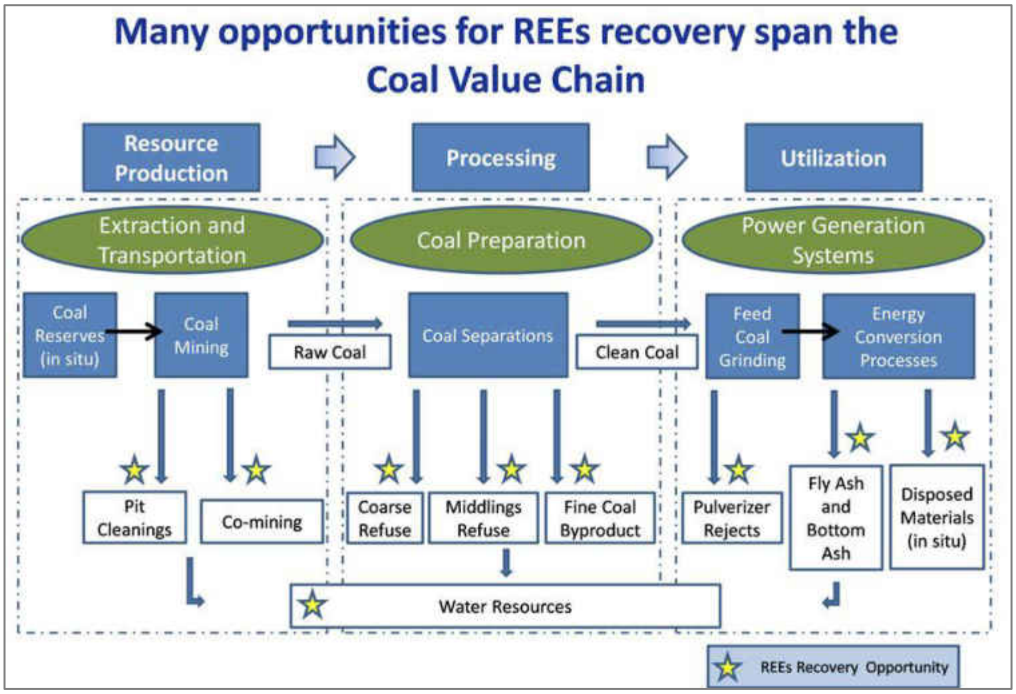


Figure 27. Potential options for for REE recovery along the coal value chain [81]

In particular, a major advantage of REEs found in coal-related materials is the relatively high proportion of the more valuable critical and heavy REE compared to traditional mineral ore deposits, such as Mountain Pass mine and Bayan Obo in China, as was previously discussed in Section 3.1.2. This is further illustrated in Figure 28 which compares various U.S. coal formation REE content distributions (ash basis) to Earth's crustal averages, the Mountain Pass carbonatite ore and the Chinese ion-adsorbed clay resource (Chinese lateritic REE ore). This data shows that coals are enriched above crustal averages, and although the content of the LREE in coal is significantly lower than the carbonatite ore, the content of less common, more critical and higher value HREE in coal exceeds that of the carbonatite, with similar concentrations as the Chinese clay (current global source of HREE).

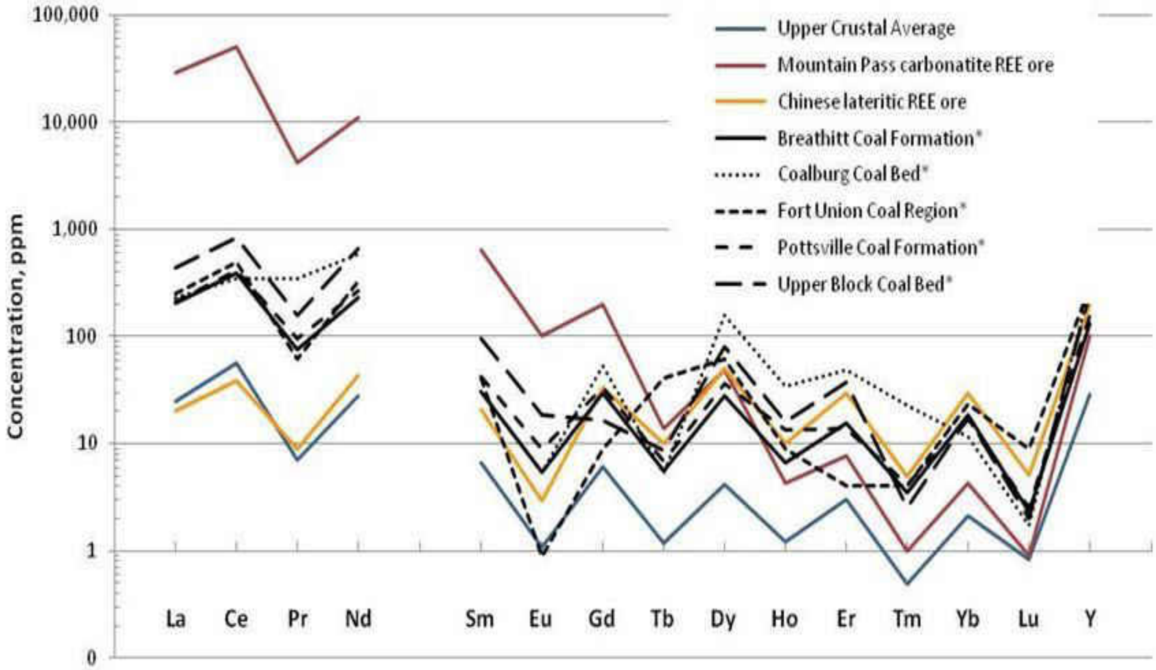


Figure 28. Comparison of the content of REEs in various geological sources including coals (ash basis) and mineral ores [81]

3.2.1 USGS Coal Quality Database

The USGS Coal Quality Database (CoalQual) [82] has been used as a source for initial assessment of coal producing regions as targets for REE recovery, as it is the most comprehensive publically available set of data regarding coal composition, including trace elements and REEs. However, it is not a perfect data set. Specifically, the data has been collected over a number of years, and the measurements were taken using the analytical tools available at the time, many of which will not have the accuracy or precision of today's techniques. Additionally, not all of the coal producing regions in the database are equally represented and not all of the samples within the database have complete REE analysis. Regardless, as an initial assessment tool, the database is useful.

Figure 29 and Figure 30 display graphically the data available nationally for REE content in the CoalQual database. In Figure 29, the REE content has been grouped into geographical regions in the U.S. and overlaid on the major coal production regions. This figure highlights specific samples with total REE content above 300 ppm (whole coal basis) and those with less than 300 ppm. This data clearly shows that the Appalachian coals are highly represented in the database, but that the locations with the highest REE content are spread out across the country in several coal regions, including North Dakota. The data shown in Figure 30 is the total REE content (whole coal basis) for all samples in the database broken town by tiers of REE content in a histogram form. The data shows that the top 25% of samples have REE content above ~90 ppm and the top 3% above 200 ppm.

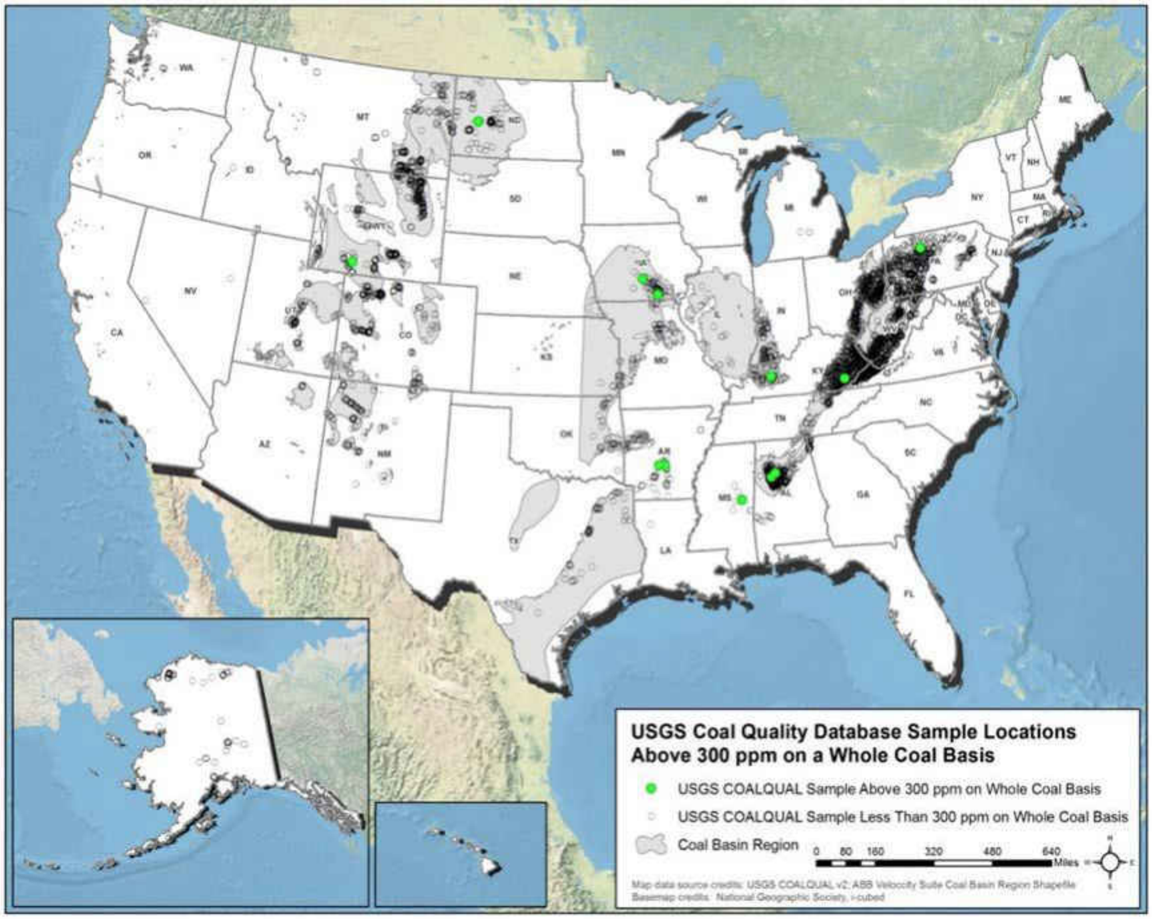


Figure 29. Summary of data in USGS CoalQual database for REE content by geographical region and coal basin [81]

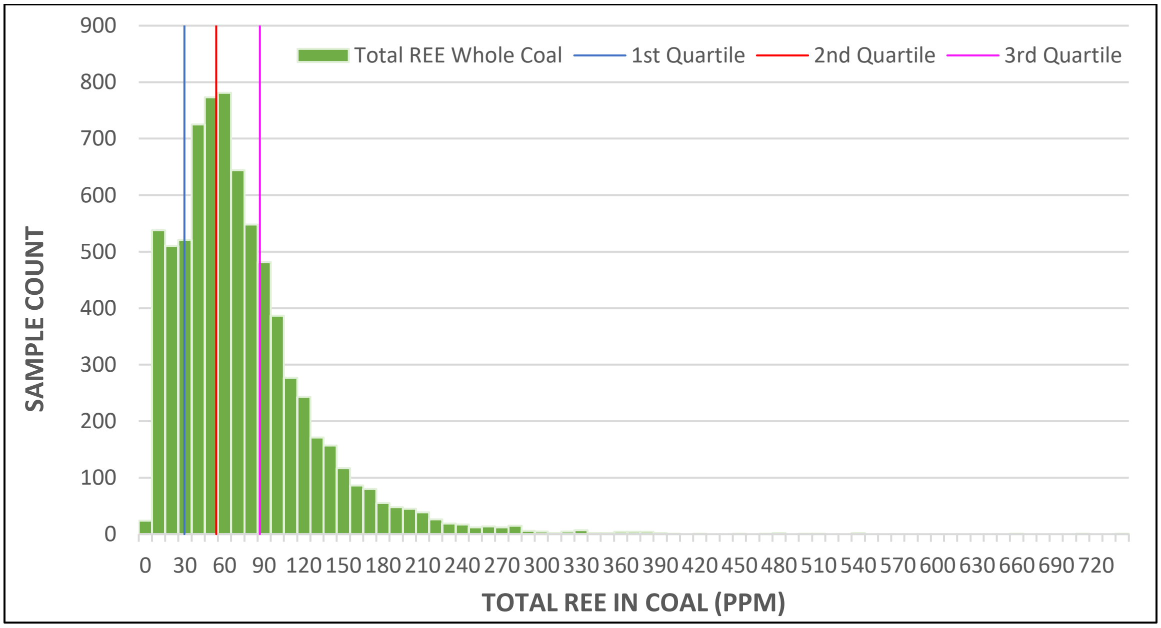


Figure 30. Histogram of REE content in coals in the USGS CoalQual database [82]

When looking specifically at the data available for North Dakota, only 180 samples in total are in the database, with only 33 of those having complete REE analysis. These 33 samples are plotted in Figure 31 which shows that on a whole coal basis, three samples are above 100 ppm, and on an ash basis, nine samples are above 700 ppm. When using the evaluation tool developed by Seredin and Dai [52], Figure 32 contains the analogous data to Figure 23 for the 33 North Dakota coal samples. These points would all fit into Cluster II, or the promising category as established by Seredin and Dai.

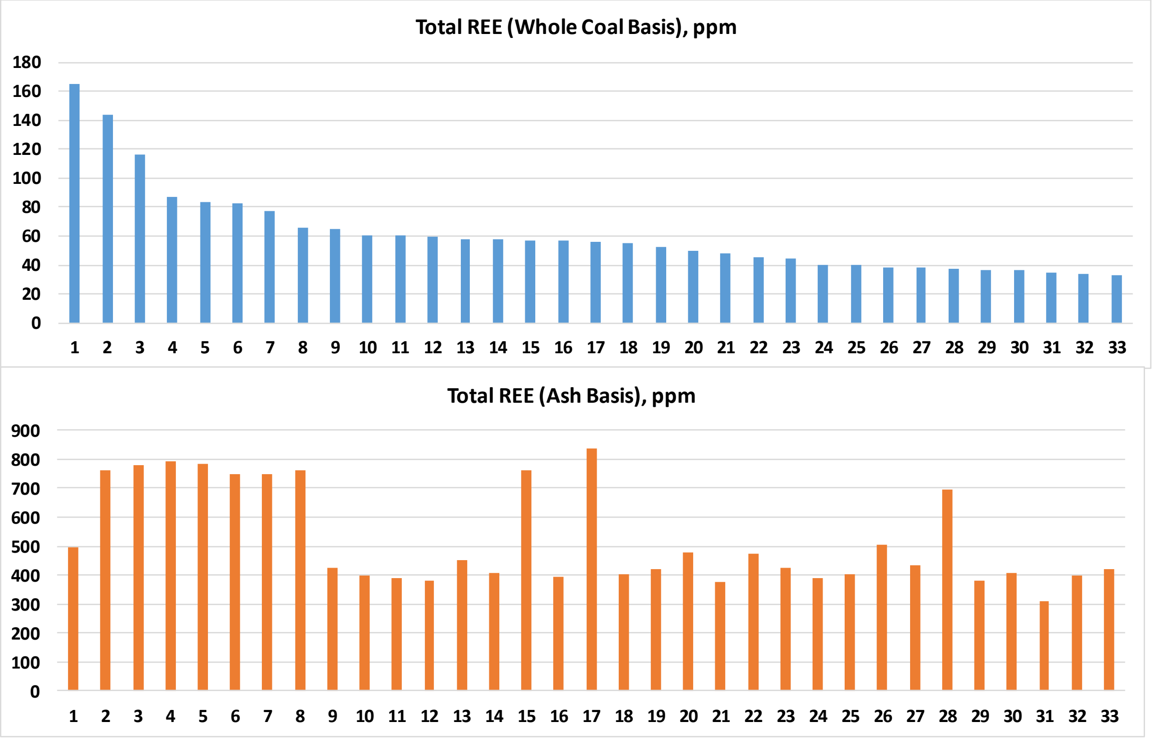


Figure 31. REE content in the 33 samples in the USGS CoalQual database for North Dakota with complete REE analysis [82]

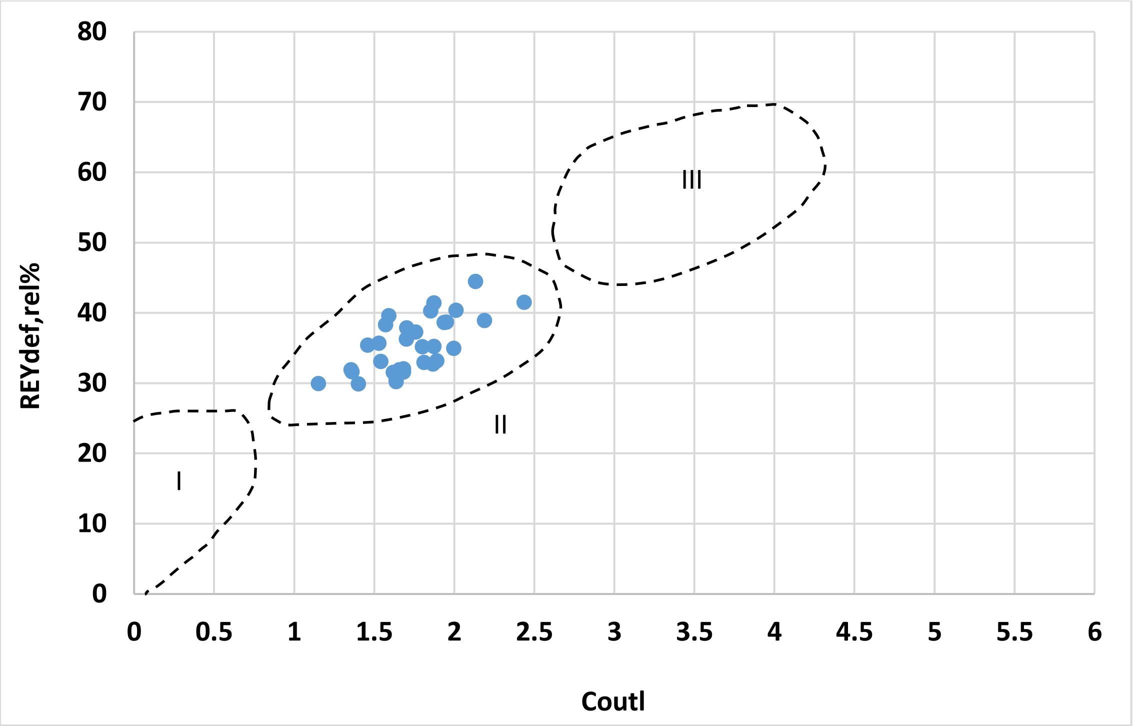


Figure 32. Seredin and Dai evaluation method [52] for North Dakota coals in the USGS CoalQual Database [82] with complete REE analysis (all fit into Cluster II in Figure 23)

As mentioned above, not all coal producing regions are equally represented, and based on the limited data available for North Dakota, one could conclude that it is one of these underrepresented regions. However, although not all of the 180 samples have completed REE analysis, all have at least Sc and Y, and most have Yb as well. Linear regressions for the 33 data sets with complete REE analysis have been calculated as shown in Figure 33 for: i) Total Sc, Y and Yb versus Total REE, and ii) Total Sc and Y versus Total REE. Both regressions show reasonable agreement and clear trends, with R^2 statistics of 0.55 and 0.57, respectively. Although obviously not perfect agreement, when using these regressions and applying them to the remaining samples in the database, the projected REE content can be calculated for all 180 samples as shown in Figure 34. These projections show that the samples in the database for North Dakota could contain a total of 36 samples with REE content higher than 100 ppm on a whole coal basis or 700 ppm on an ash basis, compared to only 10 such samples that had complete REE analysis. This includes seven samples that would exceed the top 3% threshold of 200 ppm on a whole coal basis. Of these 36 samples, most were located in either Stark or Mercer counties, as shown in Table 7. However, when looking at the specific samples with highest whole coal and ash basis REE content, Stark and Dunn counties appear to be most enriched in REEs.

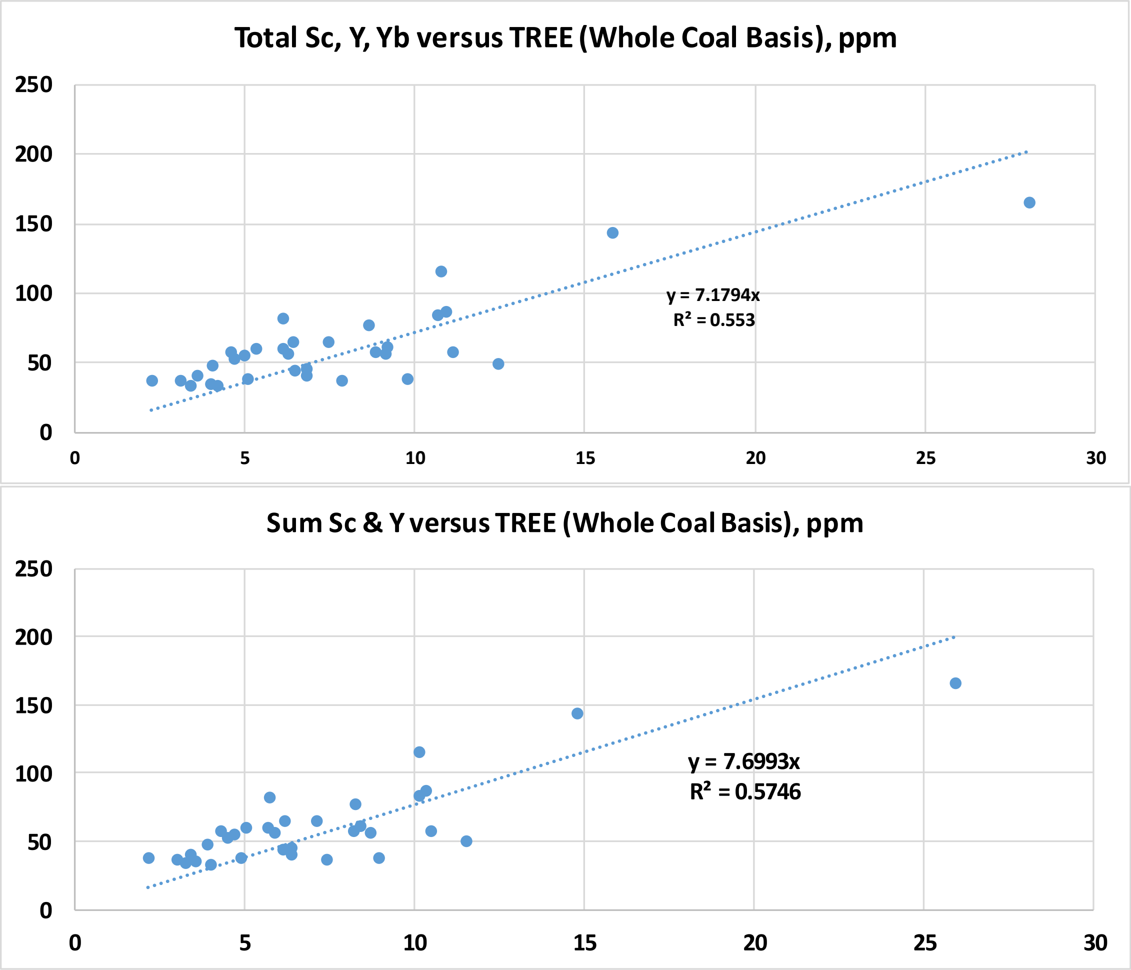


Figure 33. Regression analysis for partially complete REE analysis for North Dakota samples in the USGS CoalQual database

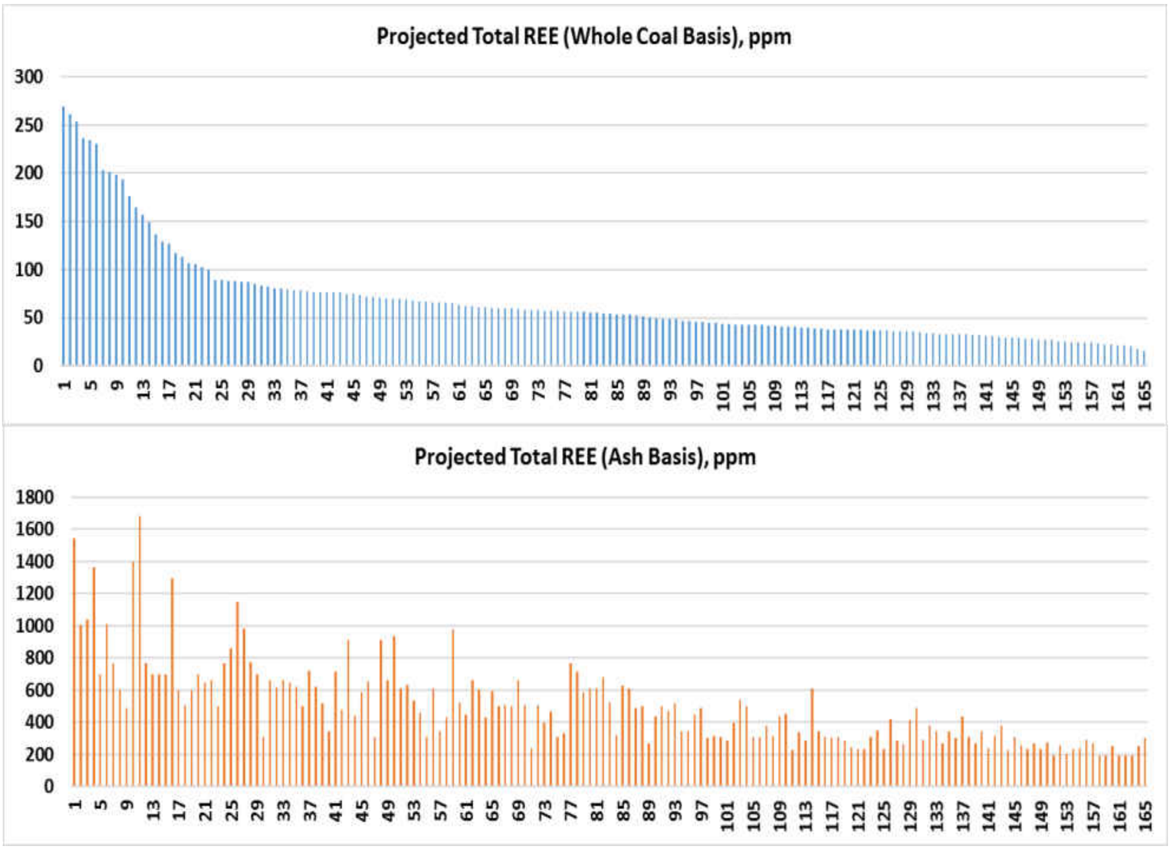


Figure 34. Projected REE content for all North Dakota samples in the CoalQual database based on regression of partially complete samples shown in Figure 33

Table 7. North Dakota counties with samples with highest projected REE content

County	**Number of Samples: > 100 ppm (whole coal) or > 700 ppm (ash)[1]**
Stark	12
Mercer	10
Dunn	5
Oliver	4
Williams	3
Golden Valley	1
McLean	1

1. REE content based on projected values from Figure 33

Overall, the data contained in the CoalQual database suggests that a large number of coals nationally would be considered targets for REE recovery evaluations. Further, given the massive lignite reserves in North Dakota, combined with the promising, yet underrepresented data for the State in the CoalQual database, it could be assumed that significant quantity of REE-rich coals are available in North Dakota, thus making North Dakota lignite a promising source for REE recovery.

4 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.

4.1 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 35 shows an overall map of the coal producing regions in North Dakota. Figure 36 shows a map of the Hagel coal zone, and Figure 37 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.

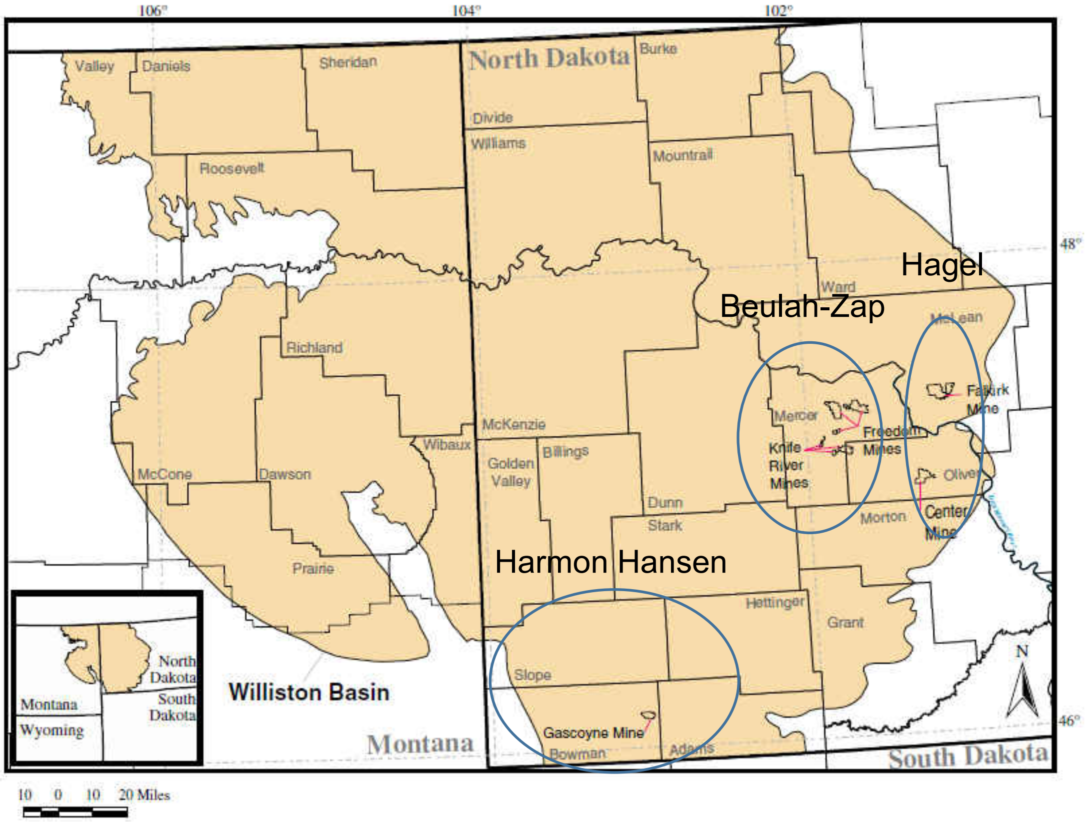


Figure 35. Map of the Williston Basin and coal zones in North Dakota [83]

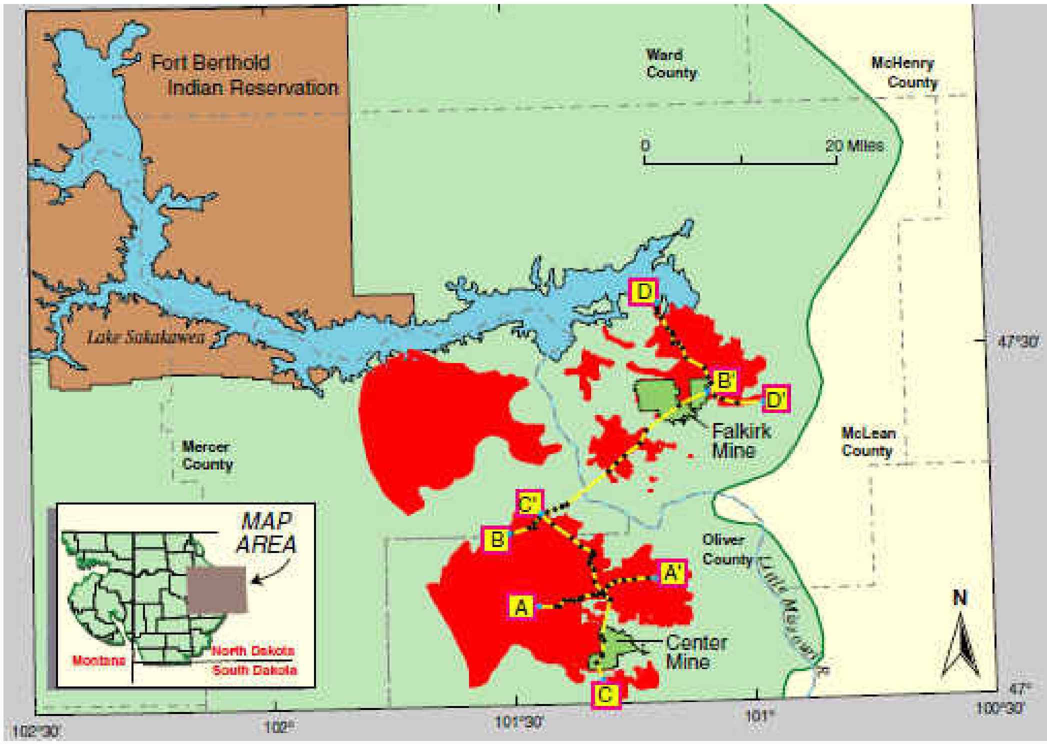


Figure 36. Map of the Hagel Coal Zone - samples collected mainly from Falkirk Mine [83]

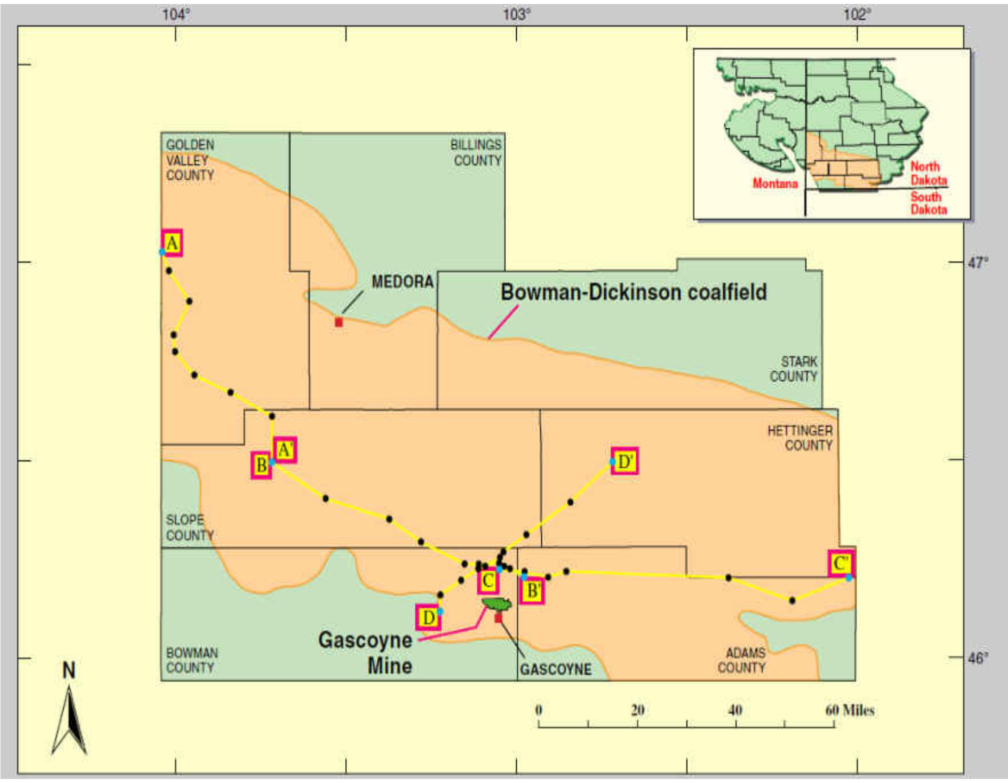


Figure 37. Map of the Harmon-Hansen Coal Zone - samples collected from Slope County [83]

The following sections provide additional details on the sampling activities at each of the above locations. The list of samples collected in the project is available in Appendix B.

4.1.1 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 38 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.

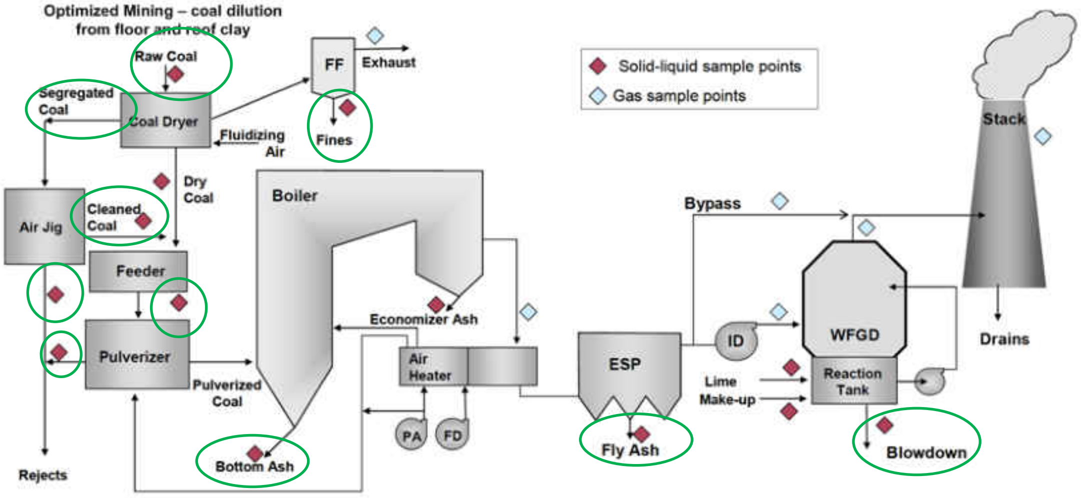


Figure 38. Schematic of the Coal Creek Station DryFining system and power system, with sampling points identified by green circles

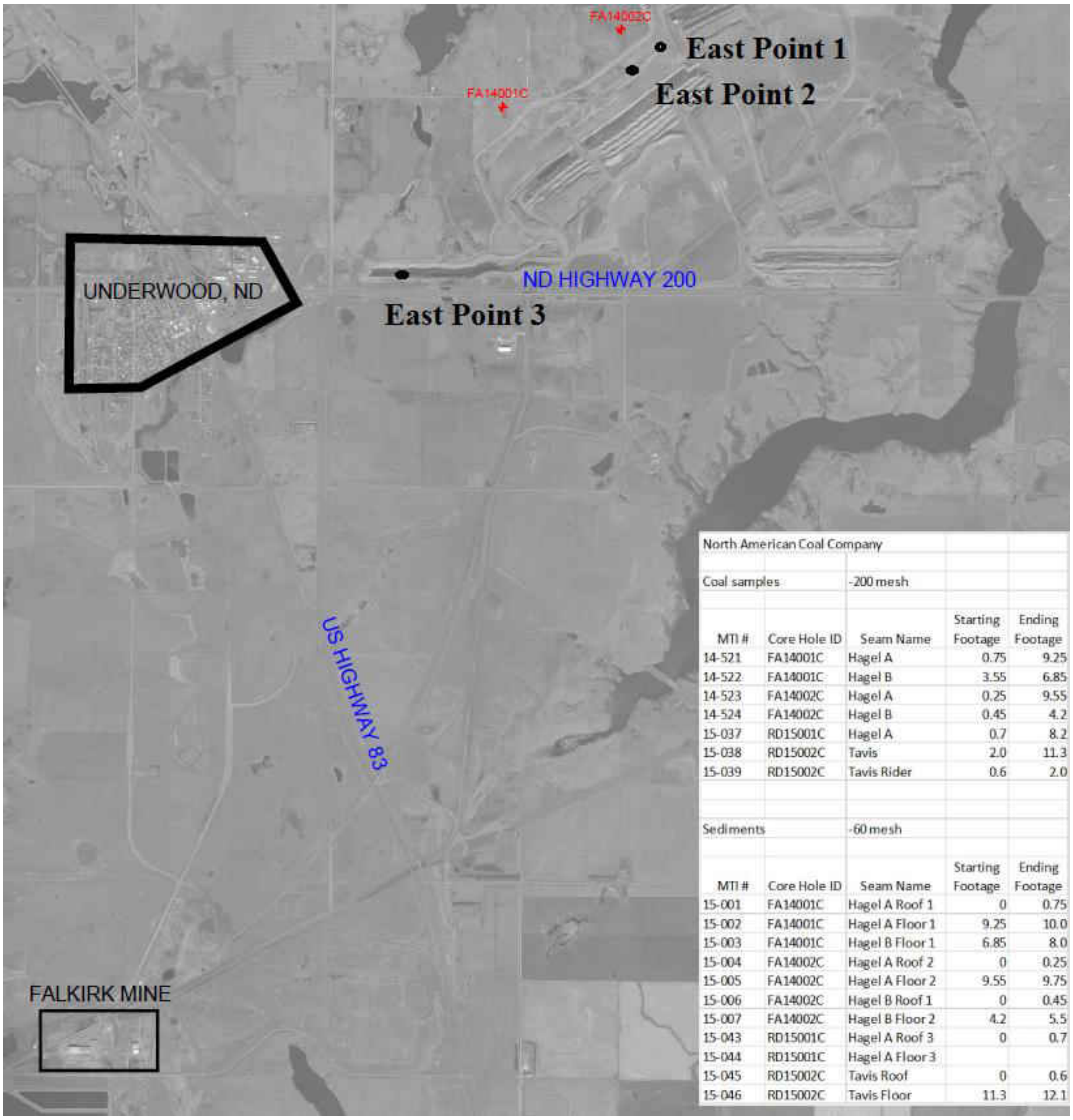
4.1.2 Sampling at Falkirk Mine

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 5 of this dissertation. 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 NAcoal 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 39 and Figure 40 show the map of sampling locations at the Falkirk mine. Figure 41 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 8.



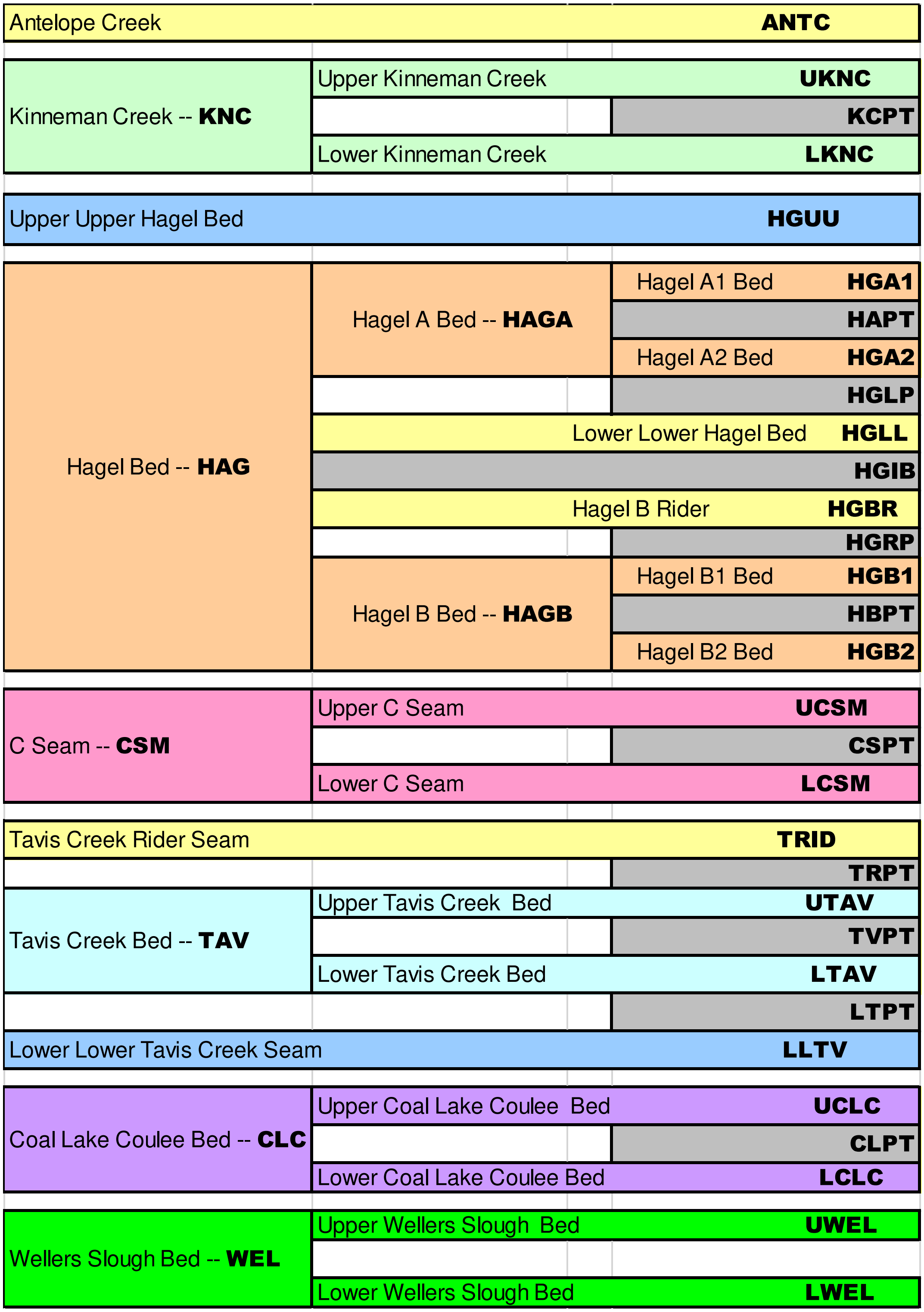
North American Coal Company

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

Figure 40. 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 41. Generalized stratigraphic column and seam codes at Falkirk mine.

Table 8. 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 40 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 39 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 39 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 8 Continued

Sampling Point	Coal Seam	Layer	Location	Mining Status (Yes/No)	Collected from	Note
East Point 3 - See Figure 39	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	

4.1.3 Other Sampling

In addition to samples collected from Falkirk Mine and Coal Creek Station, other samples were supplied 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

4.2 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 9, with additional details in the following sections.

Table 9. 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)
	Chemical Fractionation	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, Chemical Fractionation.

The following sections briefly describe each of the analytical methods used, along with equipment specifications.

4.2.1 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. Further Preparation: additional preparation was performed based on the requirement of the analysis method.

4.2.2 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) [84], 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 10. 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 [85] 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 10. 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

4.2.3 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.

4.2.4 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.

4.2.5 Chemical Fractionation

Chemical Fractionation is a sequential solvent extraction method developed to quantitatively determine the modes of occurrence of trace elements in low-rank coals [86], based on the extractability of the elements in solutions of water, 1 molar ammonium acetate, and 1 molar hydrochloric acid. This type of analysis is especially important for low-rank coals that can have significant quantities of organically bound elements which are ionically dispersed within the organic matrix of the fuel and are essentially invisible to SEM and mineralogical techniques. The flow diagram shown in Figure 42 illustrates the technique. A 75-gram sample of –45 µm (–325-mesh) vacuum-dried coal is stirred with 160 mL of deionized water to extract water-soluble minerals such as sodium chloride or sodium sulfate. After being stirred for 24 hours at room temperature, the water–coal mixture is filtered. The filtered coal is dried, and a portion is removed to be tested by ICP-MS to determine the concentration of each element remaining. The residues are then mixed with 160 mL of 1 molar ammonium acetate (NH4OAc) and stirred at 70°C for 24 hours to extract the elements associated with the coal as ion-exchangeable cations present primarily as the salts of organic acids. The ammonium acetate extractions are performed two more times to effect complete removal of the ion-exchangeable cations. After the third ammonium acetate extraction, a sample of the dried residue is analyzed by ICP-MS. The remaining residue of the ammonium acetate extractions is then stirred with 1 molar hydrochloric acid (HCl) at 70°C for 24 hours to remove the elements held in coordination complexes (chelates) within the organic structure of the coal, as well as acid-soluble minerals such as carbonates, oxides and sulfates. The hydrochloric acid extraction is repeated once. The residue is then analyzed by ICP-MS. The elements remaining in the sample after the extractions are determined by difference. The non-extractable elements are associated in the sample as silicates, aluminosilicates, sulfides and insoluble oxides.

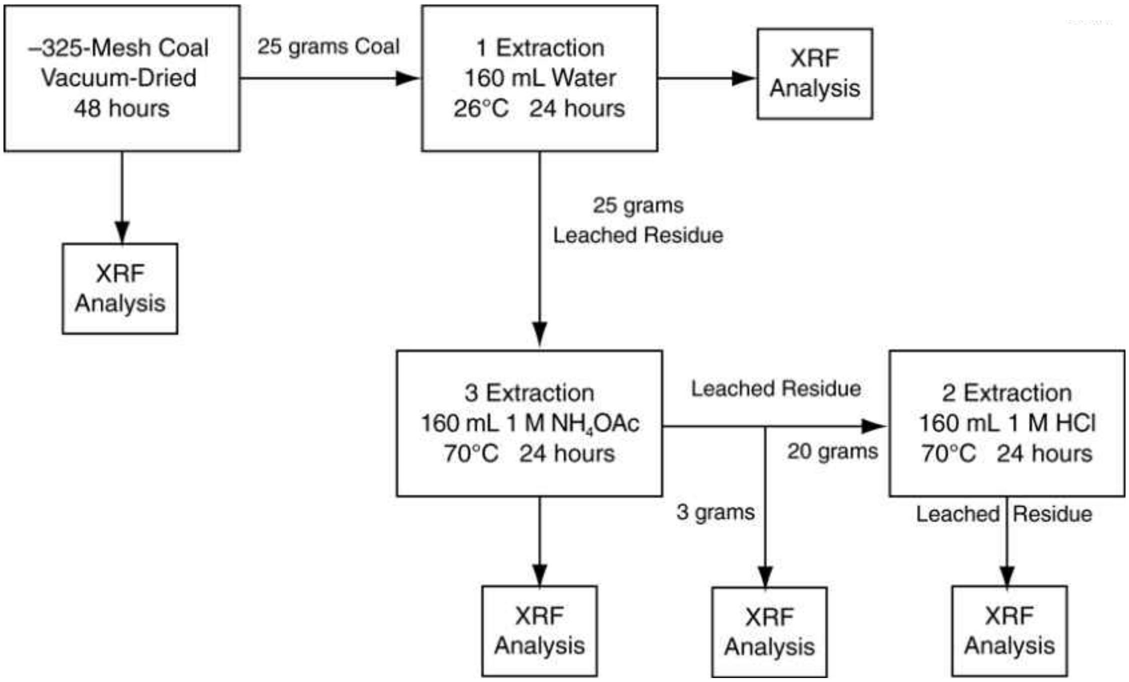


Figure 42. UND Chemical fractionation procedure - Note ICP-MS is used instead of XRF.

4.2.6 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 5 of this dissertation.

4.3 Characterization Results

The characterization results are presented in the following sections.

4.3.1 Overall ICP-MS Results and REE Classification of Samples

Appendix C contains the complete data for all of the ICP-MS analysis done in this project. Overall, 202 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 43 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.

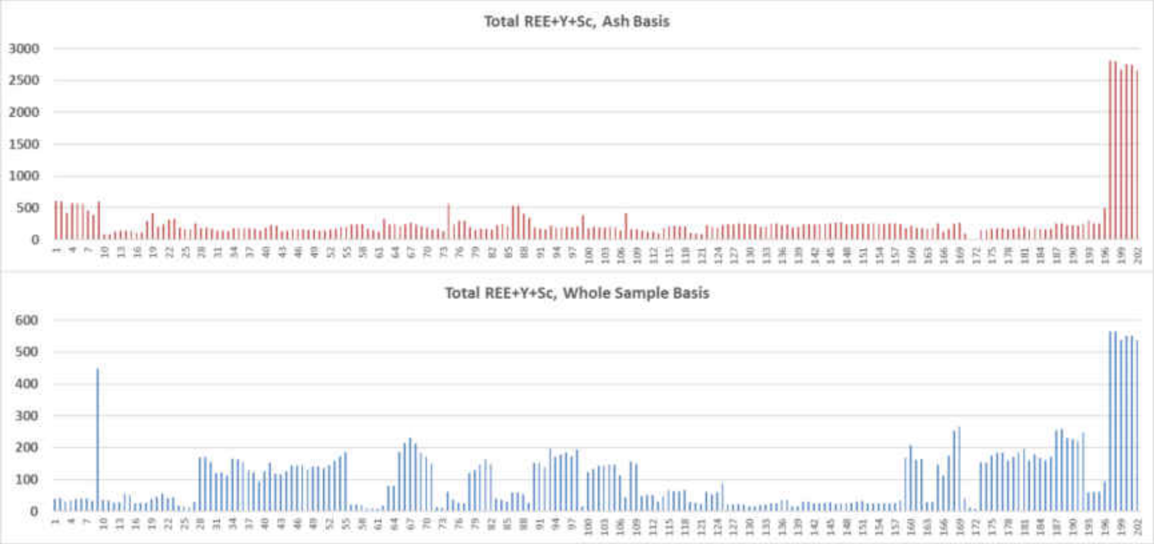


Figure 43. Results of ICP-MS for total REE content - random sample numbers on X-axis

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 44 shows all of the data from Figure 43, 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 previously discussed in Chapter 3 that concluded that the HREE have higher affinity to organic matter than the LREE.

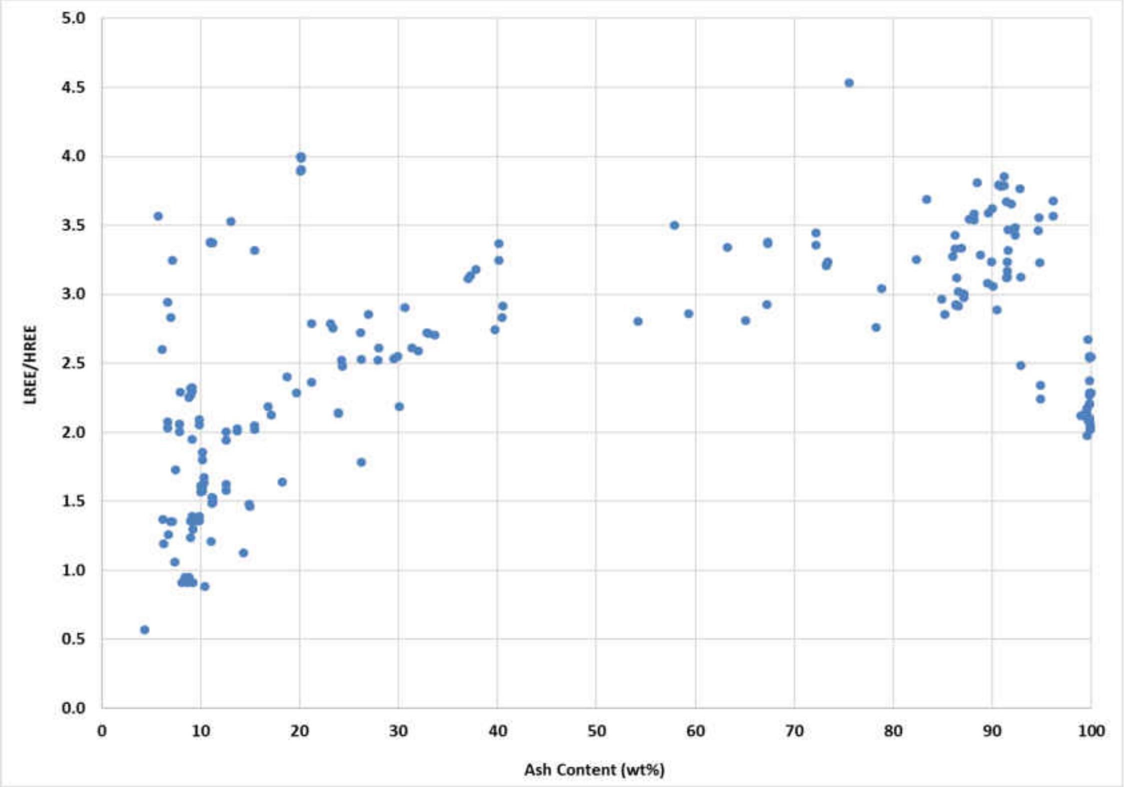


Figure 44. Ash content versus LREE/HREE for all samples analyzed in the project

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 (data provided in

Chapter 1) and have been plotted against ash content of the sample, as shown in Figure 45. 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.

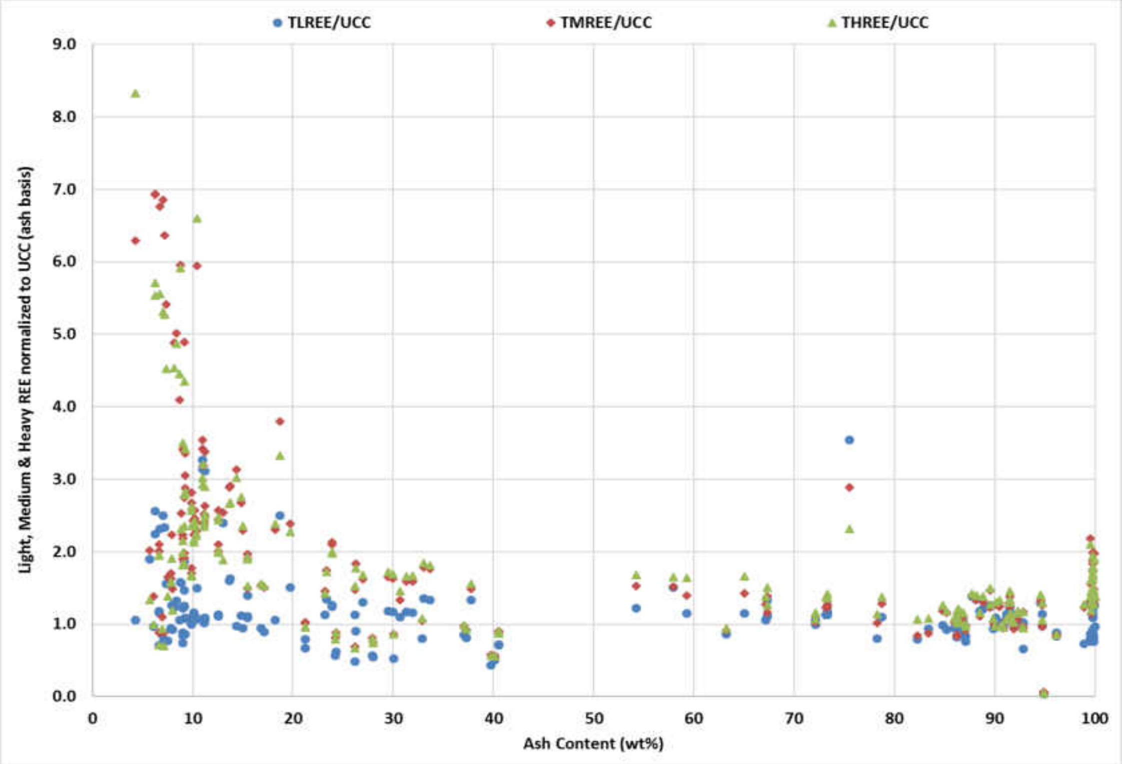


Figure 45. Total light, medium and heavy REEs normalized to crustal averages plotted against ash content for all samples analyzed

Figure 46 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 Harmon-Hansen coal sample.

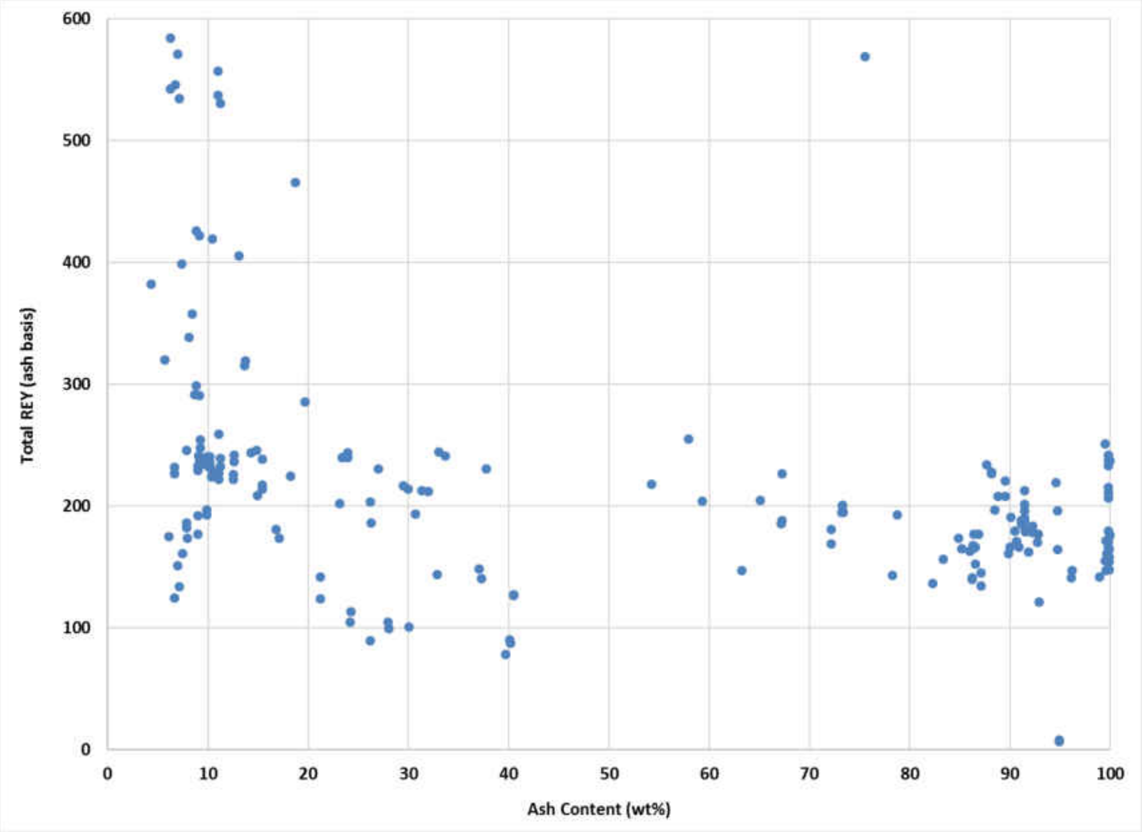


Figure 46. Total REE (ash basis) versus ash content of the sample for all samples analyzed

Chapter 3 previously described an evaluation method developed by Seredin and Dai (2012) [52] 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 47. 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 47 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 48. Again, there is a clear trend that has the low ash samples being enriched in the critical REEs.

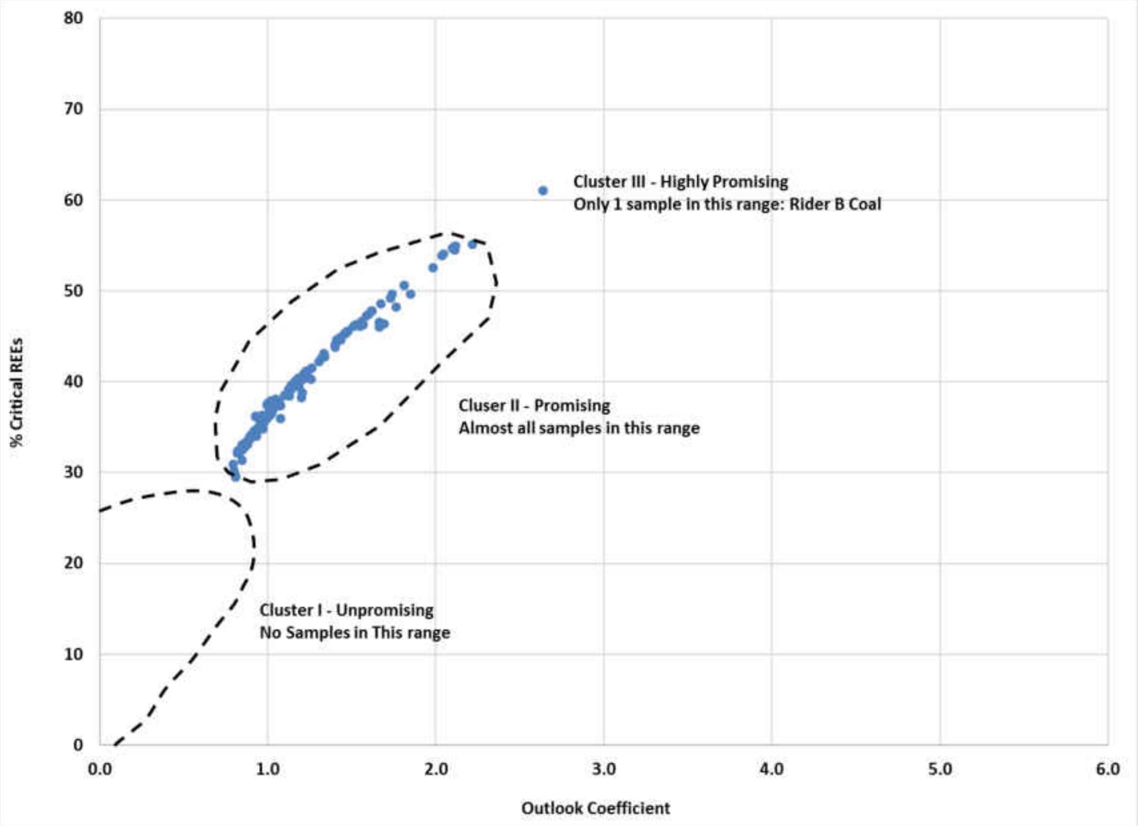


Figure 47. Method of evaluating the relative content of critical REEs within the material - Seredin and Dai method (2012) [52]; x-axis represents ratio of critical to excessive REE; y-axis represents percentage of critical REE within total REE

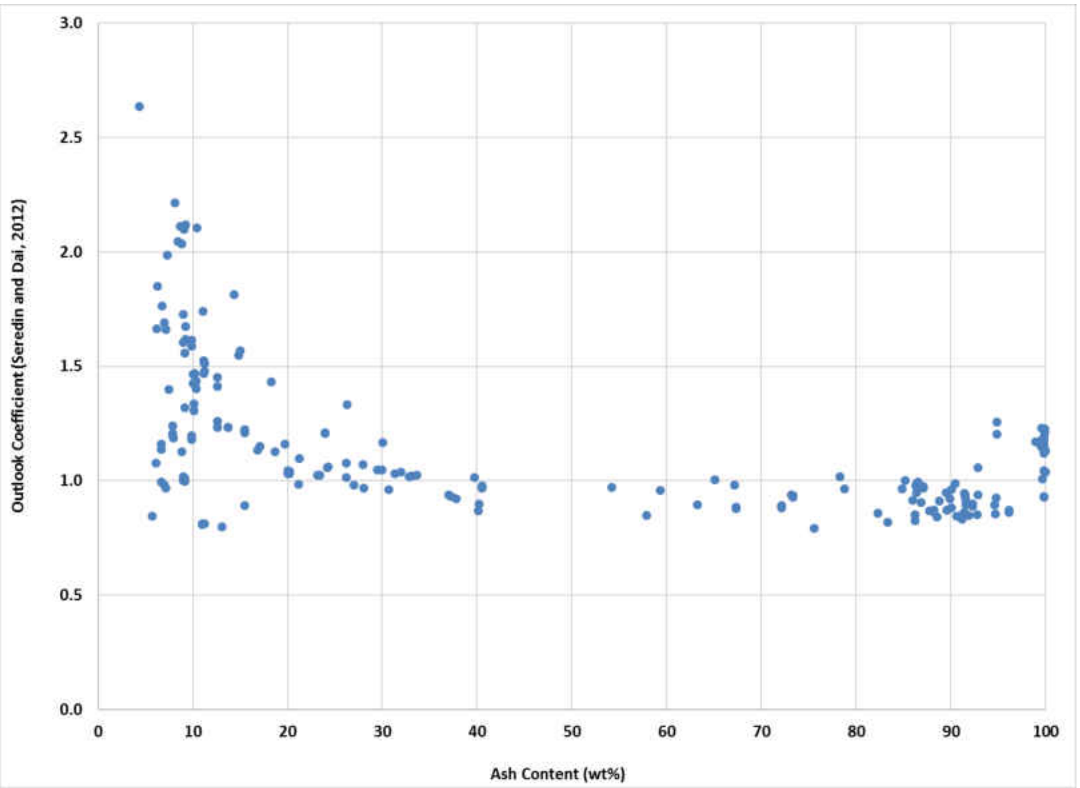


Figure 48. Seredin and Dai (2012) [52] outlook coefficient vs. ash content of the sample

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 using this approach which were discussed in Chapter 3 of this dissertation. Figure 49 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.

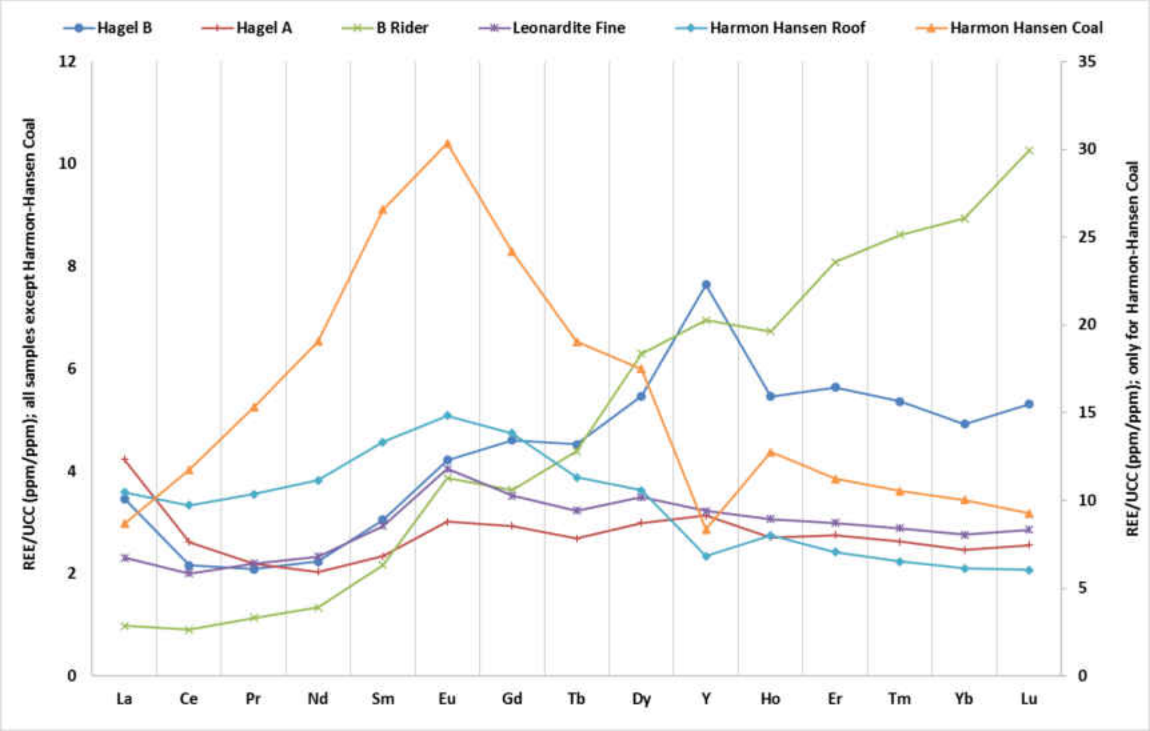


Figure 49. UCC-normalized REE distribution for selected samples

This same type of analysis method has been plotted in Figure 50 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 49). 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 and the surface water chemistry present during infiltrational accumulation of the REEs.

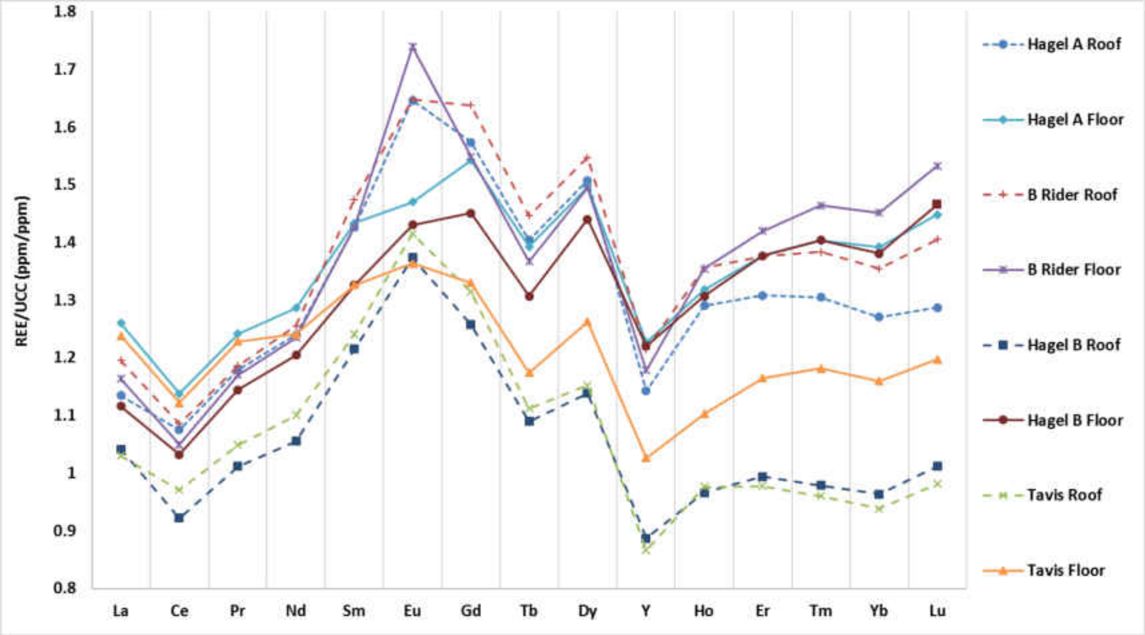


Figure 50. UCC-normalized REE distribution for selected roof/floor samples from Falkirk Mine

4.3.2 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 51 and Figure 52, respectively. Based on some prior work by Karner and others (1984, 1986) [45, 46] 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 52, 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 5).

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 11. 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 11. 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

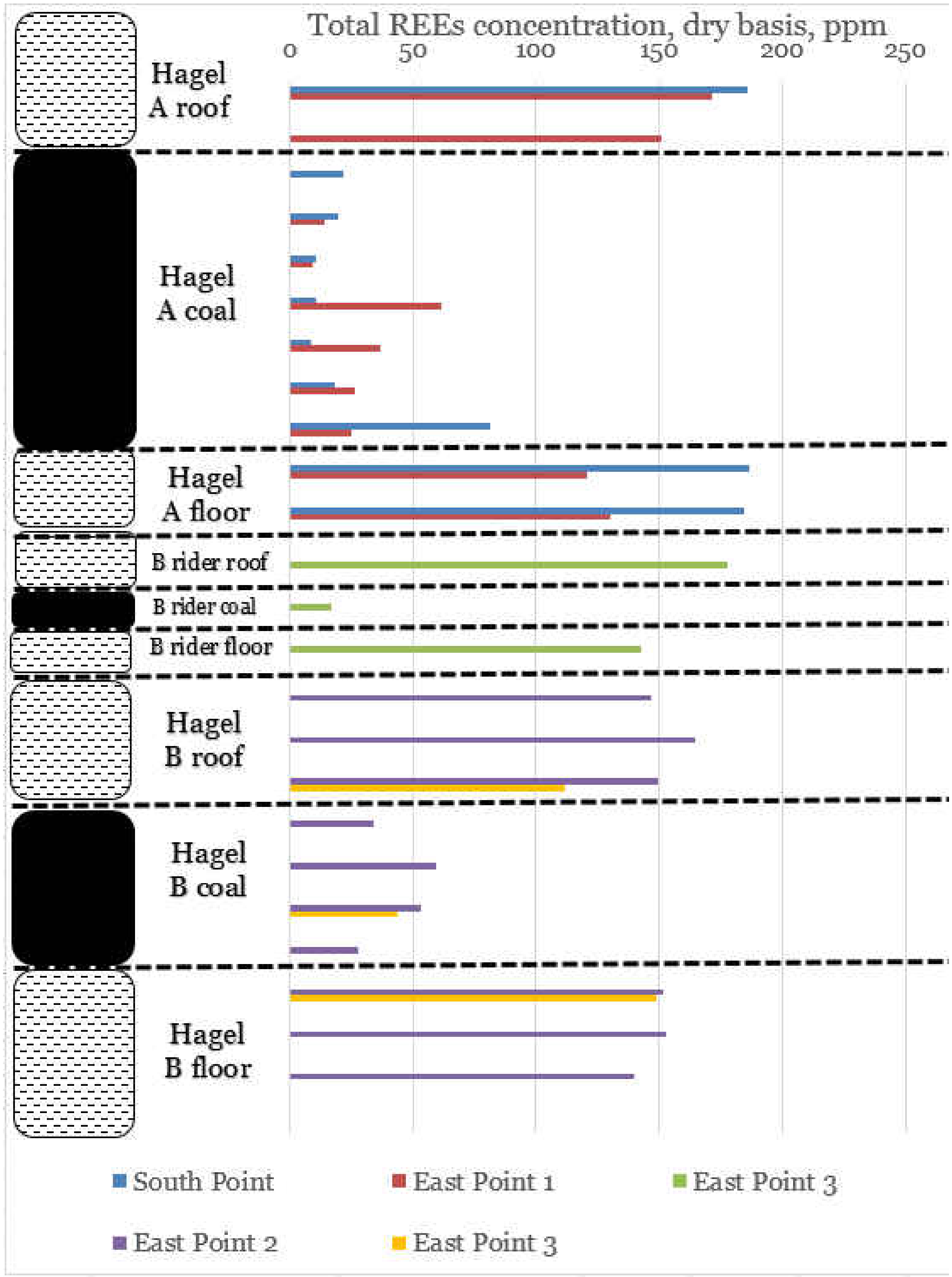


Figure 51. Total REE content in Falkirk Mine stratigraphic column as sampled (whole sample basis)

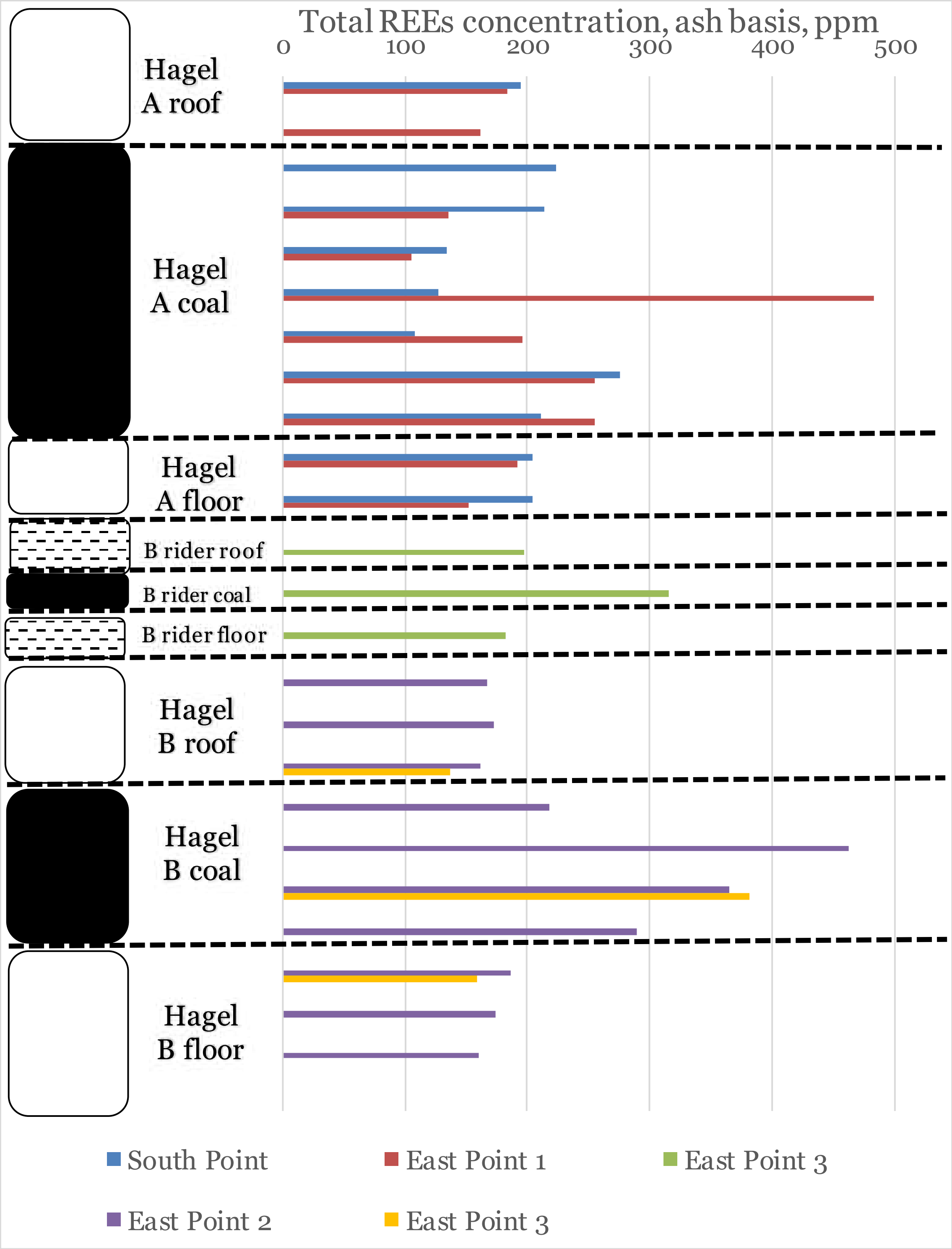


Figure 52. Total REE content in the Falkirk Mine stratigraphic column as sampled (ash basis)

4.3.3 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 12. 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 12. 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 12 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 12, 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. Maybe 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 yet again say something about the modes of occurrence of the REE in the coal.

4.3.4 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 13 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 13. 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

Table 13. 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 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 [87]. Table 14 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 14. 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) [49, 48], has been sampling lignite coal and related materials primarily in western and southwestern North Dakota and analyzing for REE content. Their efforts identified one location near

Amidon, Slope County, North Dakota that had particularly elevated levels of REE. Samples were collected from an outcropping of the Harmon-Hansen coal zone and included a coal and roof sediment sample. The coal sample was available in rather small quantity and was already ground/homogenized as supplied, but the roof sediment sample was available in a coarse grind in several pound quantity and was homogenized prior to analysis. The content in these samples is provided in Figure 53, and compared as a reference to the Hagel B from Falkirk Mine (all values are on a dry whole sample basis). Table 15 compares the Harmon-Hansen samples to Hagel B on both a whole sample and ash basis. The REE content in both of the Harmon-Hansen samples is exceptionally high, well above anything else measured in this project. Besides the high levels, one interesting finding is that the whole sample basis content of REE is actually higher in the coal than in the roof sediments. This was not the case for the Falkirk or Freedom Mine samples analyzed, indicating a likely different mode of REE occurrence and/or depositional environment for the Harmon-Hansen at this sample location.

Table 15. Comparison of total REE content of Harmon-Hansen samples and Hagel B coal

Sample	**Whole Basis, ppm**	**Ash Basis, ppm**
Harmon-Hansen Coal	551	2178
Harmon-Hansen Roof	449	595
Hagel B Coal	38	556

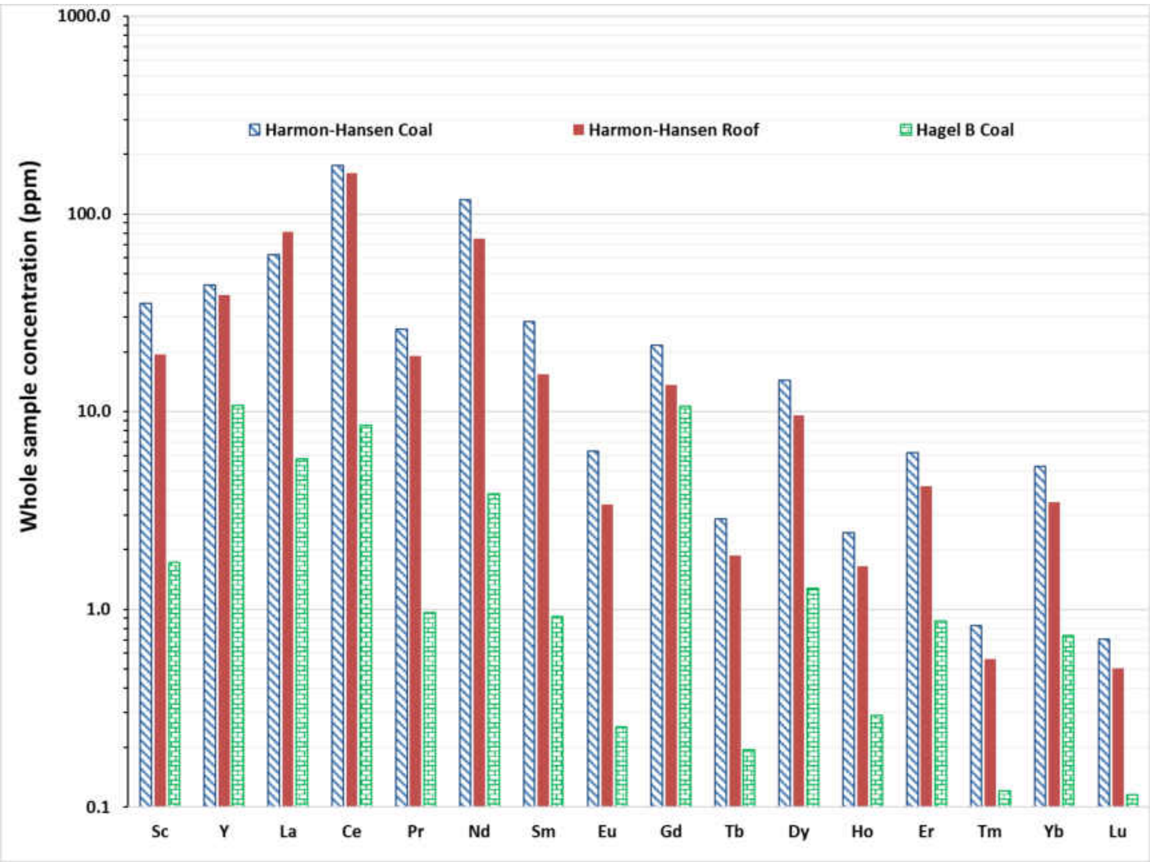


Figure 53. Comparison of REE content in Harmon-Hansen samples and Hagel B coal (y-axis on logarithmic scale)

4.3.5 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.

4.3.5.1 Manual SEM-EDS

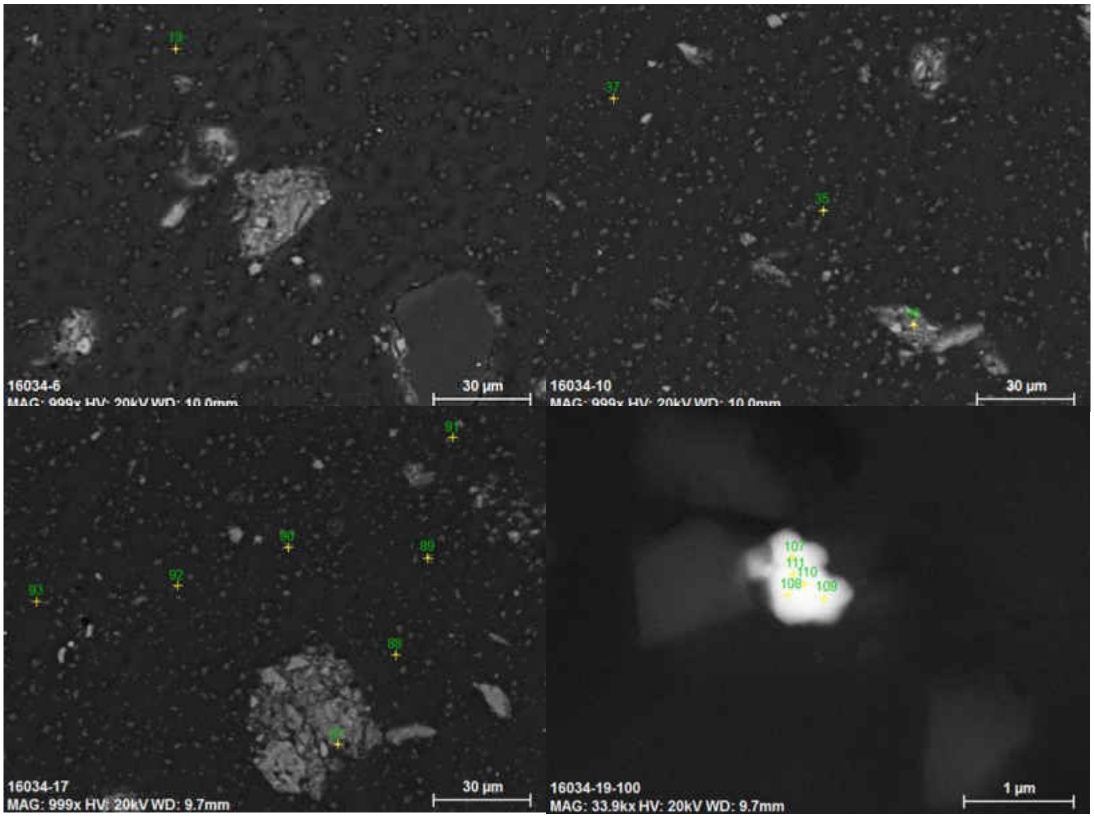
Overall, three sediment samples were analyzed by SEM-EDS in manual mode to find and type various REE-bearing mineral grains in the samples. The samples tested included:

- 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 54 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 (Chapter 3).

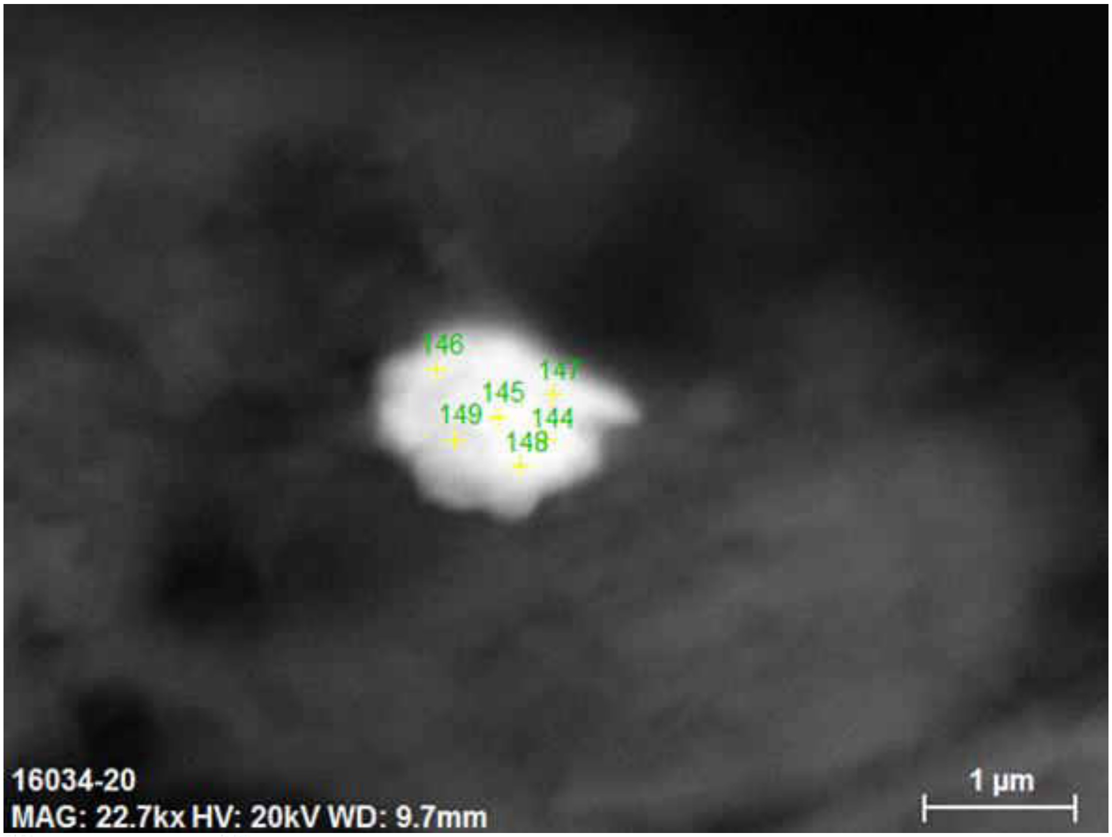
Figure 55 shows the analysis of a single mineral grain containing Ce that appears to be associated with Si, P, Fe, Mg, Al, Ca, K, Cl, Ti and oxygen. This is a much more complicated mineral form than the ones identified in Figure 54. However based on information in literature (Chapter 3), this is potentially 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.

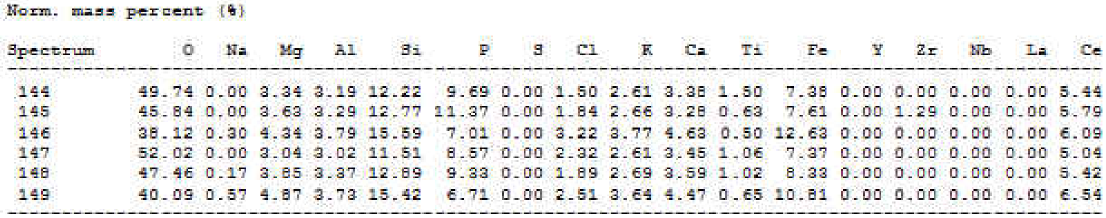
The exact mineral form in either case is not clear given these results, but it would appear that the two major forms of REEs in this particular sample (and likely the other roof/floor sediments as well) are zirconium minerals and clays.



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 54. SEM-EDS result showing REE-bearing zirconium minerals





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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
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Figure 55. SEM-EDS result of Ce-bearing mineral

4.3.5.2 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 55 above. An example is provided for sample IES16018 in Figure 56. The B Rider roof sample was somewhat different, with the primary associations appearing to be aluminosilicate and aluminophosphate minerals, as shown in Figure 57.

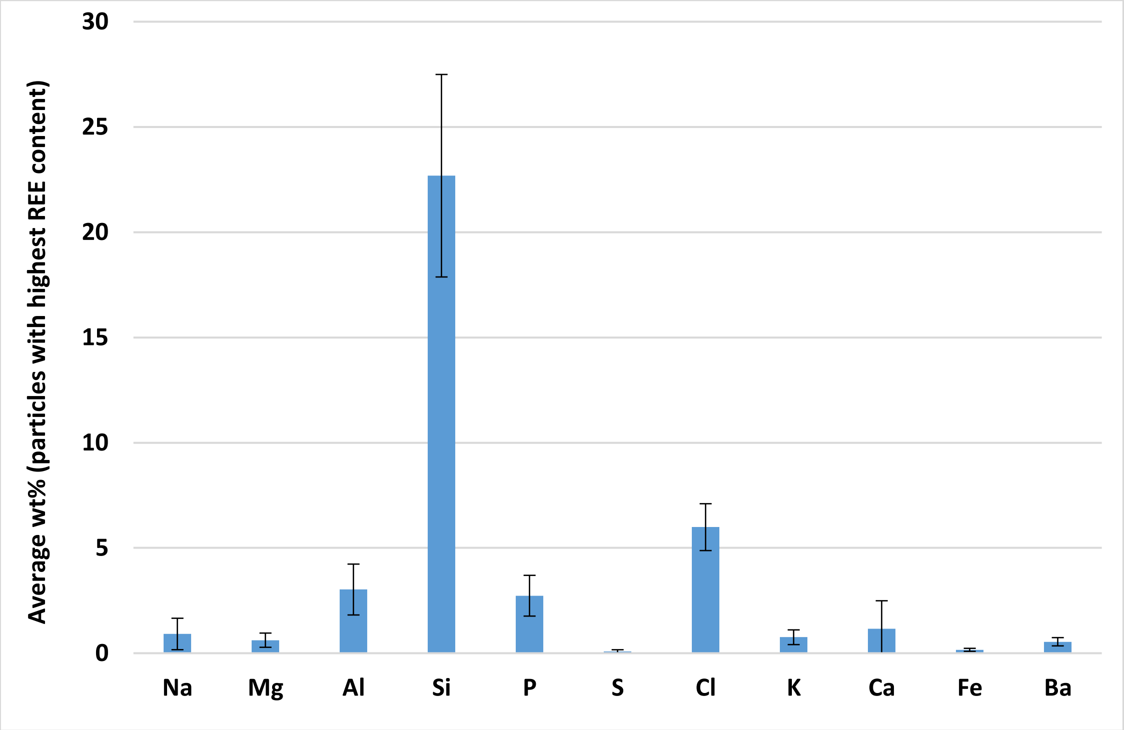


Figure 56. CCSEM analysis results for REE-bearing particles in Hagel B floor sample

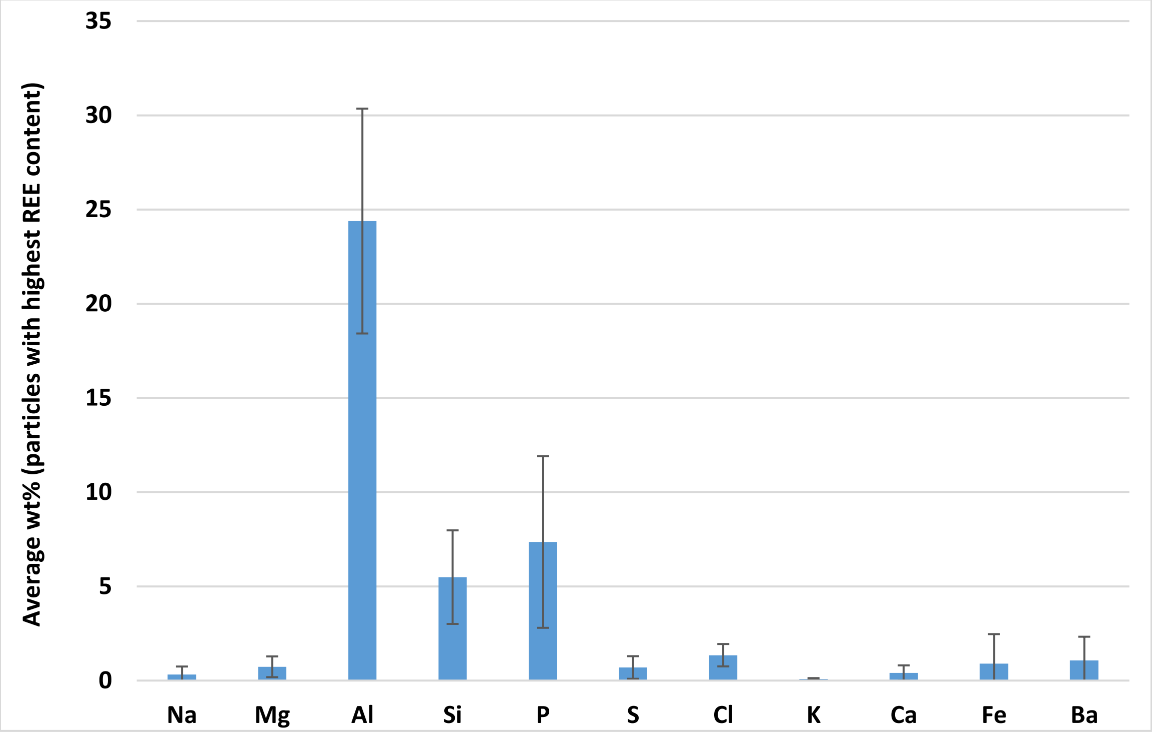


Figure 57. CCSEM analysis results for REE-bearing particles in B Rider roof sample

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 58 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 59 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.

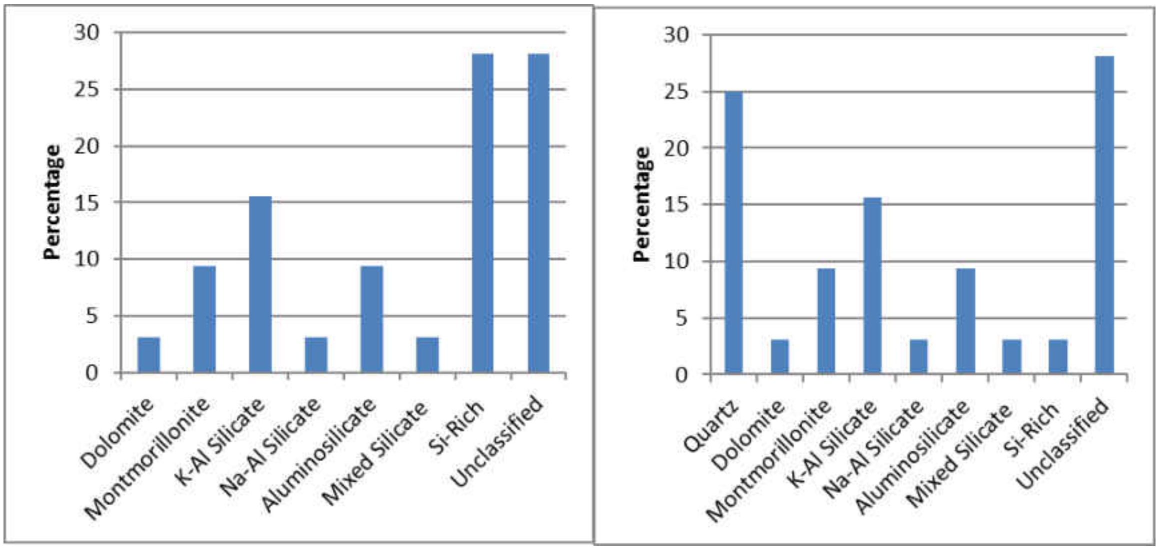


Figure 58. Mineral analysis for REE-bearing particles from CCSEM for Hagel A roof (left) and Hagel A floor (right)

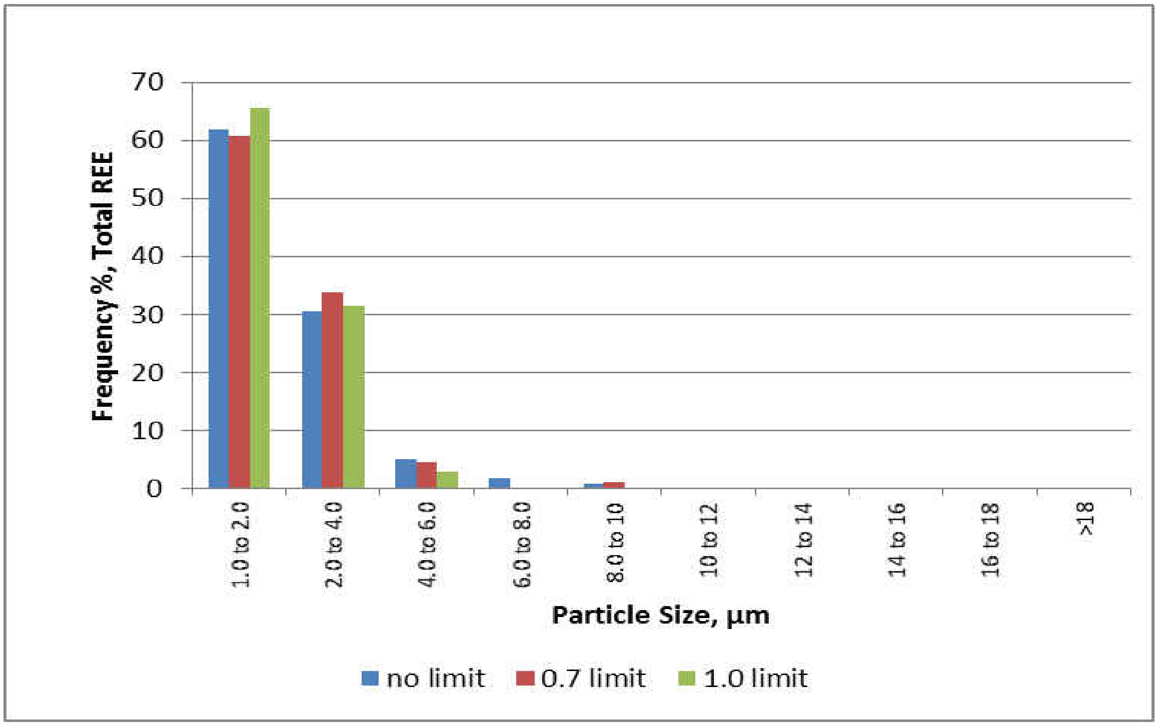


Figure 59. Size distribution of REE-bearing mineral grains based on CCSEM analysis for Hagel A roof sample - limits refer to analysis detection limits placed on the REE content of the REE-bearing mineral grains

4.3.6 Modes of Rare Earth Element Occurrence in Coal Samples

As noted above in the discussion of REE distribution classification in Section 4.3.1, as well as discussed in Chapter 3, 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 Chemical Fractionation. Each is discussed separately with results in the following sections.

4.3.6.1 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 60, 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 4.3.1, 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.

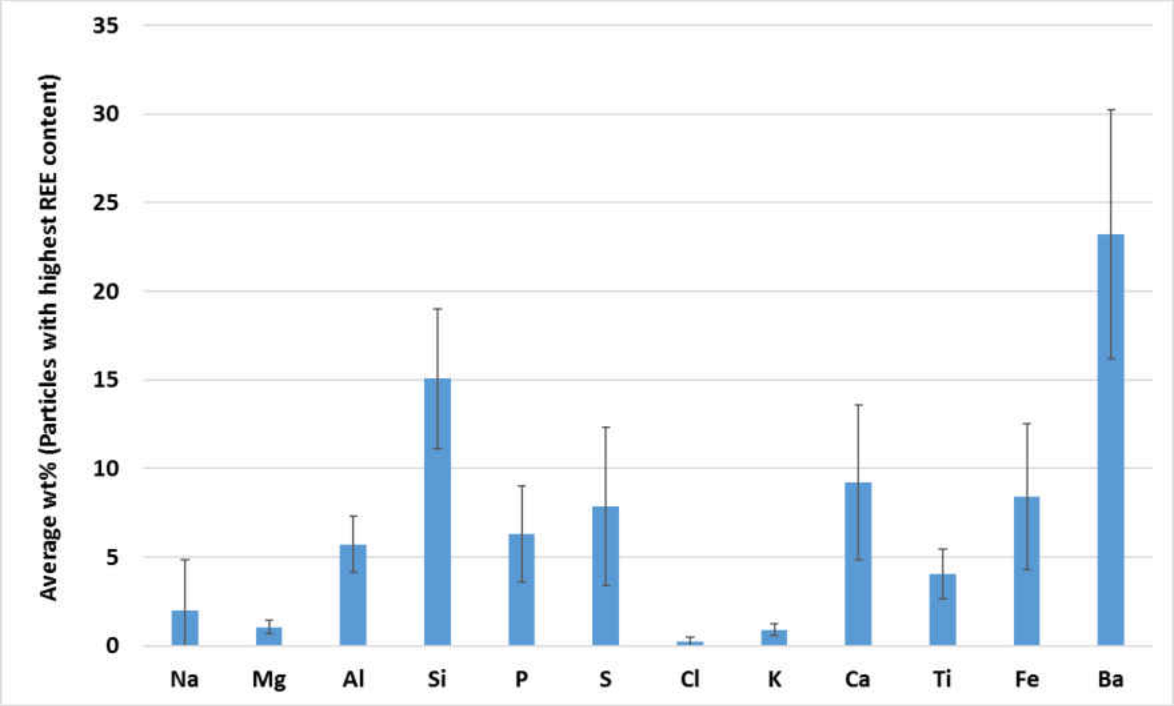


Figure 60. CCSEM analysis for REE-containing particles in Hagel A coal sample

4.3.6.2 Chemical Fractionation

Due to the inability of SEM to detect REE minerals in the coals, Chemical Fractionation was used as a quantitative method to determine REE modes of occurrence in the lignites. As described previously, 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 five coals were evaluated as shown below:

- IES16040 – Hagel A
- IES16050 – Hagel B
- IES16051 – Hagel B
- IES16060 – Hagel B
- ND15RE-6A – Harmon-Hansen

The results of the Chemical Fractionation testing for each of the coals is shown in Table 16. The results are fairly consistent for each of the coals tested, with the exception of the Hagel A sample (IES16040) which shows a very high portion (>70%) of the REEs that were either in water soluble forms or as ion-exchangeable cations. For the other samples, 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. There was some amount of ion exchangeable REEs in each of the samples except IES16050 (Hagel B coal). Overall, these results show that about 80-95% of the REEs in North Dakota lignite coal are extractable through the HCl leaching step. The remaining REEs would be associated in non-soluble minerals, such as clays, silicates, sulfides or others. When combining each of the leaching steps and plotting total REEs extracted versus molecular weight, as shown in Figure 61, there is a clear trend of decreasing extraction with molecular weight, indicating that the modes of occurrence (or potentially the kinetics of the leaching process) are a function of the REE molecular weight. Literature [10] has suggested that the stability of REE organic complexes are better for the higher weight REEs. Therefore, to fully extract the HREEs, longer contact time and/or a higher HCl concentration could be needed. Regardless, this data shows that the REEs in North Dakota lignite are easily extracted via a dilute leaching process.

Table 16. Results of Chemical Fractionation testing (water and ammonium acetate have been grouped)

Sample ID	IES 16040			IES 16050			IES 16051			IES 16060			ND 15RE-6A		
Element	Oragnically Associated (Leached by H2O/NH4OAc)	Carbonates or Coordination Complexes (Leached by HCl)	Inorganically Associated (Not leached)	Oragnically Associated (Leached by H2O/NH4OAc)	Carbonates or Coordination Complexes (Leached by HCl)	Inorganically Associated (Not leached)	Oragnically Associated (Leached by H2O/NH4OAc)	Carbonates or Coordination Complexes (Leached by HCl)	Inorganically Associated (Not leached)	Oragnically Associated (Leached by H2O/NH4OAc)	Carbonates or Coordination Complexes (Leached by HCl)	Inorganically Associated (Not leached)	Oragnically Associated (Leached by H2O/NH4OAc)	Carbonates or Coordination Complexes (Leached by HCl)	Inorganically Associated (Not leached)
Y	76.3	21.0	2.6	0.0	87.2	12.8	7.2	76.6	16.1	0.0	92.5	7.5	9.2	79.2	11.6
La	84.8	13.9	1.3	0.0	94.8	5.2	12.7	75.7	11.6	1.0	83.7	15.4	2.7	88.9	8.4
Ce	77.1	21.0	1.9	0.0	93.4	6.6	14.8	73.8	11.4	5.3	83.5	11.2	1.7	91.5	6.8
Pr	72.6	25.2	2.2	0.0	91.6	8.4	14.5	73.3	12.2	4.2	85.8	10.0	0.6	92.7	6.7
Nd	68.2	29.3	2.5	0.0	90.7	9.3	15.5	71.9	12.6	5.3	86.0	8.7	0.7	92.7	6.6
Sm	68.4	29.3	2.3	0.0	90.7	9.3	13.9	72.6	13.5	2.3	90.7	7.0	1.3	92.0	6.7
Eu	71.5	26.7	1.9	0.0	91.6	8.4	12.7	70.6	16.6	0.0	93.8	6.2	2.1	91.7	6.2
Gd	71.5	26.4	2.1	0.0	90.8	9.2	16.7	70.3	13.0	0.0	93.6	6.4	3.7	90.9	5.3
Tb	73.8	23.8	2.4	0.0	89.1	10.9	15.4	70.5	14.1	0.0	93.3	6.7	4.1	89.9	6.0
Dy	75.3	21.9	2.8	0.0	87.7	12.3	15.3	69.3	15.4	0.0	92.9	7.1	4.6	88.1	7.2
Ho	76.1	20.8	3.1	0.0	86.2	13.8	14.7	68.7	16.6	0.0	92.4	7.6	5.5	85.3	9.2
Er	76.9	19.6	3.5	0.0	84.1	15.9	16.0	66.1	17.9	0.0	91.7	8.3	6.9	81.7	11.4
Tm	76.9	19.1	4.0	0.0	81.6	18.4	15.4	64.2	20.4	0.0	90.9	9.1	6.8	80.0	13.3
Yb	76.7	18.7	4.6	0.0	79.1	20.9	15.7	61.3	23.1	0.0	89.9	10.1	6.3	79.1	14.5
Lu	76.7	18.2	5.0	0.0	76.8	23.2	14.0	60.8	25.1	0.0	89.0	11.0	7.8	75.4	16.7

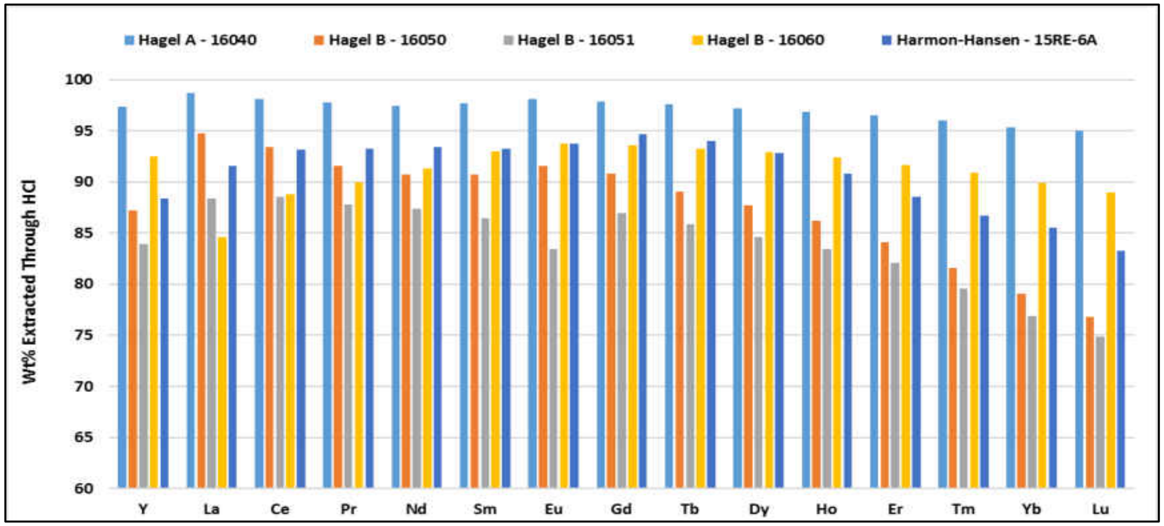


Figure 61. Total REEs extracted via Chemical Fractionation as a function of molecular weight

4.4 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 the coal at 560 ppm on a whole sample basis, or about 2200 ppm on an ash basis, 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. Further, the REE content of the Harmon-Hansen roof sediments in this location were significantly enriched as well, with a whole sample REE content of about 450 ppm, or about 595 ppm on an ash basis.
- 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. 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, 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.
- Experimental evidence of organic associations was gathered via Chemical Fractionation tests, which showed that REEs can be present in North Dakota lignites as ion-exchangeable cations, as organic complexes, in acid-soluble mineral forms, and in non-soluble inorganic forms. The Chemical Fractionation data, combined with inferred evidence and literature indicates that the REEs in North Dakota lignite appear to be primarily associated with the organic matrix. The REEs in the lignites

were also easily extracted by a dilute HCl leaching process, with extraction ranging from about 80 to 95% for the coals evaluated.

- The results, combined with data available in the USGS CoalQual database (discussed in Chapter 3) indicate the strong possibility of commercially feasible REE-rich coal resources in the State.
- Four potential feedstocks were identified for additional testing in the project:
    1. Harmon-Hansen Coal
    2. Harmon-Hansen Roof
    3. Hagel B Coal
    4. Leonardite Fine

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

This chapter details the results of REE extraction methodology development, results and conclusions. The chapter begins with a description of the extraction/concentration methods being developed in existing projects by other organizations in the U.S. DOE NETL REE portfolio and is meant to provide a frame of reference for the novel contributions in this research area established as a result of this study.

5.1 Review of Projects in U.S. DOE NETL Rare Earth Elements from Coal Program

This section is meant to provide an overview of similar work ongoing in the literature regarding development of technologies for rare earth elements recovery from coal and coal byproducts. This section will provide a brief review of the extraction/concentrating methods being investigated to provide a frame of reference for the technology developed in this study, which will be discussed in detail in later sections of this Chapter. The information contained below is taken from publically available documentation available from the DOE NETL website [88].

5.1.1 West Virginia University Research Corporation

West Virginia University (WVU) [89] is developing an REE recovery process for sludges generated during treatment of acid mine drainage (AMD) from coal mines. Their process is summarized in Figure 62, and utilizes acid dissolution followed by refining that includes selective electro-coagulation or solvent extraction/stripping. Of the projects discussed below, this one is significantly different as it is the only one focusing on anaqueous effluent-based coal byproduct. The WVU researchers claim that the REEs found in AMD in Pennsylvania and West Virginia alone represents about 25% of the global REE demand.

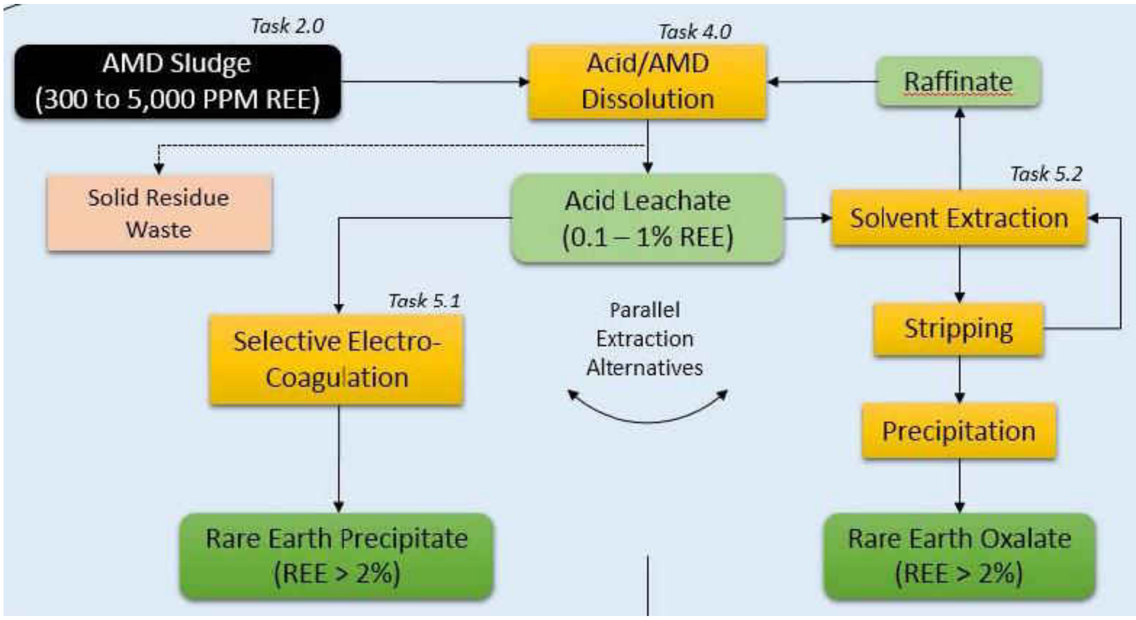


Figure 62. Schematic of the WVU process for recovery of REEs from acid mine drainage [89]

5.1.2 Duke University

Duke [90] is investigating a two-stage approach to extract and concentrate REEs from coal combustion residues (fly ash) that consists of a first stage to extract REEs using acid dissolution and a second stage that uses a membrane to selectively separate REEs from the acidic solution. They are investigating three acid extraction methods using hydrofluoric acid, alkali sintering combined with nitric acid, and nitric acid. They have shown good recovery of the REEs into the acid extracts as indicated in Figure 63.

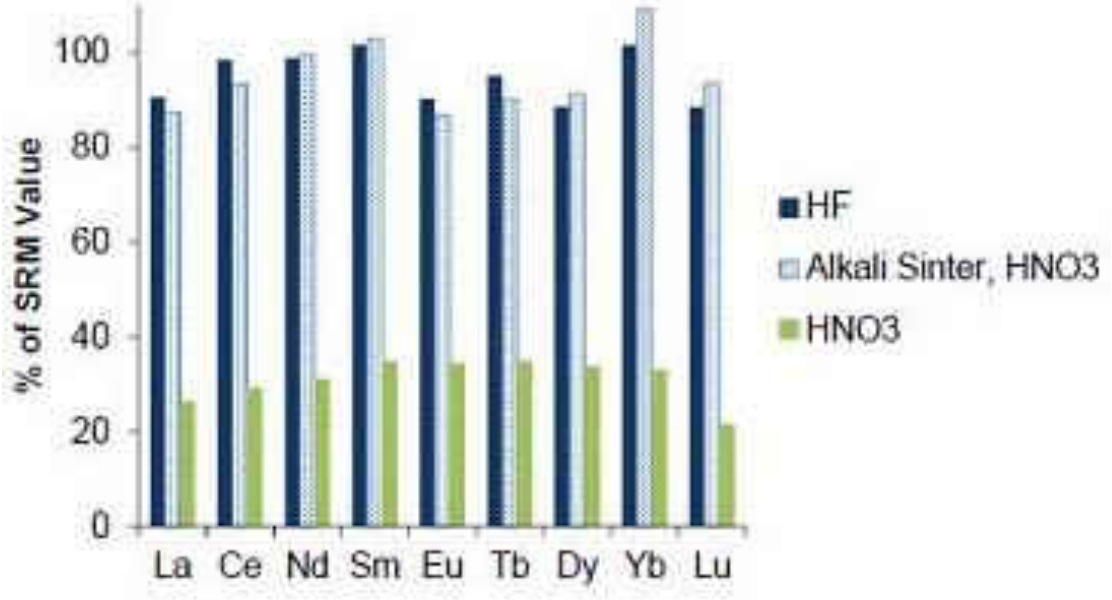


Figure 63. Duke University acid extraction results for coal combustion fly ash [90]

5.1.3 Battelle Memorial Institute

Battelle [91] is investigating the use of its proprietary closed-loop Acid Digestion Process (ADP) for recovering REEs from coal ash. The ash sources are to include power plant fly ash, low-temperature combustion ash, and residual material from Battelle's coal liquefaction process. The ADP process is a closed-loop process that uses nitric acid leaching while recovering and recycling up to 90% of the acid to reduce wastes and consumption. Using their ADP process, extraction efficiency is shown in Figure 64 and is typically in a range of 30 to 65%. Once into solution the Battelle team is investigating hydrometallurgical approaches to concentrate the REEs in the acidic solution.

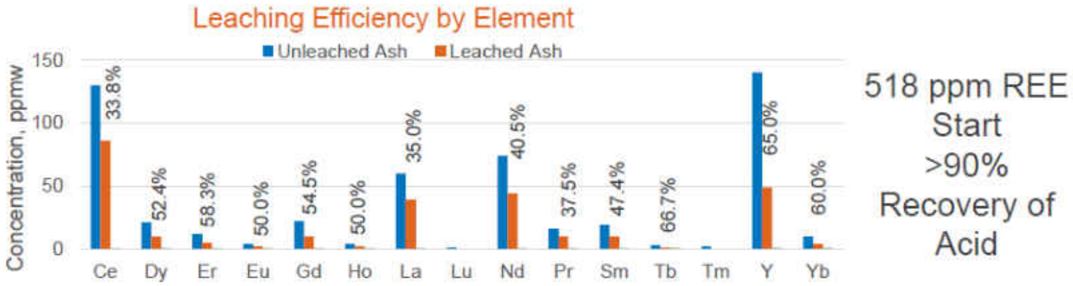


Figure 64. Results of REE extraction with Battelle's Acid Digestion Process [91]

5.1.4 University of Kentucky

University of Kentucky (UKy) [92] is developing a technology to recover REEs from the tailings streams from existing coal preparation/cleaning plants. Their process involves the use of hydrophobic-hydrophilic separation to separate and recover fine coal from the tailings, followed by froth flotation to recover REE-bearing minerals and grinding and classification to concentrate the REEs. The tailings stream from the flotation system undergoes a solvent extraction step to remove acid-soluble REEs into solution, which is then further processed and combined with the REE-mineral concentrate. An example of the developed flowsheet is provided in Figure 65. The project team is targeting REE recovery of 50% from the feedstock.

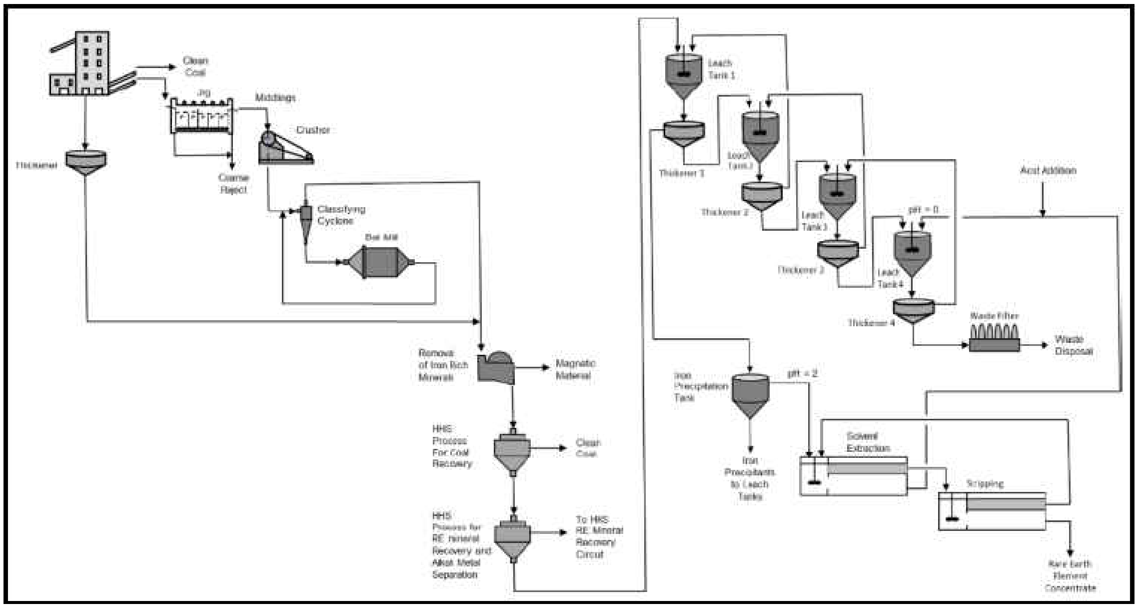


Figure 65. University of Kentucky flowsheet to separate and concentrate REEs from tailings streams of existing coal preparation plants [92]

5.1.5 University of Wyoming

University of Wyoming [93] is developing a supercritical CO_2-based REE extraction method for coal combustion ash derived from Powder River Basin subbituminous coals, as summarized in Figure 66. The leaching of REEs is performed under supercritical conditions using a promoted solvent and assisted by ultrasonics, which is followed by selective precipitation of the REEs by a flocculation process and subsequent dewatering. The research team claims at least 90% recovery of the REEs from the ash and decreased energy requirements.

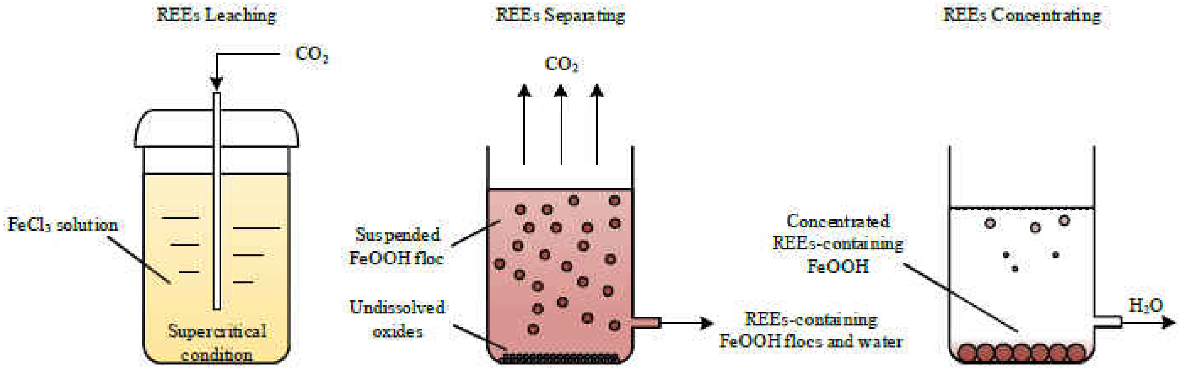


Figure 66. Schematic of the University of Wyoming process for supercritical extraction of REEs from coal ash [93]

5.1.6 Southern Research Institute

Southern Research Institute (SRI) [94] is developing a technology to recover REEs from coal combustion ash using an alternating current graphite electrode plasma arc technology. Two processes are being investigated, including a plasma smelting process and a plasma smelting process combined with volatilization and sequential condensation. The researchers claim that when combined with coal ash vitrification, the method also has the benefit of reducing coal fly ash waste volumes by 68%, and it is one of few technologies that does not require harsh chemicals in order to extract REEs from coal ash. A schematic of the vaporization and controlled condensation method is shown in Figure 67.

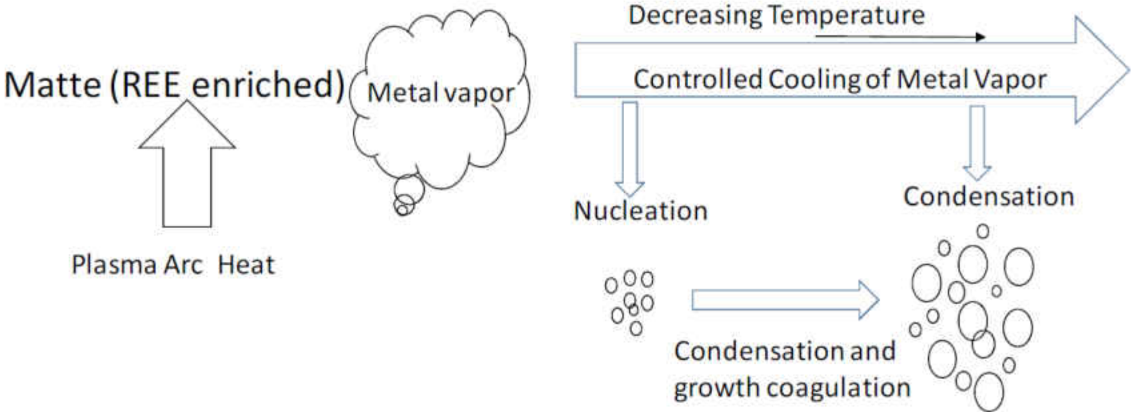


Figure 67. Schematic of the Southern Research Institute plasma-based process for REE extraction from coal combustion ash [94]

5.1.7 Tusaar Corporation

Tussar [95] is developing a technology to extract and concentrate REEs from coal byproducts, namely coal ash, using a combined solvent extraction process and a selective adsorption media to separate and concentrate REEs in the solvent extract solution. Two sorbents are used in stages with the first separating radioactive components, U and Th, and the second targeting the REEs. They claim highly selective removal of U and Th, with about 8 to 20% loss of the REEs. A schematic of their process is shown in Figure 68 along with REE separation efficiency.

5.1.1 Physical Sciences Inc.

Physical Sciences Inc. [96] is developing a technology for recovery of REEs from coal combustion ash that comprises two steps, with the first being physical beneficiation and the second being a chemical separation to produce a dry REE nitrate concentrate. The researcher’s objective is to produce an REE concentrate product with at least 5wt% REE and a target of 10wt%, as well as a beneficiated ash product. A flowsheet of the process is provided in Figure 69.

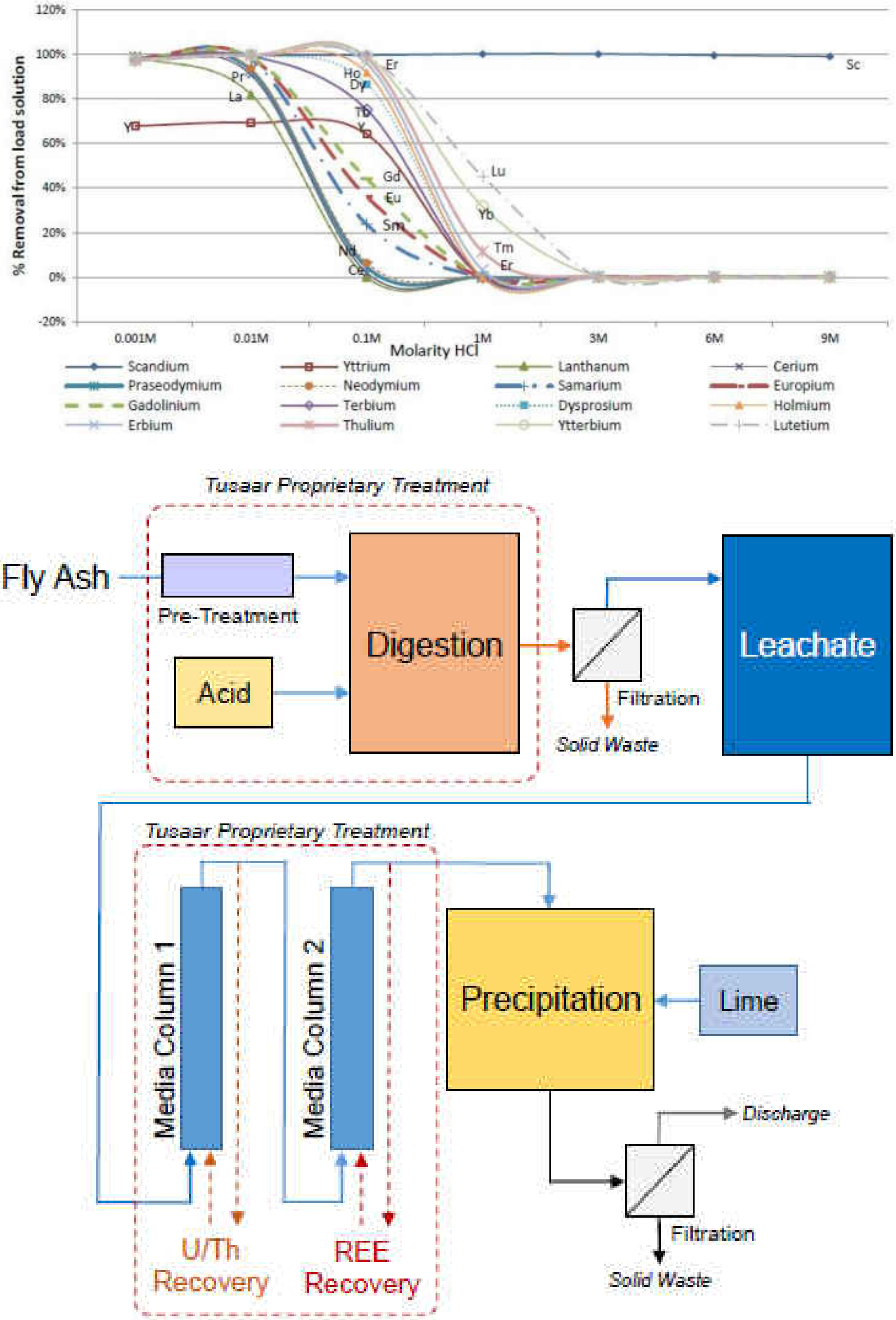


Figure 68. Schematic of the Tusaar acid digestion and adsorbent method for REE recovery from coal combustion fly ash (bottom). Top is REE adsorbent efficiency [95].

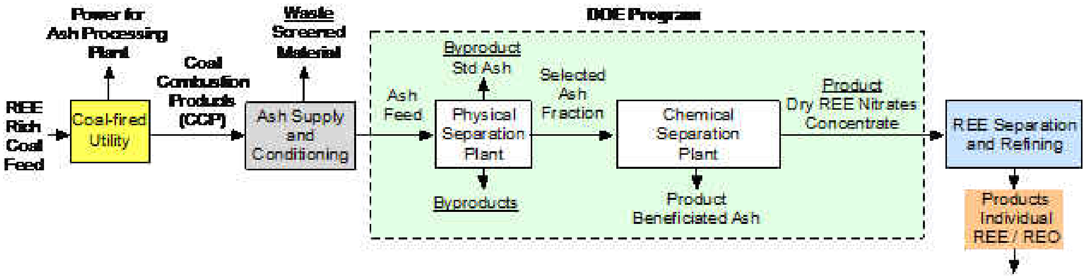


Figure 69. Schematic of the Physical Sciences Inc. process to recovery REEs from coal combustion ash [96]

5.1.2 Summary

As described above, with the exception of the WVU and UKy projects, all of the other projects are focusing on recovery of REEs from coal combustion ashes. This does make some sense conceptually for a number of reasons as summarized below:

- Combustion ash is concentrated in REEs by approximately a factor of 10 compared to the feed coal due to removal of the organic fraction during combustion
- The ash is already in a fine powder form, and thus no grinding is likely needed
- Removal of REEs or other trace elements may improve the marketability/value of the fly ash (i.e. concrete applications) or decrease disposal costs/environmental hazard

However, there are some significant challenges with fly ash. Specifically, the high combustion temperatures result in the refractory REEs being trapped in the glassy, fused ash materials, making access by leaching solutions difficult [44]. The mineral forms that were originally in the raw coal are typically not retained, which brings about serious technical challenges for any physical beneficiation processes. This results in the necessity for very harsh chemicals and high temperatures to crack the structure of the glassy ash materials and thus allow reasonable REE separation efficiency.

While WVU and UKy are both investigating alternative feedstocks, the primary mode of occurrence of the REEs in these feedstocks is likely to be in non-soluble mineral forms, namely monazite or other phosphates that are commonly found in eastern U.S. bituminous coals. Therefore, in order to effectively recover REEs, these very fine minerals (typically < 10 microns) must be liberated by energy intensive ultra-fine grinding or some other mechanical means. Physical beneficiation processes for ultra-fine particles are limited and typically carry a high cost relative to separation efficiency.

Overall, the above projects are investigating a range of novel technologies for recovering REEs from coal-related resources. There are challenges primarily with the choices of feedstocks, with the REEs either locked in fused combustion ash materials or tightly bound in non-soluble ultra-fine mineral forms. Therefore, in order to effectively recover REEs from these types of sources, complex flowsheets are needed and environmental issues will be a challenge when using harsh chemicals and high temperatures that are required to extract REEs from these types of feedstocks.

5.2 Experimental Methods

As described in Chapter 2, 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. However, with the understanding of the extreme challenges of recovering REEs from combustion ash, an approach was taken to look at a low-temperature combustion process that would result in removal of the organic fraction without melting/fusing the ash product and keeping the mineral forms intact. Some limited testing was completed using this method. Finally, with the data gathered from Chemical Fractionation testing (described in Chapter 4), it was discovered that the REEs are loosely bound in the raw coal and could be removed by a simple dilute acid leaching process at low temperature. 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.

5.2.1 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 provided to Hazen Research of Golden, Colorado, who screened the samples into -10 micron, 10 to 25 micron, and +25 micron size fractions. The samples were returned for 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 [97]. 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 70), 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.

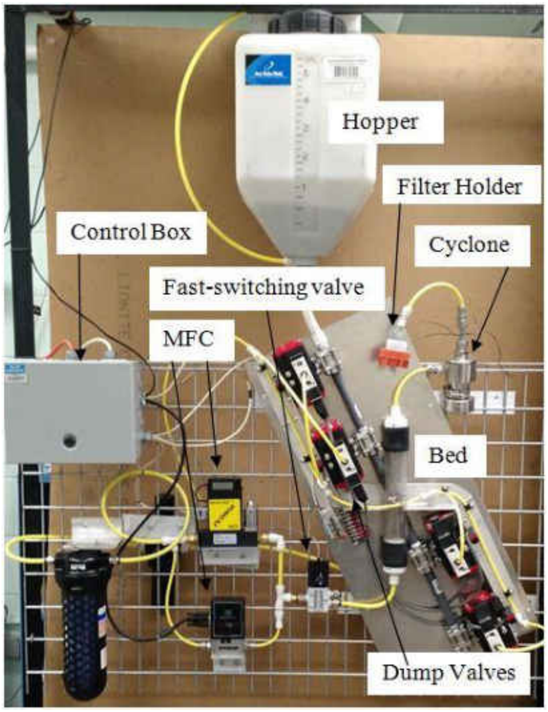


Figure 70. Dry elutriation test system.

5.2.2 Low-temperature Combustion Tests

Limited low-temperature combustion tests were performed. The testing involved use of an externally heated two-inch diameter fluidized bed equipped with a screw feeder for coal feed, a gas cooler, a multi-cyclone particulate classifier, and a bulk filter. The goal of this testing was to operate the fluidized bed at sufficiently low temperature (i.e. 750-850°C) to be able to completely burn off the organic matter in the coal without forming a fused ash product. Due to the organic associations of REEs in the lignite coal, it was expected that the REEs would be associated with the ion-exchangeable inorganic components in the coal (i.e. Na, Ca, K, Mg) and were likely to end up in the largest size fraction in the ash. Thus, the multi-cyclone system was installed to be able to simultaneously capture the ash particulate and classify it by size. Once classified, the ash would be analyzed for REE content to determine the partitioning of the REEs and identify any concentrated products. However, even though a series of tests were completed using these methods, no analysis was done. This was due to success in the leaching methods discussed later. Because no data on REE content in the ash products was generated, the low-temperature combustion testing will not be discussed hereafter.

5.2.3 Leaching Tests

Leaching tests followed many of the same procedures as established for Chemical Fractionation testing discussed previously in Chapter 3. 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 at surface temperature of 70°C (solution temperature of about 40°C)
- After finishing desired leaching duration, the slurry was filtered using a vacuum-assisted Buchner funnel
- For most tests, after filtering, a second extraction was performed using the residual solids and a fresh quantity (125 mL) of leaching solution.
- Once extraction was complete, the separated residual material was rinsed extensively with DI water, collected and dried in a convection oven at about 105°C to dryness. The liquid solution was discarded.
- 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.

Overall, four lignites or lignite-related materials were tested and three acid types (HCl, H_2SO_4, H_3PO_4) were tested each with two concentrations (two of 0.1, 0.5 or 1.0M). Additionally, ammonium acetate and ammonium sulfate solutions were evaluated using the Leonardite feedstock.

Initial leaching tests focused on screening acid types and concentrations that were effective in extracting REEs. One acid type and concentration was subsequently down-selected for continued testing with three lignite-related materials. 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.

5.3 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.

5.3.1 Physical Beneficiation

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

5.3.1.1 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 5.2.1. 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 with the hope that some natural partitioning of the ultra-fine REE-bearing mineral grains would occur during the grinding process. The ICP-MS results shown in Table 17, however, do not show any detectable enrichment in either material fraction generated. However, as indicated in the PSD data in Figure 71 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.

Table 17. 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

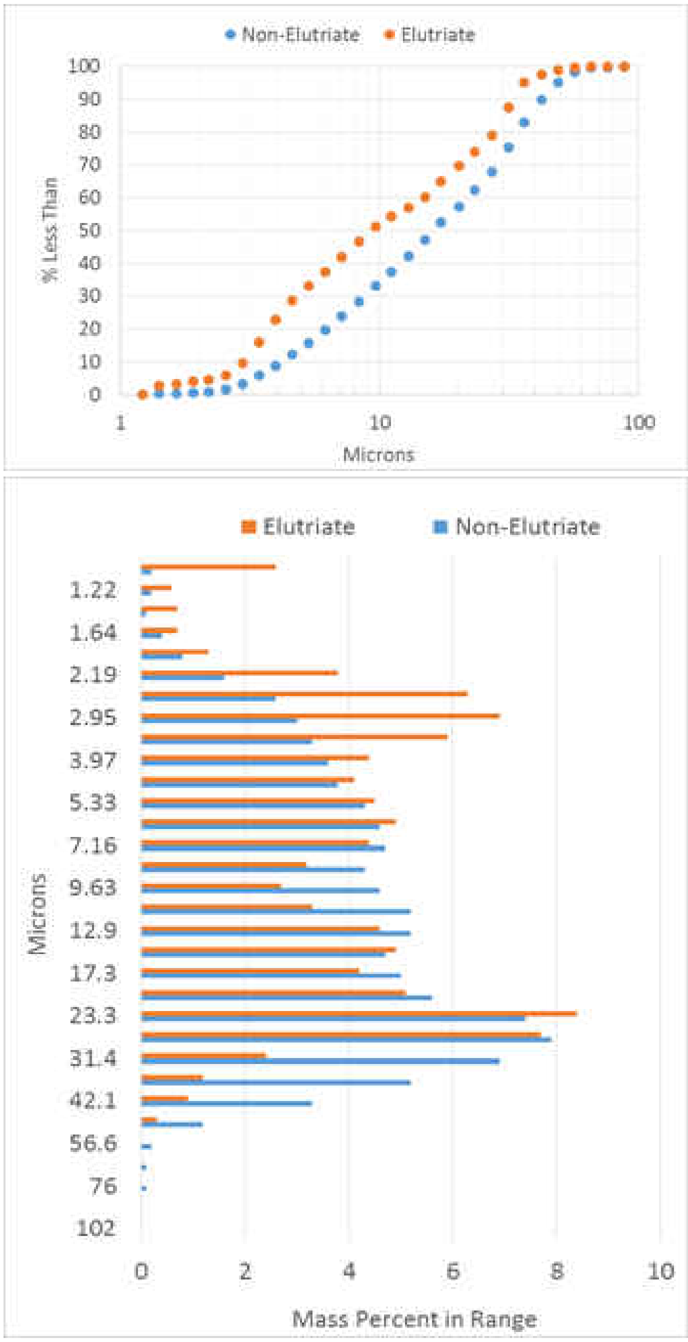


Figure 71. Particle size distributions of the elutriate and non-elutriate fractions generated from dry elutriation-based physical benefication testing for Falkikrk Mine roof/floor sediments

5.3.1.2 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 18. 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, which would be expected given the organic association of the REEs in the raw coal. However, only about 28% of the starting REEs reported to that size range.

Table 18. 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.

5.3.2 Leaching Tests

The results of Chemical Fractionation testing discussed in Chapter 3 provided strong evidence that a solvent-based approach using a leaching process on the raw coal or unprocessed feedstocks was worth further investigation. Three series of leaching tests were accomplished: i) initial screening of acid types and concentrations, ii) additional testing with down-selected acid type and concentration, iii) leaching kinetics testing. Each is described separately in the following sections.

5.3.2.1 Screening Tests – Hagel B and Harmon-Hansen Roof

Based on the results of the Chemical Fractionation (Chapter 4) testing that showed high efficiency extraction of REEs from raw ND lignite was possible by dilute acid leaching at low temperature, additional testing with a range of acid types and acid concentrations was performed to identify an operating window with best combination of performance, with extractability of target elements, economics and environmental factors considered. Table

19 and Table 20 display leaching test results for two feedstocks, respectively: i) raw Hagel B coal, and ii) Harmon-Hansen roof sediments. Three acid types (HCl, H_2SO_4 and H_3PO_4) were tested in two concentrations each. Tests were conducted using a coal/sediment particle size of -10 mesh, a leaching temperature of approximately 40°C and a purposefully long contact time of about 48 hours. The long contact time was used to ensure equilibrium extraction was achieved (or nearly achieved). The first 24 hours for each test and the second 24 hours of each test utilized fresh quantities of acid, with filtering and rinsing with DI water in between.

Table 19. Acid leaching screening test results for Hagel B coal

	wt% Extracted					
	0.1 M HCl	1.0 M HCl	0.1 M H2SO4	0.5 M H2SO4	0.1 M H3PO4	1.0 M H3PO4
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	11.04	86.81	4.50	70.94	7.90	64.56
LREE wt% extracted	11.17	83.86	4.31	63.79	7.59	60.35
HREE wt% extracted	10.83	91.84	4.82	83.13	8.41	71.73
CREE wt% extracted	10.94	90.80	4.66	78.95	8.09	69.16

NOTE: CREE denotes critical REE

Table 20. Acid leaching screening test results for high-ash Harmon-Hansen roof sediments

	wt% Extracted					
	0.1 M HCl	1.0 M HCl	0.1 M H2SO4	0.5 M H2SO4	0.1 M H3PO4	1.0 M H3PO4
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

NOTE: CREE denotes critical REE

The Harmon-Hansen roof sediments (Table 20) exhibited very intriguing results. Even though the ash content of the material was about 80%, a large fraction of the REEs were still extractable via the dilute acid leaching. This is behavior that is similar to the HREE market-dominating Chinese ion-adsorbed clays. It is possible that a similar REE mode of occurrence exists (i.e. ions adsorbed on the clays) that could make the clay-rich roof sediments of the Harmon-Hansen another promising feedstock for REE recovery. It may also be possible that a large fraction of the REEs in this material is contained in acid-soluble mineral forms. Also notable is that extraction with the most dilute acid concentration for both HCl and H_2SO_4 resulted in 20 to 30% REE extraction, a significantly better performance than with Hagel B coal as discussed below, and also a potential indicator of adsorbed REEs. Although these results are interesting and deserve consideration in future work, the remaining work in this project focused on lignite coal feedstocks.

The results shown for the Hagel B coal in Table 19 indicate that overall, 1.0M HCl had the highest recovery of REEs, ahead of 0.5M H_2SO_4 and 1.0M H_3PO_4. In each case the 0.1M acid concentrations did a poor job of REE extraction. The data is shown in graph form in Figure 72 for the three higher concentration acid tests. The behavior of scandium was significantly different among the acid types, with phosphoric acid producing the best extraction. With the exception of sulfuric acid, the extraction was fairly uniform across the LREE and HREE. Sulfuric acid, however, showed a strong selectivity towards the HREE, which, in fact is an opposite trend observed for HCl, which showed a slightly decreasing extraction in the heaviest REE with the exception of Y. However, for all three acid 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.

An interesting result from this testing is a comparison of the results of total REE extraction through the 1.0M HCl step for previous Chemical Fractionation testing results in a noticeably different extraction profile that when leaching with HCl by itself (i.e. without leaching by H_2O and 1.0M ammonium acetate beforehand), as shown in Figure 73. The Chemical Fractionation total extraction showed high REE extraction through the middle weight REEs, but a steadily declining performance in the HREEs. However, with HCl only, there appears to be a slightly worse extraction in the middle weight REEs, but a better performance in the HREEs. The cause of these differences aren’t completely clear, but it seems possible that leaching first with water and ammonium acetate has somehow changed the modes of REE occurrence prior to HCl extraction.

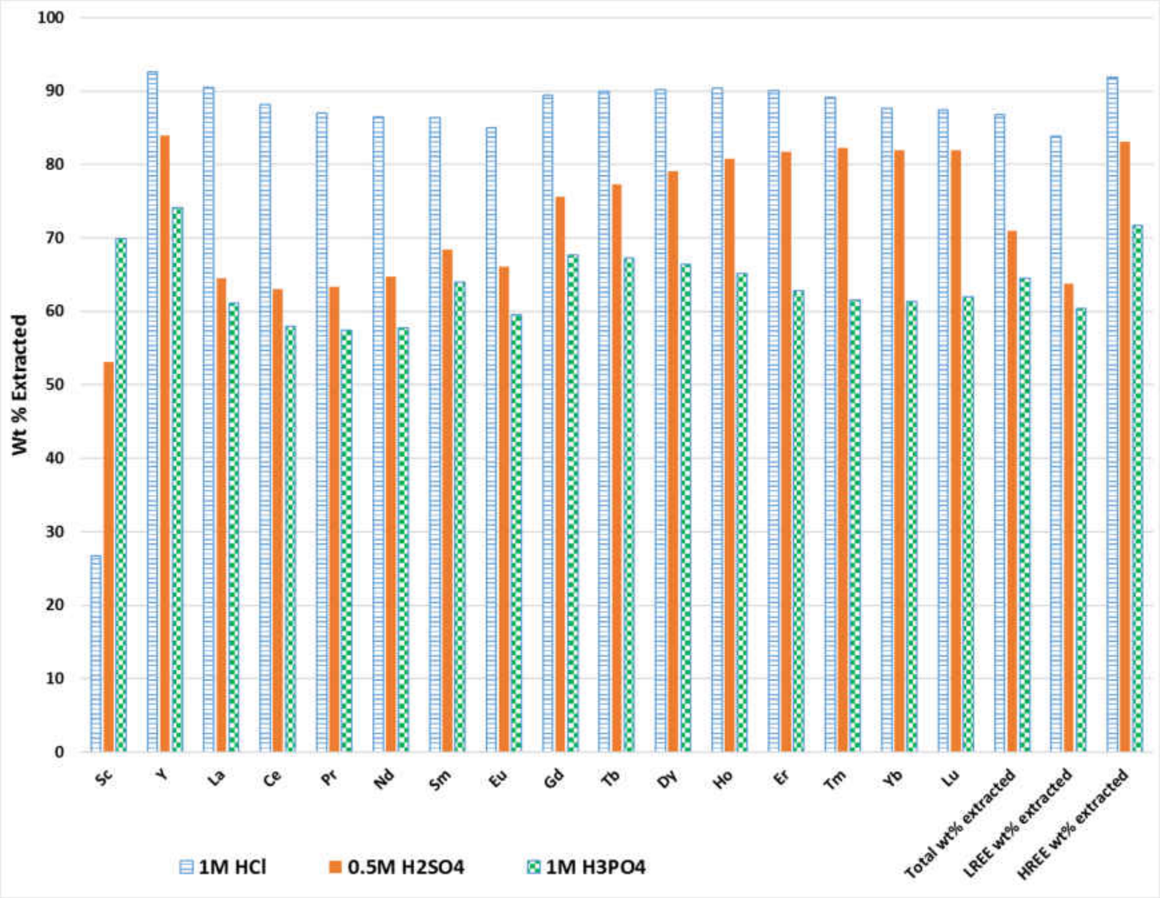


Figure 72. REE extraction results for 1M HCl, 0.5M H_2SO_4 and 1M H_3PO_4

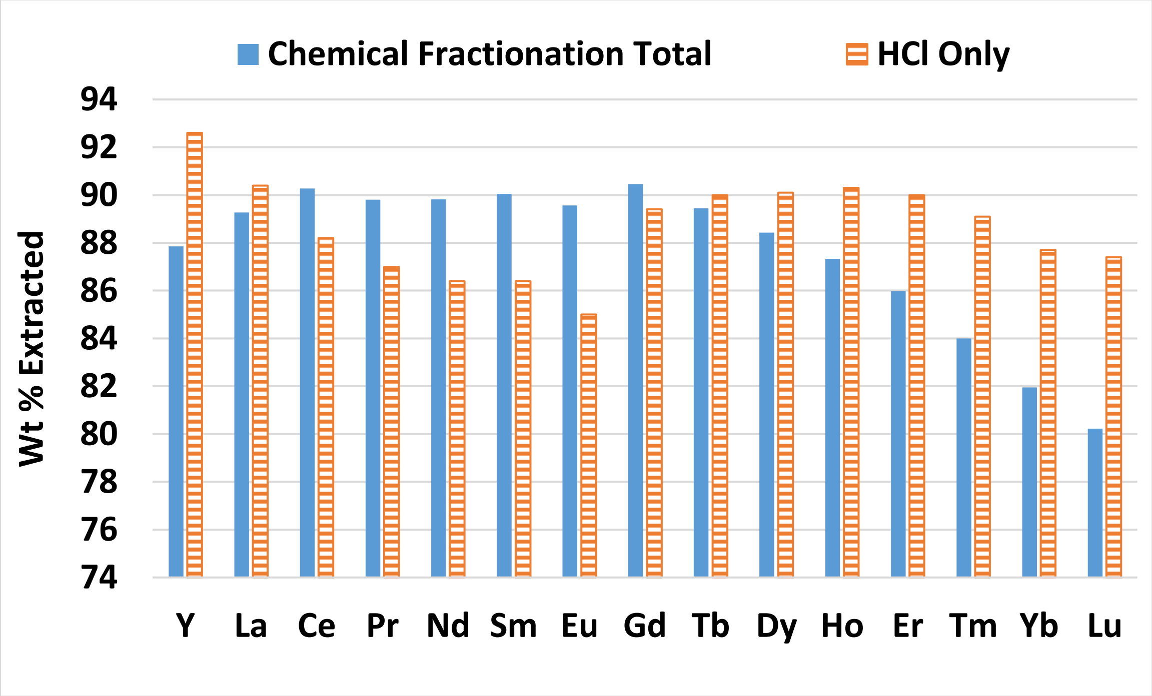


Figure 73. Comparison of leaching extraction for Chemical Fractionation and HCl only

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 21. Here, it is clear that although the 1.0M HCl 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 0.1M phosphoric acid 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 0.5M sulfuric acid test 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 21. 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	-	-	-
0.1M HCl	5.9	18.1	11	0.03
0.1M H_2SO_4	6.9	4.3	4.5	0.06
0.1M H_3PO_4	7.2	0.6	7.9	**0.74**
1.0M HCl	1.7	76.1	86.8	0.07
0.5M H_2SO_4	6.1	15.6	70.9	**0.25**
1.0M H_3PO_4	3.1	56.4	65.6	0.06

Although HCl was the most effective in extraction of REEs, the 0.5M H_2SO_4 acid was chosen for additional investigation in the project for the following reasons:

- Higher recovery of the extremely valuable scandium than HCl
- Higher recovery of total REE than H_3PO_4

- Very good REE-selectivity (i.e. lowest extraction of impurities for 0.5M or 1.0M acids)
- Lowest concentration acid that had good REE extraction efficiency
- H_2SO_4 is the least expensive of the strong mineral acids used in mineral processing
- Very good selectivity to the more valuable HREE
- Potential for on-site production of H_2SO_4 to reduce acid costs (i.e. SO_2 contained in flue gas from a co-located combustion plant)

5.3.2.2 0.5M Sulfuric Acid Leaching Tests

As described above, based on the results of screening tests, 0.5M sulfuric acid 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 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 0.5M H_2SO_4. 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 22. 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 22. Extractions for 0.5M H_2SO_4 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
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

Table 22. Extractions for 0.5M H_2SO_4 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)	
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 74, 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. These results are similar to extraction by HCl for the Harmon-Hansen coal as presented previously in Chapter 3. 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 or potentially just more susceptible to an oxidizing acid such as H_2SO_4.

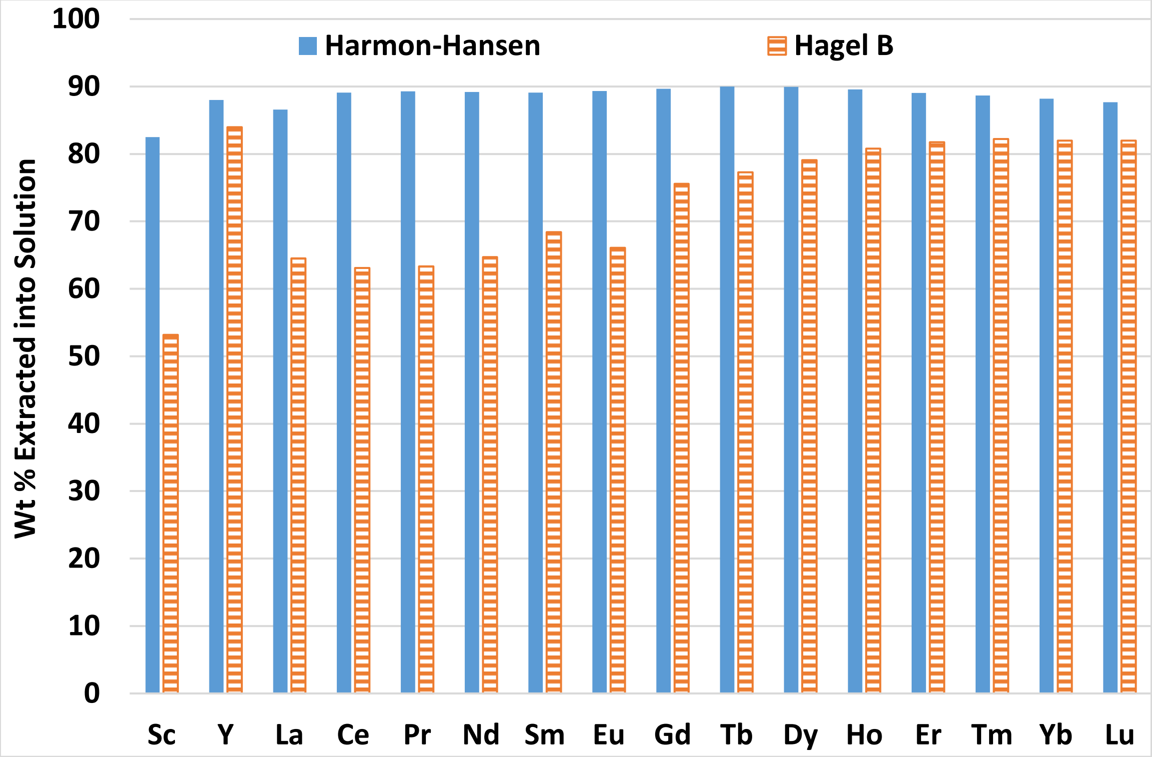


Figure 74. Comparison of REEs extraction by 0.5M H_2SO_4 for Harmon-Hansen and Hagel B coals

For the major ash-forming elements shown in Figure 75, 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. A theory for the differing extractions of the alkali and alkaline earth elements could be the distribution of these elements as ion-exchangeable cations within the coals versus clay or mineral associations. With this theory, it would appear that a higher proportion are found as ion-exchangeable cations in the Hagel B coal, with the exception of Ca.

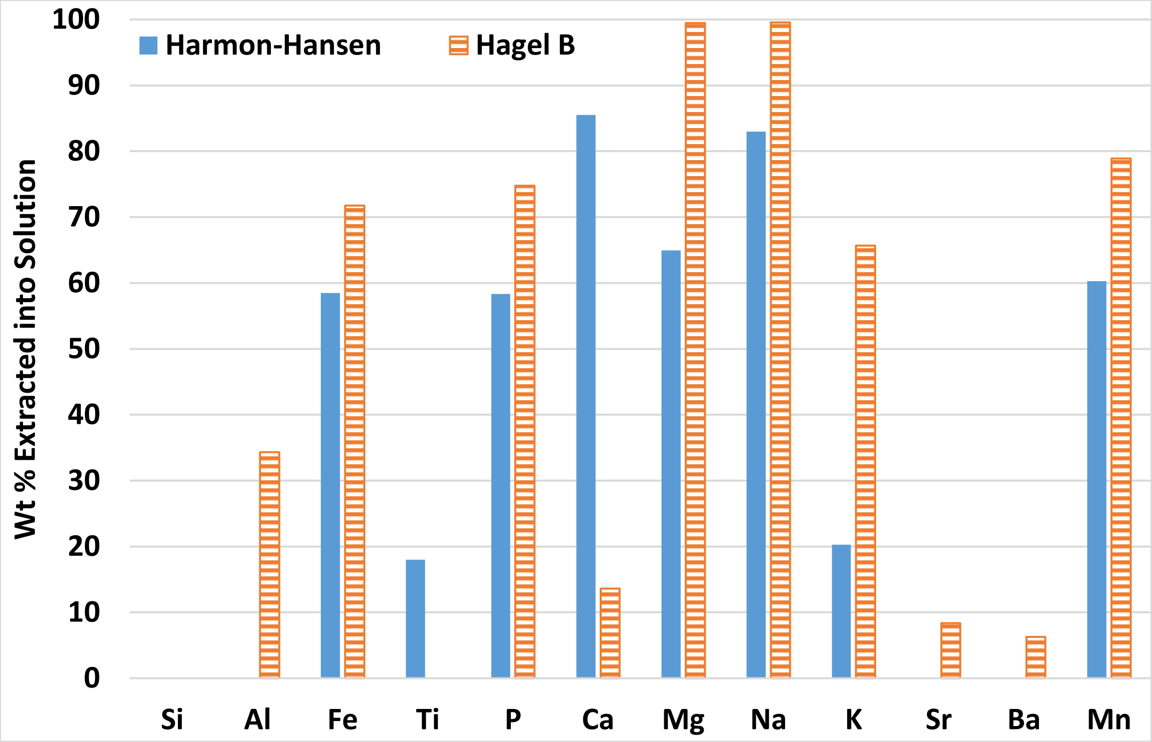


Figure 75. Comparison of the extraction of the bulk ash species by 0.5M H_2SO_4 leaching for Harmon-Hansen and Hagel B coals

When looking at the remaining species shown in Figure 76, 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.

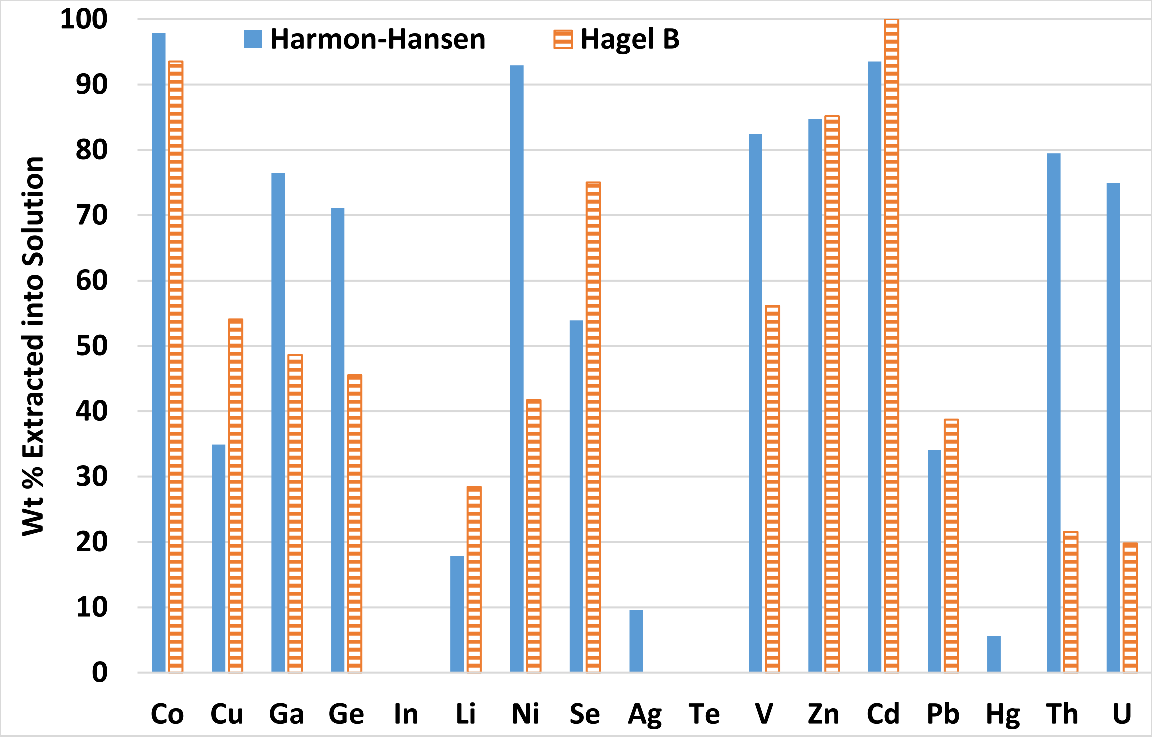


Figure 76. Comparison of the extraction of non-REE species by 0.5M H_2SO_4 leaching for Harmon-Hansen and Hagel B coals

Based on the results shown above, the mass balances can be calculated as shown in Table 23. 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 23. Overall mass balances for 0.5M H_2SO_4 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

5.3.2.3 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 with fresh acid being used during each of the two 24 hour periods. 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 0.5M H_2SO_4 as the leaching solution. Besides the contact time, methods described previously for the leaching tests were used. Table 24 and Figure 77 display the results for extraction as a function of leaching contact time for the individual REEs. Figure 78 displays the results for groupings into Total REE, LREE, HREE and critical REE (CREE).

Table 24. Leaching kinetics results for Hagel B coal with 0.5M H_2SO_4

	Mass % Extracted by 0.5M H_2SO_4 @ 40°C						
	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
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

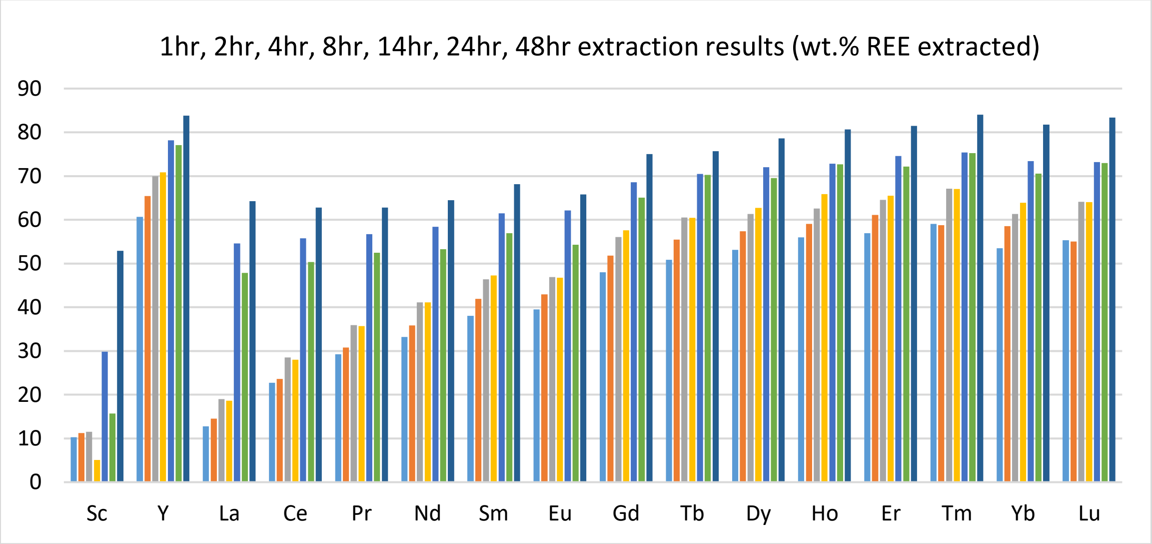


Figure 77. REE leaching kinetics for Hagel B coal with 0.5M H_2SO_4

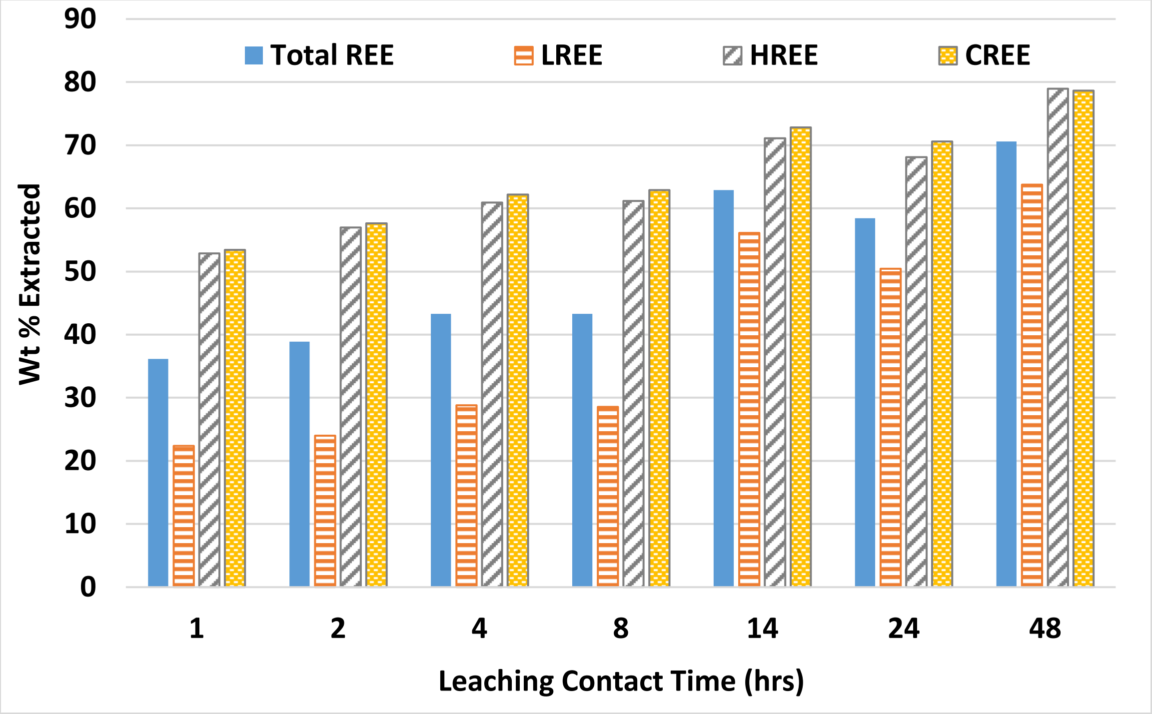


Figure 78. Leaching kinetics for groupings of REE for Hagel B coal with 0.5M H_2SO_4

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. While the data is grouped by molecular weight, it appears likely that the differing behavior as a function of the molecular weight is due to the decreasing ionic radius with increasing molecular weight (i.e. the lanthanide contraction). The smaller HREEs could be more mobile (i.e. faster mass transfer) during the extraction process. 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, or more likely the ionic radius.

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 some form of acid-soluble mineral that after 8 hours of contact time became solubilized.

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.

5.3.2.4 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 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 79 for the REEs and Figure 80 for all other elements.

For the REEs shown in Figure 79, 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. The increase between 14 and 48 hours is likely the result of the fresh quantity of acid that was used for the second 24 hour period in the 48 hour test. 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.

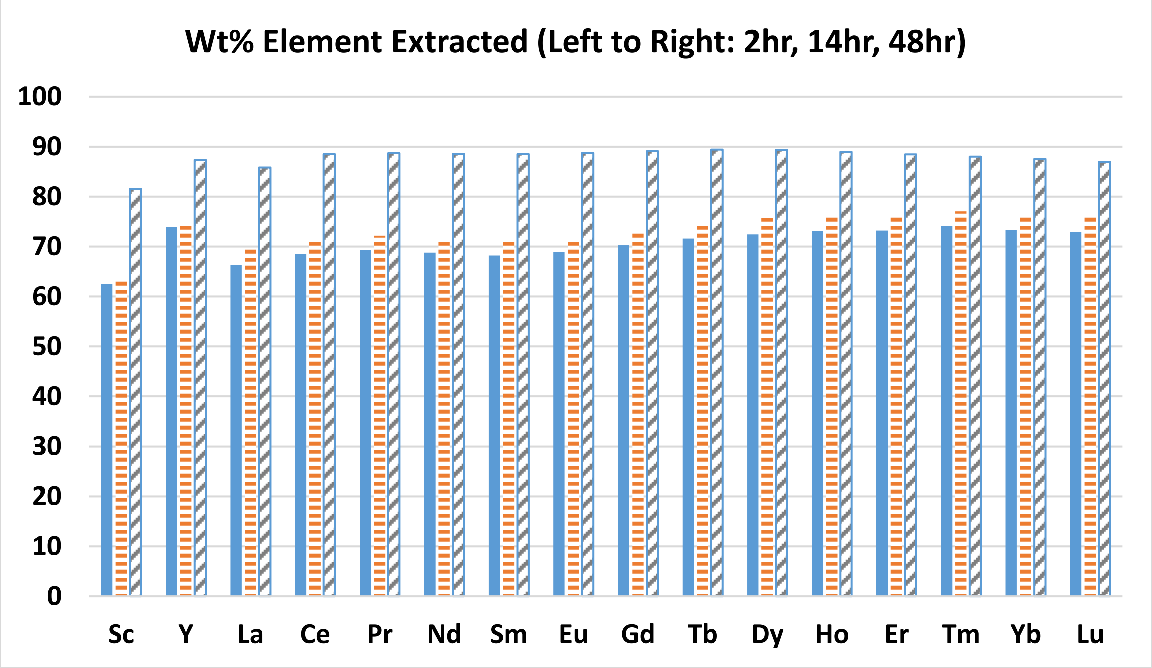


Figure 79. Results of REE extraction kinetics testing for Harmon-Hansen coal

For the other elements analyzed, consisting both of monetizable target elements and impurities, results are shown in Figure 80. 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 25. This result shows that with only the acid leaching step, 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.

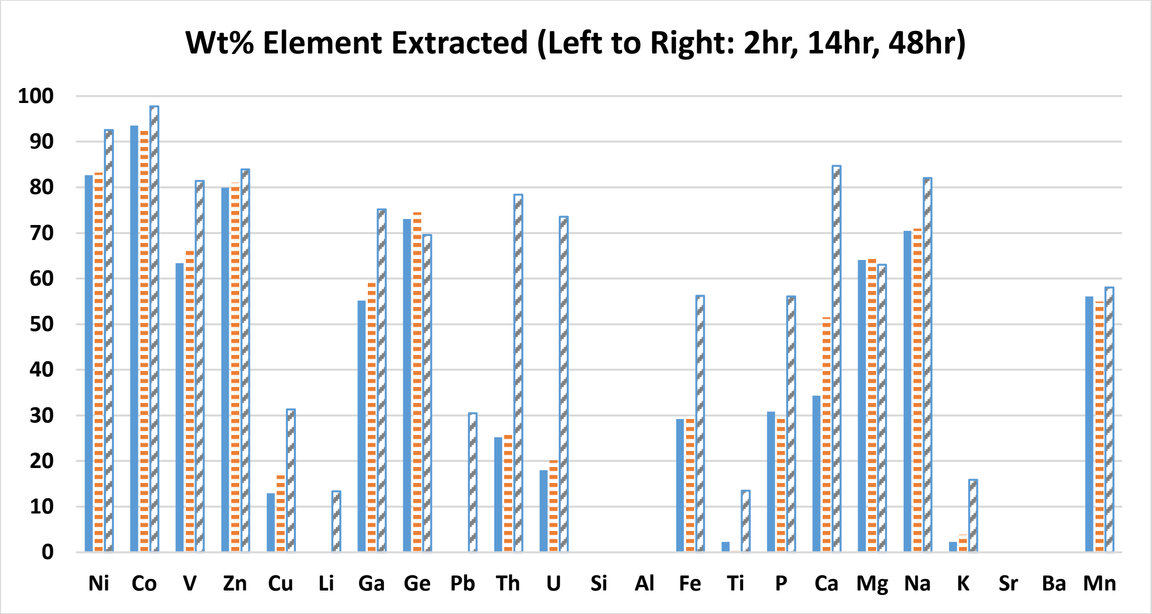


Figure 80. Results of extraction kinetics testing for other elements for Harmon-Hansen coal

Table 25. 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

5.3.2.5 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 as follows:

- 1M Ammonium Acetate @ 40°C and 24 hr contact time
- 1M Ammonium Sulfate @ 40°C and 24 hr contact time
- 0.5M H_2SO_4 @ 40°C and 24 hr contact time.

The ammonium acetate and ammonium sulfate are both ion-exchange solutions, the ammonium acetate having been used previously in the Chemical Fractionation testing, and the ammonium sulfate being the primary leaching reagent for the Chinese ion-adsorbed clays. Besides the contact time and the leaching solutions, all procedures followed previous leaching tests.

The results showed that no measurable extraction of the REEs occurred with either of the ion exchange solutions, but that there was some extraction with the sulfuric acid, as shown in Figure 81. 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 26, and shows that there is very low concentration of REEs in the extract solution after sulfuric acid 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.

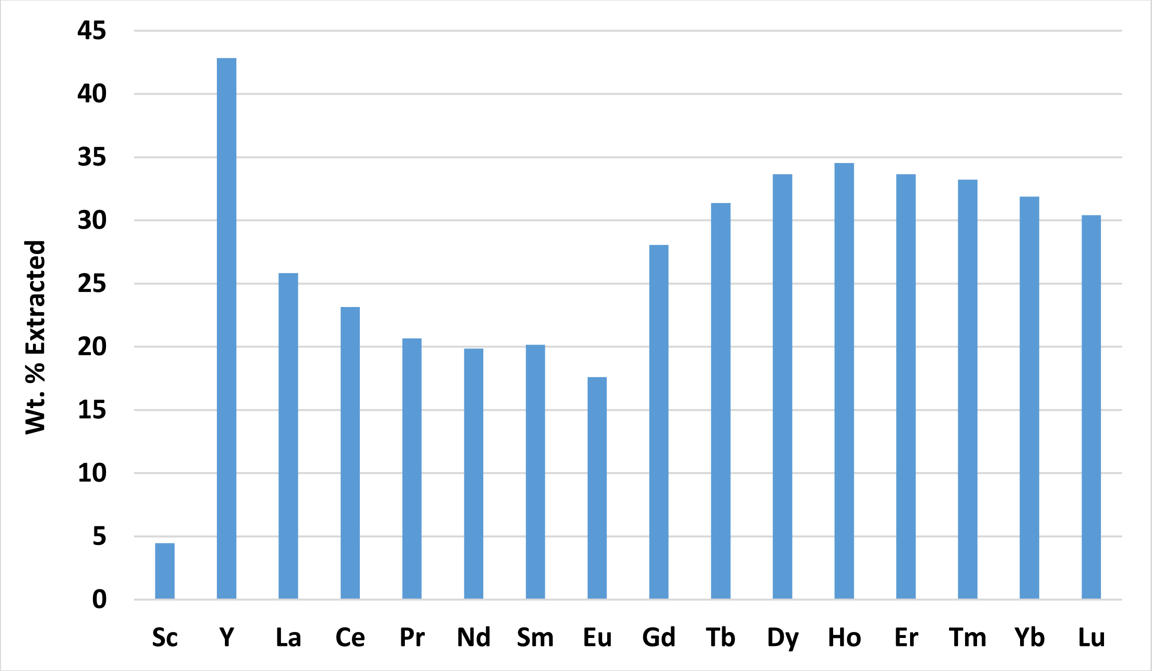


Figure 81. 0.5M sulfuric acid extraction results for Leonardite Fine material

Table 26. Mass balance for Leonardite REE extraction tests

Sample	Ash Content (wt%)	% Ash Reduction	% REE Extraction	REE Concentration (wt%)
Unleached	21.6			
Ammonium Acetate	20.1	6.9	-	-
Ammonium Sulfate	19.3	10.7	-	-
Sulfuric Acid	18.0	16.6	25.7	0.05

5.4 Summary and Conclusions

Two types of extraction methods were evaluated that included grinding and classification for roof/floor sediments and combustion fly ash, and dilute acid 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.
- Based on the results of Chemical Fractionation testing that showed high efficiency extraction of the REEs directly from the raw lignite coals was possible with dilute and low temperature leaching processes, a series of tests was performed to identify an acid type and acid concentration with the best performance also in the context of environmental and economic considerations. Results indicated that 0.5M sulfuric acid provided the best combination of high REE extraction and REE-selectivity while also being the lowest concentration acid that proved effective in extracting REEs. When considering economic and environmental factors, 0.5M sulfuric acid was chosen for additional evaluation in the project.
- Although only limited testing was completed with the Harmon-Hansen roof sediments, extraction of REEs from the clay-rich materials was about 50-70% for dilute acid leaching tests, indicating a potentially similar mode of REE occurrence as with the market dominating Chinese ion-adsorbed clays. The Harmon-Hansen clay materials are thus a target for future investigation.
- 0.5M sulfuric acid 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 acid-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 acid leaching step.
- Extraction of REEs from Leonardite proved ineffective using ion exchange solutions of either ammonium acetate or ammonium sulfate. Further, the REE extraction with 0.5M sulfuric acid was considerably less than with Hagel B or Harmon-Hansen coal samples, indicating that the modes of REE occurrence in the Leonardite are different, likely due to the oxidation process having transformed the bonding.

6 PROCESS DESIGN, ECONOMICS AND OPTIONS FOR COMMERCIALIZATION

This chapter details work associated with performance of a technical and economic feasibility assessment of REE extraction/concentration from North Dakota lignite coal. The first section of this chapter details the process design as conceptualized based on laboratory-scale testing described in Chapter 5 and highlights the novel aspects and advantages of this process design. The second section provides a summary of the economic assessment performed by a third party Engineering and Architecture Firm (Barr Engineering). Finally, some initial concepts for commercialization are laid out and discussed.

6.1 Process Design to Extract and Concentrate REEs from North Dakota Lignite

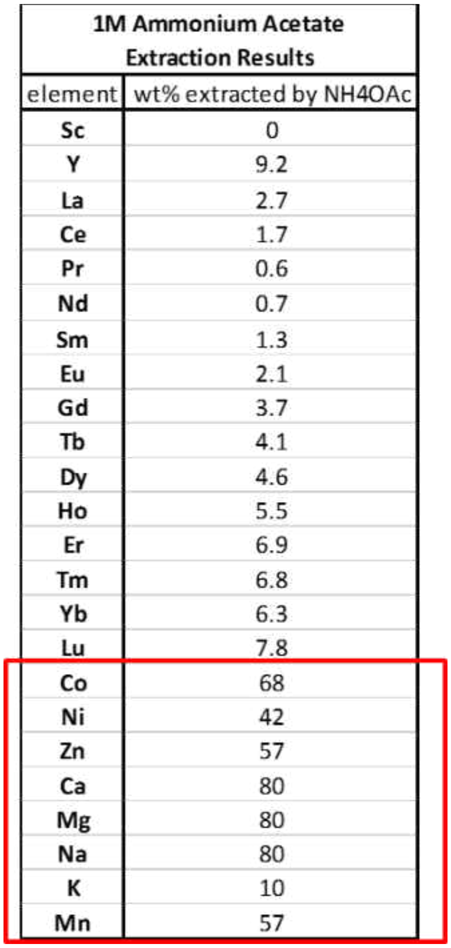
Based on the laboratory-scale testing described previously in Chapter 5, a process design has been conceptualized to extract and concentrate REEs in North Dakota lignite coal to a target of two percent by weight on a dry elemental basis. Only the extraction and concentration unit operations were evaluated. Additional processing will be required to take the two weight percent product and arrive at salable REEs or REE products. The following section provides the details of this process design.

6.1.1 Impurities Removal Options

The elemental analysis of the pre- and post-leaching coal has shown that the primary impurity forms (not likely monetizable) extracted into the REE-solution are iron, calcium, sodium, potassium and magnesium. The alkali and alkaline earth elements can be taken care of through a pre-removal process using an ion-exchange solution, such as ammonium acetate in a pre-leaching step prior to leaching of the REEs. The previous Chemical Fractionation tests (Chapter 4) showed that dilute and low temperature ammonium acetate leaching resulted in very good extraction of these impurities (along with some of the transition metal elements), with very minimal losses of the REEs, as shown in Table 27 for Harmon-Hansen coal. For the case of Hagel B coal, there was zero loss of REEs with ammonium acetate leaching.

In the case of iron impurity, it can either be removed prior to or after the leaching process. The bulk of iron in lignites is in the form of pyrite mineral that has a significantly higher density than the coal. Therefore, processes, such as the GRE DryFining™ process that utilizes density-based separation (i.e. pneumatic air jig) may be applicable to remove coarse pyrite minerals that have been liberated during the initial crushing at the plant. As discussed previously in Chapter 4, the air jig reject stream contained very low levels of REE compared to the feed coal, and thus it is likely that the REEs are not associated with the pyrite/heavy mineral fraction, making this type of configuration a possible option to reduce iron impurity in the REE-containing leach solution without loss of a significant fraction of the REEs. Although not evaluated experimentally, for post leaching removal, this study investigated methods that included pH adjustment and forced oxidation to render the iron species insoluble and selectively precipitate them, while leaving the REEs in solution. Based on a literature review [98, 99, 100, 101, 102], these methods appear feasible. Future work will be required to finalize/optimize the iron impurity removal approach.

Table 27. Extraction of REEs and impurities (red box) by 1M ammonium acetate



1M Ammonium Acetate Extraction Results	
element	wt% extracted by NH4OAc
Sc	0
Y	9.2
La	2.7
Ce	1.7
Pr	0.6
Nd	0.7
Sm	1.3
Eu	2.1
Gd	3.7
Tb	4.1
Dy	4.6
Ho	5.5
Er	6.9
Tm	6.8
Yb	6.3
Lu	7.8
Co	68
Ni	42
Zn	57
Ca	80
Mg	80
Na	80
K	10
Mn	57

6.1.2 Process Description

Combined with the impurities removal strategies identified in the previous section, to maximize the concentration of REEs in the REE concentrate product, the following processing steps can be implemented, as shown in Figure 82:

1. Selectively mined coal with high REE content is delivered to the process. Depending on the as-received particle size of the delivered/selected coal feedstock, some grinding may be needed prior to the extraction process. This will provide sufficient surface area for the leaching steps and will also allow liberation of the heavy mineral content from the coal-rich particles. A top size of about 10 mesh is anticipated, although additional testing is needed to confirm. Grind size will affect the ability to slurry the coal and the leaching solution effectively and will likely affect the kinetics of the REE extraction. A tradeoff between energy usage for grinding/slurry mixing and REE recovery is likely.
2. Gravity concentration to reject heavy mineral content (i.e. pyrite, oxidized iron species) that has been shown to be REE-depleted. This results in an initial concentrating step, and also removes much of the iron content that would be otherwise extracted with the REEs into the concentrate product.
3. Ammonium acetate/ion-exchange leaching to remove ion-exchangeable cations associated with the organic matrix in the coal. This step primarily targets rejection of the alkali and alkaline earth elements (Na, Ca, Mg, K) that would otherwise be extracted with the REEs into the concentrate product. Some of the transition metals and a small fraction (< 5 wt.%) of the REEs are lost to the tailings in this step.
4. Acid leaching (0.5M H_2SO_4) to extract the majority of REEs (70-90 wt.%) into solution

5. Impurities removal step that can include methods such as pH adjustment or forced air oxidation to render target species (i.e. iron) insoluble and selectively precipitate, leaving the REEs and other desired elements in solution.

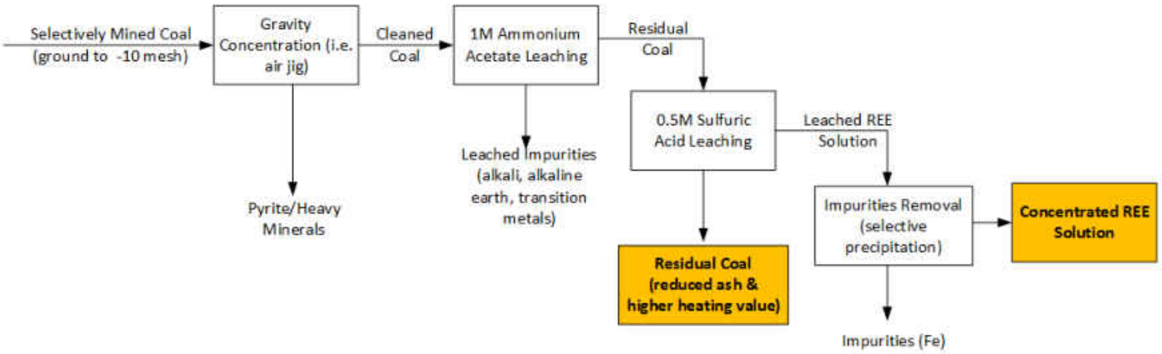


Figure 82. Simplified novel approach to extract and concentrate REEs from North Dakota lignite coal

Two saleable/utilizable products are generated via the above processing steps: i) residual coal byproduct with reduced inorganic content, but preserved organic content, and ii) REE concentrate solution that can be sold to an outside refiner, or could be further processed on-site to arrive at either mixed or separated rare earth oxides and other high value compounds.

6.1.3 Mass Balances

The concentration of REEs in the concentrated REE solution product are shown in Table 28 for both the Hagel B and Harmon-Hansen coals based on the process configurations and the assumptions used for impurities removal efficiency detailed in Table 29. These results indicate that the target of REE concentration of two weight percent is achievable using the methods described above for the Harmon-Hansen coal. However, for the Hagel B coal, additional processing would be needed to achieve the target. The main impurities left in solution after Case 7 for Hagel B are aluminum and the residual amounts of iron and the alkali and alkaline earth elements. Neutralization of the acidic leach solution after REE extraction is likely to achieve the two percent target, but may come at the expense of some REE loss. The target could alternatively be achieved by selectively precipitating some of the monetizable elements prior to REE extraction from the solution. Future experimental work will be required to finalize the entire process flowsheet and mass balances.

Table 28. Concentration of REEs in solution for various cases and assumptions

Case No.	Wt% REEs in Solution (dry basis)	
	Harmon-Hansen Coal	Hagel B Coal
1	0.8	0.2
2	0.9	0.3
3	1.0	0.5
4	2.3	0.4
5	2.7	0.6
6	4.1	0.4
7	5.5	0.7

Note: Based on 48 hour contact time laboratory data. All values are likely to increase with shorter contact times

Table 29. Description of the cases and assumptions used in Table 28

Case No.	Configuration & Assumptions
Case 1	0.5M sulfuric acid leaching only - assumes laboratory-scale 48 hour contact time results
Case 2	To Case 1: Adds 1M ammonium acetate pre-leaching step with 50% removal of Σ (Ca, Na, K, Mg, Zn, Co, Ni, Mn)
Case 3	To Case 1: Adds 1M ammonium acetate pre-leaching step with 80% removal of Σ (Ca, Na, K, Mg, Zn, Co, Ni, Mn)
Case 4	To Case 2: Adds iron removal method with 70% Fe removal
Case 5	To Case 3: Adds iron removal method with 70% Fe removal
Case 6	To Case 2: Adds iron removal method with 90% Fe removal
Case 7	To Case 3: Adds iron removal method with 90% Fe removal

NOTE: Cases 2-7 each assume 5% total REE loss with the ammonium acetate pre-leaching and the iron removal

6.1.4 Process Design Advantages

Although the above process has been presented in the four step configuration shown in Figure 82 (gravity concentration, ion-exchange leaching, acid leaching, impurities removal), substantial room for improvement exists that can further simplify an already exceptionally simple process. Specifically, by optimizing the acid leaching step (acid type, concentration, coal particle size, contact time, solution temperature), one or more of the above steps can likely be eliminated. This author believes that the weakly bonded REE association in the lignite coal combined with mild leaching conditions will allow the possibility to sufficiently tune the process to offer a very high degree of REE-selectivity by minimizing impurities that are extracted into solution. For instance, the association of the dominant impurity, iron, is as an oxidized or reduced species in mineral forms (i.e. pyrite or iron oxides), and thus to extract it into solution the mineral must be solubilized. It is likely that the kinetics of such dissolution are significantly slower than the REEs which are organically bound, and thus control of the contact time could prevent iron dissolution. Ultimately, it may be possible to utilize only the acid leaching step while still achieving the target REE concentration of 2wt% in the concentrate product. This is the type of optimization that is needed in future development.

Some of the key benefits/differentiators of this novel and low-cost process are summarized below:

- The weakly-bonded association of REEs in ND lignite presents a unique opportunity. The REEs in higher rank coals are mainly mineral-bound and are not easily extracted. In lignite, the REEs are primarily associated with the organic matter or in soluble REE-bearing compounds, making them easily extractable from the raw coal with fast leaching kinetics. The process is similar in some respects to the ion-adsorbed clays in China that dominate the HREE market.

- Extensive physical beneficiation is not required. For example, traditional mineral ores and other forms of coal-related feedstocks such as higher rank coals or combustion fly ash require complex, expensive and often inefficient physical beneficiation steps. These can include: i) energy intensive ultra-fine grinding to liberate the micron-size REE-bearing minerals, ii) separation of organics, iii) magnetic separations, and iv) flotation. In particular, the physical beneficiation of coal-related feedstocks is a significant technical/economic challenge because the REE minerals are typically 10 microns or smaller and separation processes in this size range are limited, questionably effective, and costly. One of the major advantages of the ion-adsorbed clay deposits in China is that these processes are not needed. Instead the REE extraction is performed on the as-mined or more recently on the in-situ ore. The process developed in this study is expected to take a similar approach once fully optimized
- A dilute/mild leaching process of the **raw coal** at low or room temperature is utilized. In comparison, hard rock ores, coal fly ash or high rank coals require highly concentrated (i.e. > 80wt%) acid or caustic baking at very high temperatures (i.e. 200-600°C) to achieve reasonable REE extraction. These processes must "crack" or dissolve the REE-bearing minerals into solution. This is a technically complex, expensive and environmentally challenging approach. Coal fly ash in particular is very challenging because during the high temperature combustion process, the REEs

become trapped in the glassy matrix of the ash-related materials, making extraction expensive and technically difficult.

- Because REEs are extracted directly from the raw coal and its organic content is preserved while the inorganic content is decreased, a high value coal byproduct is created that can be sold or utilized to augment the economics of REE recovery.
- The mild leaching process offers potential for a more REE-selective extraction than aggressive leaching methods that must completely dissolve the target mineral(s). By tuning chemistry/contact time, the project team expects to limit extraction of impurities along with the REEs. This is likely not possible with higher rank coals.
- All of the processing steps are commercially proven at large scales and are commonly employed in metallurgical processing/mining operations. There are no first-of-a-kind or novel equipment configurations as were described previously in Chapter 5 in the review of projects by other organizations in the DOE portfolio. This will reduce scale-up risks and significantly decrease the time to market readiness.
- In essence, this technology has "flipped" the conventional notion of REE recovery from coal and coal byproducts. Conventionally, the REE feedstock is a byproduct of another coal process that has little/negative value. This technology uses the raw coal as the feedstock, and thus allows ability to dictate the value-added use of the coal to augment economics, and maximize efficiency and synergies.
- The REE extraction process can also be considered a coal beneficiation process. In the case of the model where activated carbon is produced from the coal byproduct (described later in this Chapter), the purity of the carbon, and hence its value, is increased because a portion of the ash content in the feed coal is removed during the

REE recovery process. However, if the coal is to be used as combustion fuel there are several other important benefits:

1. Ash content can be reduced by 10-75% depending on leaching process(es) used, resulting in an increased heating value per unit mass of coal. The REE recovery itself is optimized by minimizing the ash reduction, but depending on the targeted use of the coal byproduct (i.e. for high purity carbon products such as premium activated carbons or metallurgical coal), the leaching process can be modified or augmented to target the higher end of this range.
2. Nearly 100% of the alkali species are removed, which will mitigate/eliminate alkali aerosol-based issues for solvent-based CO_2 scrubbers. Addition of a gravity concentration step ahead of the leaching processes would also result in a decrease in sulfur and mercury emissions during combustion, as the heavy mineral pyrite is a carrier of these species and would be separated.
3. Reduced fouling/slagging/opacity issues and improved plant reliability
4. Reduced burden on particulate control devices
5. Removal of some toxic/hazardous species, resulting in decreased disposal costs or increased value/marketability of combustion fly ash.

6.2 Technical and Economic Feasibility Analysis (TEA) – Barr Engineering

A third party Engineering and Architecture Firm (Barr Engineering) was contracted to perform a technical and economic feasibility analysis based on the laboratory-scale testing results and feedstock characterization results that were presented in Chapters 4 and 5 of this dissertation. The complete study is attached as Appendix D, and the following sections provide a summary of the methods, major assumptions and results. It should be noted that although Barr Engineering was contracted for the study and they prepared the report, this author in particular was extensively involved throughout the process to prepare flow sheets, set process conditions and determine mass and energy balances.

6.2.1 Scope of the TEA

The scope and basis of the TEA were derived from the work completed during this study. As part of this effort, a potential commercial facility configuration for the economic modeling was identified. The overall concept for first-of-a-kind commercial implementation of this REE recovery process is to combine the REE recovery with activated carbon production co-located at a combined heat and power plant. The integration of activated carbon production with steam generators is a concept developed to replace aging district heating systems at North Dakota University System (NDUS) campuses with systems that co-produce activated carbon and steam [103]. The activated carbon can be sold for municipal water treatment and mercury capture at coal-fired power plants. The steam is used for district heating and for activating the carbon. The concept is being evaluated for implementation at Valley City State University (VCSU) in North Dakota (Senate Bill 2196) [104], which is currently constructing a new steam generation plant. This is a concept that has very favorable economics and has generated tremendous support within the State of North Dakota. 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.

As part of separate research work, in which this author has been a key contributor, technical support and design work is being provided in the VCSU efforts to move forward with the above activated carbon/steam combined plant. The design for the activated carbon components were derived from this separate project and applied to the TEA. Appendix E contains the business plan (Pro-Forma) prepared as part of this separate research work detailing the design basis for the TEA.

For the purposes of the TEA in this work, the scope of the economic modeling is shown in Figure 83 with major assumptions identified below:

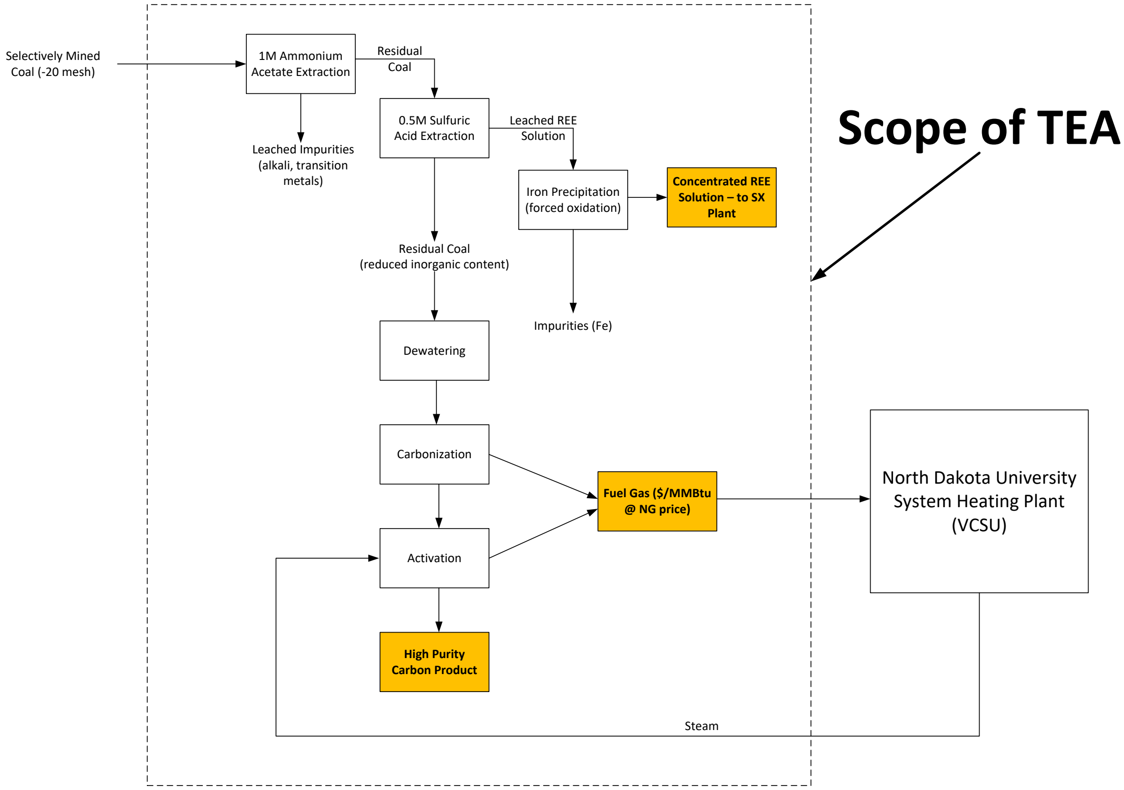


Figure 83. Schematic of the scope of economic modeling for the TEA

- Selectively mined coal from the Harmon-Hansen coal zone is purchased (additional locations for selective mining have been identified, but the Harmon-Hansen was used as the base case in this evaluation)
- Concentrated REE solution is sold to a commercial processor for final purification
- Fuel gas generated via the activated carbon production process is sold to the VCSU steam plant
- Activated carbon is sold wholesale to a distributor (i.e. Calgon Carbon)
- Steam for activation is purchased from the VCSU steam plant

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

- Uses smaller quantity of fuel than large-scale power plants (i.e., 1100 MW Coal Creek Station), which will enable selective mining to prevent dilution of the REE content in the feed coal.
- Integration of activated carbon production and steam production is a transformational approach that significantly reduces cost of carbon production.
- The REE extraction process reduces the inorganic content in the coal, thus resulting in a higher 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 plant scale evaluated in the TEA can be considered a first-of-a-kind demonstration. With successful implementation, support would be expected for additional and larger facilities that will offer scale-up potential.

6.2.2 Design Basis

The design basis is detailed in Appendix D, but below is a summary:

- Coal Feed Rate: 5,000 lb/hr as-received Harmon-Hansen coal – 560 ppm total REE content on dry whole coal basis
- Plant Operating Factor: 50 weeks per year
- Total REE Production: 12.6 tons/year on a pure oxide basis
- Total Activated Carbon Production: 7,450 tons/year
- Total Fuel Gas Production: 230,000 MMBtu/year

Detailed process flow diagrams and mass balances are contained in Appendix D. However, processing steps included are summarized below:

- Process Unit 1: Crushing and milling as-received coal to size of -200 mesh, or the approximate size of powdered activated carbon that would be suitable for use as a mercury control sorbent in coal-fired power plants. It was assumed the coal would be trucked or railed to the VCSU facility in size of approximately 2 to 4 inches.
- Process Unit 2: Leaching to extract REEs and other target elements
- Process Unit 3: Separation of the leach solution and residual coal

- Process Unit 4: Impurity removal via selective precipitation of iron by forced oxidation
- Process Unit 5: Dewatering of the residual coal
- Process Unit 6: Carbonization of dewatered coal to produce a char and fuel gases
- Process Unit 7: Activation of the char to produce activated carbon and fuel gases

Note that the TEA evaluated only the acid leaching step and the impurities removal step, and did not include any gravity concentration of the feed coal or ammonium acetate pre-leaching. These are items that need additional testing in future development work.

6.2.3 Results of Economic Analysis

The TEA focused on evaluating the cost of leaching and impurity removal steps to extract and concentrate REEs and other target elements from coal in conjunction with activated carbon production. In conducting the TEA the principal process drivers such as material price, resource composition/concentration, leaching efficiency, and operating and maintenance expenses were considered. The estimates are considered a Class 5 accuracy range according to AACE International, Cost Estimate Classification System with an expected accuracy range of -20% to -50% (low) and +30% to +100% (high).

The TEA accounted 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 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 this process), evaluation was on 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, it is not needed to know the sales price of the 2 wt% REE concentrate, which is the product of the processing plant. Instead, that value is wrapped into the larger calculation of net profit. The cost of the offsite refinery is addressed by assigning a processing cost per ton of element produced which includes the refiner's operating cost plus profit. Since the refiner would process the concentrate on a contract basis, this analysis does not include any capital expense for the refinery – it is assumed to be built and available for contract processing. This approach allows use of 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 the scope of the project. This provides a net revenue stream (after accounting for internal OPEX) that can be used, along with the estimated extraction plant CAPEX to determine economic metrics.

Overall, the results of the economic analysis are provided in Table 30 for the base case scenario, as described in detail in Appendix D. As shown in the table, the major revenue source is the activated carbon, at about \$10.4 Million/year, but the REEs and the other target elements provide significant revenue as well at about \$3.3 Million/year. The fuel gas is the lowest source of revenue at \$0.8 Million/year. Overall these results indicate that this combined plant configuration is highly profitable, even at the relatively small scale evaluated in this study. The incremental economics of the REE extraction by itself are presented later in Section 6.2.6.

Table 30. Economics of the combined REE/activated carbon/steam plant concept

Economic Metric	Amount
CAPEX	($28,300,000)
OPEX	($4,700,000)
REE/target element and Base Metal Payable Amount per year	$3,300,000
Activated Carbon Payable Amount per year	$10,400,000
Syngas Payable Amount per year	$800,000
Net Annual Revenue per year	$9,800,000
Simple Payback (years)	2.9
IRR (10 years)	32%
ROI (10 years)	21%
NPV (10 years) @15% discount rate	$18,600,000
IRR (20 years)	35%
ROI (20 years)	28%
NPV (20 years) @15% discount rate	$32,600,000
CAPEX/annual dry ton feed	$1,800
OPEX/annual dry ton feed	$300
Net Revenue/annual dry ton feed	$620

IRR: Internal Rate of Return   ROI: Return on Investment   NPV: Net Present Value
Simple Payback = CAPEX/Net Annual Revenue Per Year

An interesting finding is shown in Table 31, which breaks down the revenues generated for each of the target elements recovered from the REE extraction process. The data shows that the three highest revenue generators are scandium (58.6%), germanium (16.7%) and cobalt (8.8%). These are elements that are not in the lanthanide series, which are the primary targets of this technology, but are providing nearly 85% of the total revenue from the REE extraction. Based on discussions with others investigating REE recovery processes, this appears to be fairly standard in the industry. Even though the REEs are the technology drivers, the economic drivers are actually the byproducts produced with the REEs. Therefore, it is critical that technologies be developed that are able to monetize products besides the REEs for them to be economically viable given the current market pricing.

Table 31. Breakdown of revenues generated by each element contained in the REE concentrate product

Element	**% of Total**	**Salable Revenue**
Cerium Ce 58	0.1%	$4,627
Cobalt Co	***8.8%***	***$288,948***
Copper Cu 29	0.1%	$3,498
Dysprosium Dy 66	2.4%	$79,383
Erbium Er 68	0.3%	$10,385
Europium Eu 63	1.0%	$31,462
Gadolinium Gd 64	0.3%	$10,354
Gallium Ga	3.2%	$105,658
Germanium Ge	***16.7%***	***$550,705***
Holmium Ho 67	0.1%	$3,216
Lanthanum La 57	0.1%	$3,067
Lutetium Lu 71	0.6%	$18,289
Manganese Mn 25	0.0%	$525
Neodymium Nd 60	3.5%	$114,724
Praseodymium Pr 59	1.1%	$34,697
Samarium Sm 62	0.1%	$1,784
Terbium Tb 65	2.0%	$64,330
Thulium Tm 69	0.6%	$19,458
Scandium Sc 21	***58.6%***	***$1,929,223***
Ytterbium Yb 70	0.2%	$6,113
Yttrium Y 39	0.3%	$10,385
Zinc Zn 30	0.0%	$394

In addition to the base case evaluation, a series of *independent* sensitivity points were evaluated to identify the impact of parameters on overall plant economics. These are summarized as follows, with results shown in Table 32.

- Hagel B Results – used Hagel B coal instead of Harmon-Hansen and the associated laboratory-scale leaching results. This results in lower REE and target element production, as well as lower concentration in the product, thus requiring increased refining costs.

- Base Case Half Element Price – each sale price for the REEs/target elements was halved
- Base Case Double Element Price – each sale price for the REEs/target elements were doubled
- Higher Activated Carbon Sale Price – increased from $1400/ton to $2000/ton
- Lower Activated Carbon Sale Price – decreased from $1400/ton to $1000/ton
- Scandium Excluded From Saleable Products (discussion in Section 6.2.4)
- Sale Price of Germanium Halved (discussion in Section 6.2.4)
- CAPEX Decreased by 50%
- CAPEX Increased by 50%
- Reduced Plant Operating Factor – 45 weeks instead of 50 weeks

Table 32. Results of economic sensitivity analysis

Economic Parameter	**Net Annual Revenue**	**Simple Payback (years)**	**IRR (10 years)**	**ROI (10 years)**	**NPV (10 years) @15% DR**	**IRR (20 years)**	**ROI (20 years)**	**NPV (20 years) @15% DR**
Base Case	$9,820,000	2.9	32%	21%	$18,600,000	35%	28%	$32,600,000
Hagel B Results	$6,960,000	4.1	20%	12%	$4,900,000	24%	18%	$14,800,000
Base Case Half Element Price	$8,170,000	3.5	25%	16%	$10,700,000	29%	22%	$22,300,000
Base Case Double Element Price	$13,110,000	2.2	45%	32%	$34,300,000	46%	39%	$53,000,000
Higher Activated Carbon Price	$14,290,000	2.0	49%	35%	$39,900,000	50%	43%	$60,300,000
Lower Activated Carbon Price	$6,840,000	4.1	19%	12%	$4,300,000	24%	18%	$14,100,000
No Sale of Scandium	$7,890,000	3.6	24%	15%	$9,300,000	28%	21%	$20,600,000

Table 32. Results of economic sensitivity analysis

Economic Parameter	Net Annual Revenue	Simple Payback (years)	IRR (10 years)	ROI (10 years)	NPV (10 years) @15% DR	IRR (20 years)	ROI (20 years)	NPV (20 years) @15% DR
Germanium Half Price	$9,540,000	3.0	31%	20%	$17,200,000	34%	27%	$30,800,000
Base Case CAPEX Decrease by 50%	$9,820,000	1.4	69%	52%	$32,700,000	69%	61%	$46,700,000
Base Case CAPEX Increase by 50%	$9,820,000	4.3	18%	11%	$4,400,000	23%	17%	$18,400,000
86% Capacity (45 wks/yr)	$9,810,000	2.9	32%	21%	$18,500,000	35%	28%	$32,500,000

The sensitivity analysis indicates that although revenue is obtained from the sale of REEs and base metals, payable revenue due to generation of the activated carbon product has the largest impact on overall profitability. The sensitivity shows that increasing/ decreasing the sale price of the activated carbon has simple payback from 1.9 to 4.0 years compared to 2.1 to 3.3 years for increasing/decreasing sale price of REEs and base metals. The most drastic change comes from increasing/decreasing the CAPEX with a simple payback from 1.4 to 4.2 years, which is expected with larger cash amounts. The sensitivity analysis also shows that the choice of feedstock impacts the economics dramatically. The Harmon-Hansen coal is considerably more favorable. However, even the Hagel B coal, with relatively low total REE content results in an overall profitable plant. It is important to recognize, though, that in the case of the Hagel B coal, that the economics of the activated carbon production process subsidize the production of REEs (i.e. incremental economics of the REE components produce negative cash flow). However, this may not necessarily be a deal-breaker for Hagel B in the event that REE prices increase in the future due to decrease in supply from foreign sources, or in the event of government subsidies stemming from national security concerns.

6.2.4 Discussion of Market Impacts

The following section briefly discusses the market implications of introducing new sources of domestic production of REE as well as other metals that have a large impact on the economics of the proposed plant. Data is obtained from the 2016 USGS Mineral Commodities Report [33]. It is important to note that these discussions are based on production rates from the plant evaluated within the TEA. 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 in the United States has increased from 11,000 to 17,000 metric tons from 2011 to 2015. In 2015, the U.S. was a net importer with about 4,100 metric tons produced from the Mountain Pass Mine in 2015, most of which consisted of the light REE. A larger proportion of the heavy REE were imported. For instance, for Yttrium, the content within the Mountain Pass Mine ore is estimated at about 0.12% of the total REE content, and due to this low concentration was not processed/produced. Total domestic consumption of Yttrium was about 200 metric tons in 2015, all of which was imported. As of 2016, the U.S. was 100% import reliant for REEs, as the Mountain Pass Mine was no longer in operation. Approximately 11 tons per year of REE oxides are produced from the plant evaluated in this study after final purification. 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 1 ton/year of Scandium oxide, 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 10 to 15 tons in 2015. 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 to expand the market utilization. To understand the impact of Scandium sale price on the overall economics of the proposed plant, a sensitivity analysis point was included that excludes Scandium from the list of saleable products.

Another major contributor to sales from the proposed plant is Germanium oxide, with a production rate of about 0.5 ton/year from the proposed plant. According to the USGS Mineral Commodities Report, total domestic consumption of Germanium was about 30 metric tons in 2015, down from 38 metric tons in 2012. The U.S. is a net importer of Germanium, with total imports of about 37 metric tons in 2015. 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. To understand the impact of Germanium sale price, a sensitivity analysis point was included that reduces the price by half for only Germanium.

6.2.5 Evaluation of Worst, Likely and Best Case Scenarios

To provide an indication of the spectrum of possible outcomes for the economics of the plant evaluated within the TEA, estimates of the worst, likely and best case scenarios were prepared. The technical and economic data presented in the TEA were purposefully conservative, and thus the economics are likely to be more towards the ‘worst-case’ scenario. However, these three scenarios were evaluated both from a technical and economic standpoint with details presented in the following sections.

6.2.5.1 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, iii) complexity/number of processing steps, and iv) effectiveness of impurity removal to reduce costs of purification. Each of these categories are discussed below.

- *REE Recovery Efficiency*: Since the REE recovery efficiency presented in this study is based on actual laboratory testing data performed, these results are classified 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, as was described in the discussion on leaching kinetics in Chapter 5. 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 purification processes (i.e. increase recovery efficiency from solvent extraction steps). REE recovery efficiency also depends on the feedstock chemistry. The Harmon-Hansen coal had better recovery than the Hagel B coal. Other elements such as Scandium and Germanium were extracted with good efficiency as well and because of their high market prices have a large impact on overall economics. The worst-case scenario was estimated at about 70-75% recovery in the leaching step(s), and the best-case scenario at about 90% recovery in the leaching step(s).

- *REE Content in the Feedstock*: The TEA evaluated the Harmon-Hansen coal, which to date, is the highest REE content coal sampled. It also has an attractive ratio of critical and heavy REE to light REE. However, based on the discussion previously provided in Chapters 3 and 4, this author believes that other coals in the state have the necessary quantity/distribution of REE, as well as being present/mineable in sufficient quantity, to be commercially feasible. Therefore, the Harmon-Hansen coal is classified as the likely scenario. The Hagel B coal, which was shown to be significantly less profitable in this study, but still profitable, can be considered the worst-case scenario. The best-case scenario is to identify large quantity of high REE content coal with the desired REE modes of occurrence in an existing mine (the Harmon-Hansen coal zone has not been mined since 1997) that has good/uniform distribution to minimize costs of selective mining.
- *Complexity/Number of Processing Steps:* This study presented the two-step approach to generating a 2wt% REE concentrate solution – sulfuric acid leaching

followed by forced oxidation to remove iron impurity. The option of adding a third step in the form of a pre-leach using ammonium acetate was also investigated. The presented configuration is believed to be the likely case, but optimization of the acid leaching step may result in sufficient REE purity to eliminate the iron oxidation component. The worst-case scenario can be considered the 3-step process that also needs an acid neutralization step to increase the kinetics of iron oxidation. The best-case scenario is an optimized acid leaching process that eliminates the pre-leach and impurities removal steps. An alternate best-case scenario could be implementation of a processing approach that significantly increases the concentration of the REE in the product (i.e., ~5.5 wt% as shown in Case 7 in Table 28), which could sufficiently reduce the cost of downstream purification to justify the added capital/operating costs for extraction and initial concentration.

- *Effectiveness of Impurity Removal*: The primary impurity in the leach solution is iron for the Harmon-Hanson coal. This study presented the case with 70% iron removal efficiency via forced oxidation, which is believed to be the likely case. A worst-case scenario is slow iron oxidation kinetics that require an acid neutralization step. The best-case scenario would be not needing iron removal at all due to prevention of extracting iron into the solution, either by optimizing the leaching steps or by identifying a feedstock with more stable or lower iron content.

6.2.5.2 Economic Scenarios

The primary economic drivers are: (i) CAPEX/OPEX, (ii) REE/target element and carbon sales price, (iii) purification costs, and (iv) plant scale. Each are discussed briefly below.

- *CAPEX/OPEX*: This study made conservative assumptions for capital and operating expenses to account for the early stage of technical development, and thus the data presented is considered the likely case, but erring slightly towards the worst-case. The main driver dictating capital and operating expenses is process complexity. As discussed above, three complexity scenarios are envisioned – one-step, two-step and three-step, the two-step having been presented in this study.
- *Product Sales Prices:* 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. The sensitivity analyses have evaluated ½ and double the current prices to understand the impact. While it is not believed that 2011 prices are realistic in the near-term, a major decline in prices is also not expected. The sale price for activated carbon used in this study is based on wholesale prices derived from discussions 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.

- *Purification Costs*: For the purposes of this study, the downstream element purification costs were not defined, and estimates were applied to appraise the "value" of the 2-wt% REE concentrate product. At this stage of development it is difficult to quantify the uncertainty in the estimates, but they are believed to be conservative based on consultation with industry experts.
- *Plant Scale:* As discussed previously, the plant scale evaluated within the TEA is considered a first-of-a-kind pilot that, if successful, will encourage installation at additional and larger facilities. To investigate the impact of scale, the economics of the application of REE extraction co-located with activated carbon production and steam production to a range of coal feed rates from "small demo" to scaled-up installations has been estimated. CAPEX was scaled using the $^6/_{10}$ ths rule and OPEX and revenues were scaled linearly with throughput. The results are shown in Figure 84. Using these projections, the 10-year 'break-even' plant scale is about 1,000 lb/hr in terms of NPV (at 15% discount rate), but net revenues (cash flow) are positive even at the smallest 100 lb/hr scale.

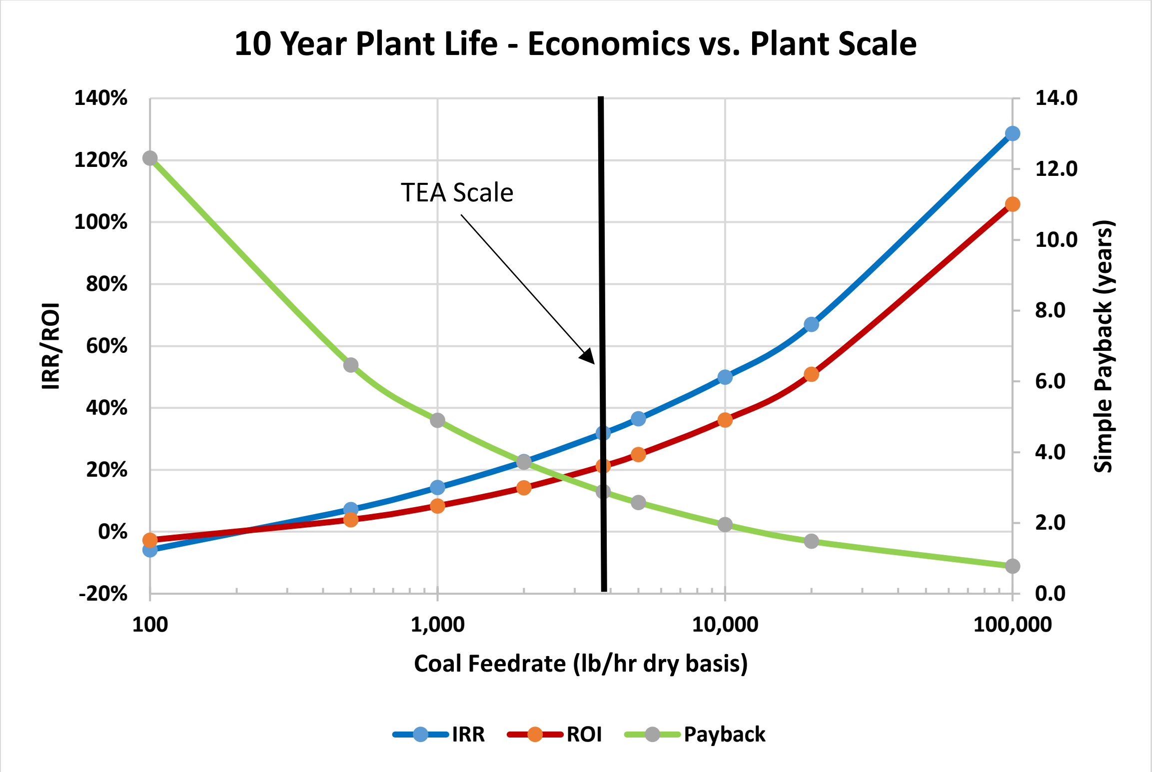


Figure 84. Projection of economics for multiple plant scales with TEA scale noted

6.2.5.3 Quantified Results

The data presented in the TEA can reasonably be assumed as the likely or average scenario, accounting for conservative assumptions based on limited process definition to date. Best-case scenarios would involve: (i) simplifying the processing scheme to eliminate pre-leaching and impurities removal steps, or to significantly increase the concentration of REEs in the product, (ii) identification of an improved feedstock with either higher total REE content, higher critical or heavy REE content, more stable impurity forms or lower cost mining, (iii) increases in REE/target element sales prices, and (iv) scaling up the technology beyond the first implementation. Worst-case scenarios would involve: (i) increased process complexity to achieve 2-wt% REE concentration,

(ii) less desirable feedstock, and (iii) lower REE/target element and activated carbon sales prices.

The <u>best-case scenario</u> could be estimated as the following combined sensitivity case:

- Decrease in CAPEX/OPEX, including REE/target element purification costs by 10%
- Increase in REE/target element sales price by 10%
- Increase in activated carbon sales price by 10%

When combining the above, best-case economic metrics are as follows:

- 20 year IRR: 46%
- 20 year ROI: 38%
- Simple Payback: 2.2 years
- 20 year NPV (15% discount rate): $46,700,000

The <u>worst-case scenario</u> could be estimated as the following combined sensitivity case:

- Increase in CAPEX by 50%
- Increase in OPEX, including REE/target element purification costs by 10%
- Decrease in REE/target element sales price by 10%
- Decrease in activated carbon sales price by 10%

When combining the above, worst-case economic metrics are as follows:

- 20 year IRR: 18%
- 20 year ROI: 13%
- Simple Payback: 5.3 years
- 20 year NPV (15% discount rate): $6,900,000

The results clearly show that even in the estimated worst-case scenario the combined REE/activated carbon/steam plant configuration still has very attractive overall economics at the scale evaluated in the TEA.

6.2.6 Evaluation of the Stand-Alone Economics of REE Extraction

The overall concept for initial commercial-scale implementation of this novel rare earth element extraction technology for North Dakota lignite-related feedstocks includes co-location and integration of the REE extraction with activated carbon production and steam/electricity production. The economics of this configuration are very attractive according to the TEA. A primary benefit of the technology is that since it recovers REEs directly from the raw as-mined coal and preserves its organic content, the economics of REE extraction can be significantly augmented through value-added use of the coal byproduct. However, the following discussion presents the economic results of the stand-alone REE extraction technology that does not take credit for the value-added use of the coal byproduct produced by the technology. The goal of this analysis was to identify the stand-alone economics for the base case scenario as evaluated in the TEA, as well as to investigate several other scenarios that impact economics.

Costs and revenues associated with the activated carbon and syngas production components evaluated in the TEA have been stripped from this analysis, leaving only the costs and revenues associated with the REE extraction by itself. To investigate plant scale, CAPEX has been scaled according to the $^{6}/_{10}$ ths rule, and OPEX and revenues have been scaled linearly. Although this analysis does not include value-added use of the coal byproduct, it is assumed to have zero cost for the feedstock (i.e. will be able to sell the coal byproduct at the same price as the purchased feed coal). This is believed to be a conservative assumption as the quality (ash content, heating value) of the coal byproduct is significantly better than the feed coal, and grinding has already occurred as part of the process. The analysis also assumed 50% labor/operator cost than that used in the TEA for the full combined plant. The following describes each of the independent scenarios evaluated in this analysis:

- **Case 1**: Base case CAPEX, OPEX and revenues (only for the REE extraction) evaluated in the TEA
- **Case 2**: Decrease base case CAPEX by 10%
- **Case 3**: Target only highest value/largest revenue generating elements for final purification
    - Co, Dy, Er, Eu, Ga, Ge, Lu, Nd, Pr, Tb, Tm, Sc, Y
    - TEA assumed purification of all elements listed in the economic model (Appendix D). The above elements provide more value relative to refining costs and thus improve economics.
- **Case 4**: Target only highest value/largest revenue generating elements for final purification *AND* decrease base case CAPEX by 10%
- **Case 5**: Increase revenue by 10%
    - Either through higher quality feedstock or increases in sales prices
- **Case 6**: Co-location of final purification (i.e. solvent extraction plant)
    - Allows 60% acid recycle via the barren liquor post extraction of target elements
- **Case 7**: Increase revenue by 25%

    - Either through higher quality feedstock or increases in sales prices
- **Case 8**: Peak REE oxide sales prices (2011 data) [33]
    - Ce: \$20/lb
    - Dy: \$645/lb
    - Eu: \$1,727/lb
    - Gd: \$91/lb
    - La: \$24/lb
    - Nd: \$91/lb
    - Pr: \$112/lb
    - Tb: \$1,282/lb
    - Y: \$64/lb
    - All other elements use base case sale prices from the TEA

Table 33 (Cases 1-4) and Table 34 (Cases 5-8) provide the results of the economics calculations/estimates for each of the above scenarios. The data is also shown in Figure 85 for cases 1-7 for the 20-year internal rate of return (IRR) metric. For a reference to plant scale, 200,000 lb/hr of coal feed is approximately equivalent to a 100-150 MW North Dakota lignite-fired power plant. Note that 3,772 lb/hr was the scale used in the TEA.

As shown in Table 33 and Table 34, cash flows are positive for every plant scale and case evaluated. However, 20-year net present value (NPV) is not positive when using 10% discount rate or higher for any scale in either Case 1 or Case 2. With 5% discount rate for Case 1 and 2, the NPV becomes positive at scale above 100,000 lb/hr feedstock throughput. At 10% discount rate, positive NPV isn't shown until Case 3 at the largest scale. Each subsequent case has improved economics, with Case 8 (2011 peak REE prices) having extremely attractive economics, with positive NPV even at the smallest scale evaluated. Although 2011 prices may not be realistic in the short term, in the event of a decrease in foreign supply due to export limitations from China (as occurred in 2010), the market may see a significant increase in prices. For instance, Case 7, with 25% increase in revenue has very attractive economics above 20,000 lb/hr scale (~10-15 MW equivalent lignite-fired power plant). An interesting finding from this exercise is the significant impact of co-locating the purification plant with the extraction plant that allows recycling of the barren liquor back to the leaching process (Case 6). The TEA assumed 100% acid makeup, even though laboratory testing showed only about 40% of the acid is consumed during the leaching process. Co-location would allow 60% acid recycle and a significant reduction in OPEX.

The primary conclusions from this evaluation are summarized below:

- Stand-alone economics of this REE extraction technology are less attractive without value-added use of the coal byproduct
- Targeting only high price elements for purification (Cases 3 & 4) can improve economics over the base case
- Economic sensitivity to revenue (limited to REE/target element sales for this analysis) is larger than CAPEX – a 10% increase in revenue results in a profitable plant, but a 10% decrease in CAPEX does not.

- In the event of future increases in REE sales prices such as those that have occurred in the recent past, the economics of the technology are very attractive, especially at larger scale than evaluated in the TEA.
- Although the TEA evaluated a relatively small-scale plant (3,772 lb/hr feedstock), the REE-rich lignite resources in North Dakota are believed to be commercially feasible for significantly larger plants, such as those evaluated in this study.
- Economic recovery of REE from coal and coal byproducts (for any technology) will be an extremely challenging prospect without higher sales prices or value-added use of byproducts generated. The technology developed in this study is unique in that it produces multiple high-value and monetizable byproducts.

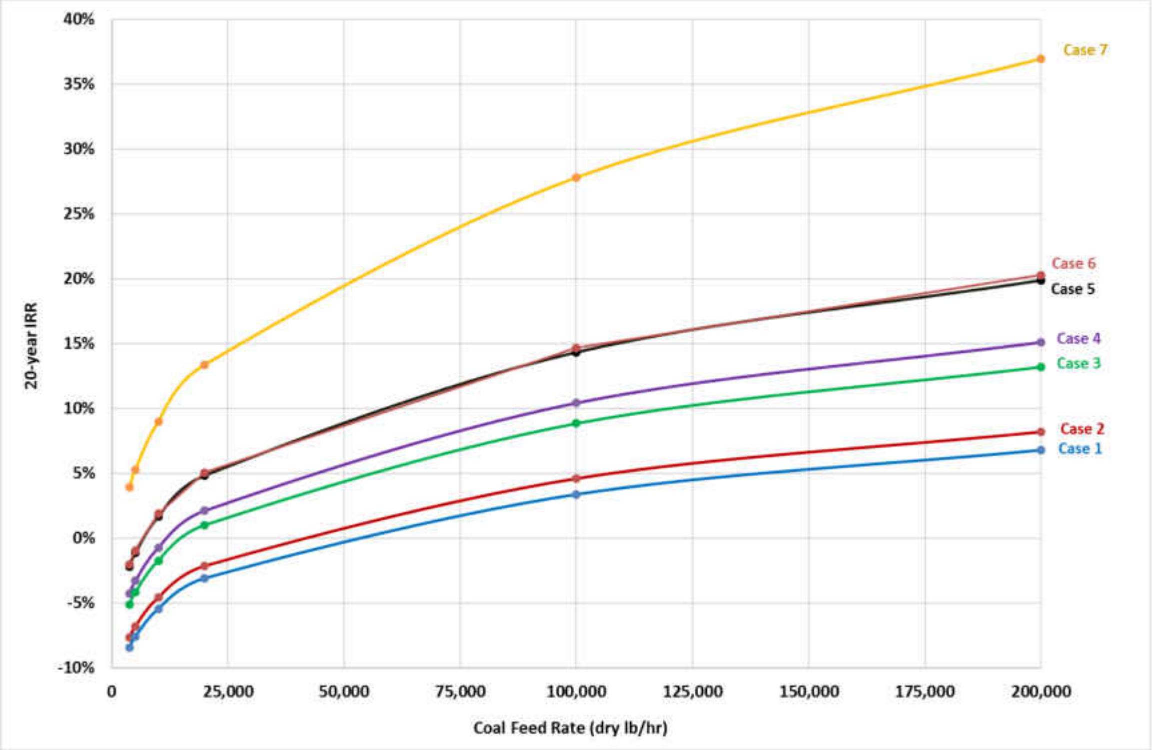


Figure 85. Estimates of economics of stand-alone REE extraction

Table 33. Cash flow sheet and 20-year economic metrics for stand-alone REE extraction - Cases 1- 4

Case Description	Case No.	Plant Size (lb/hr coal feed)	CAPEX	OPEX	REE/element Revenue	Cash Flow	IRR	ROI	Simple Payback	NPV (15%)	NPV (10%)
Base Case	**1**	3,772	($14,600,000)	($3,000,000)	$3,300,000	$300,000	-8%	-3%	48.7	($12,900,000)	($12,200,000)
		5,000	($17,300,000)	($4,000,000)	$4,400,000	$400,000	-8%	-3%	43.3	($15,000,000)	($14,200,000)
		10,000	($26,300,000)	($8,000,000)	$8,700,000	$800,000	-5%	-2%	32.9	($21,600,000)	($20,000,000)
		20,000	($39,800,000)	($15,900,000)	$17,500,000	$1,500,000	-3%	-1%	26.5	($30,500,000)	($27,200,000)
		100,000	($104,500,000)	($79,700,000)	$87,300,000	$7,500,000	3%	2%	13.9	($57,800,000)	($41,500,000)
		200,000	($158,400,000)	($159,400,000)	$174,500,000	$15,100,000	7%	4%	10.5	($65,000,000)	($32,300,000)
Decrease CAPEX by 10%	**2**	3,772	($13,200,000)	($3,000,000)	$3,300,000	$300,000	-8%	-3%	44.0	($11,400,000)	($10,800,000)
		5,000	($15,600,000)	($4,000,000)	$4,400,000	$400,000	-7%	-3%	39.0	($13,300,000)	($12,400,000)
		10,000	($23,600,000)	($8,000,000)	$8,700,000	$800,000	-5%	-2%	29.5	($19,000,000)	($17,300,000)
		20,000	($35,800,000)	($15,900,000)	$17,500,000	$1,500,000	-2%	-1%	23.9	($26,500,000)	($23,200,000)
		100,000	($94,100,000)	($79,700,000)	$87,300,000	$7,500,000	5%	3%	12.5	($47,400,000)	($31,000,000)
		200,000	($142,600,000)	($159,400,000)	$174,500,000	$15,100,000	8%	5%	9.4	($49,100,000)	($16,500,000)
Target only: Co, Dy, Er, Eu, Ga, Ge, Lu, Nd, Pr, Tb, Tm, Sc, Y	**3**	3,772	($14,600,000)	($2,800,000)	$3,300,000	$400,000	-5%	-2%	36.5	($11,900,000)	($11,000,000)
		5,000	($17,300,000)	($3,700,000)	$4,300,000	$600,000	-4%	-2%	28.8	($13,700,000)	($12,500,000)
		10,000	($26,300,000)	($7,500,000)	$8,600,000	$1,200,000	-2%	-1%	21.9	($19,100,000)	($16,600,000)
		20,000	($39,800,000)	($15,000,000)	$17,300,000	$2,300,000	1%	1%	17.3	($25,500,000)	($20,400,000)
		100,000	($104,500,000)	($74,800,000)	$86,400,000	$11,600,000	9%	6%	9.0	($32,800,000)	($7,700,000)
		200,000	($158,400,000)	($149,600,000)	$172,700,000	$23,100,000	13%	9%	6.9	($15,000,000)	$35,100,000
Target only: Co, Dy, Er, Eu, Ga, Ge, Lu, Nd, Pr, Tb, Tm, Sc, Y **AND** **CAPEX reduced by 10%**	**4**	3,772	($13,200,000)	($2,800,000)	$3,300,000	$400,000	-4%	-2%	33.0	($10,500,000)	($9,500,000)
		5,000	($15,600,000)	($3,700,000)	$4,300,000	$600,000	-3%	-1%	26.0	($12,000,000)	($10,800,000)
		10,000	($23,600,000)	($7,500,000)	$8,600,000	$1,200,000	-1%	0%	19.7	($16,500,000)	($14,000,000)
		20,000	($35,800,000)	($15,000,000)	$17,300,000	$2,300,000	2%	1%	15.6	($21,500,000)	($16,500,000)
		100,000	($94,100,000)	($74,800,000)	$86,400,000	$11,600,000	10%	7%	8.1	($22,400,000)	$2,700,000
		200,000	($142,600,000)	($149,600,000)	$172,700,000	$23,100,000	15%	10%	6.2	$800,000	$51,000,000

Table 34. Cash flow sheet and 20-year economic metrics for stand-alone REE extraction - Cases 5-8

Case Description	Case No.	Plant Size (lb/hr coal feed)	CAPEX	OPEX	REE/element Revenue	Cash Flow	IRR	ROI	Simple Payback	NPV (15%)	NPV (10%)
Increase Revenue by 10%	**5**	3,772	($14,600,000)	($3,000,000)	$3,600,000	$600,000	-2%	-1%	24.3	($10,800,000)	($9,500,000)
		5,000	($17,300,000)	($4,000,000)	$4,800,000	$800,000	-1%	-1%	21.6	($12,300,000)	($10,500,000)
		10,000	($26,300,000)	($8,000,000)	$9,600,000	$1,600,000	2%	1%	16.4	($16,200,000)	($12,700,000)
		20,000	($39,800,000)	($15,900,000)	$19,200,000	$3,300,000	5%	3%	12.1	($19,600,000)	($12,600,000)
		100,000	($104,500,000)	($79,700,000)	$96,000,000	$16,300,000	14%	10%	6.4	($3,700,000)	$31,500,000
		200,000	($158,400,000)	($159,400,000)	$192,000,000	$32,500,000	20%	15%	4.9	$43,200,000	$113,700,000
Co-location of SX-EW (60% acid recycle to leaching process)	**6**	3,772	($14,600,000)	($2,700,000)	$3,300,000	$600,000	-2%	-1%	24.3	($10,800,000)	($9,400,000)
		5,000	($17,300,000)	($3,500,000)	$4,400,000	$800,000	-1%	0%	21.6	($12,200,000)	($10,400,000)
		10,000	($26,300,000)	($7,100,000)	$8,700,000	$1,700,000	2%	1%	15.5	($16,000,000)	($12,400,000)
		20,000	($39,800,000)	($14,100,000)	$17,500,000	$3,300,000	5%	3%	12.1	($19,300,000)	($12,100,000)
		100,000	($104,500,000)	($70,700,000)	$87,300,000	$16,600,000	15%	10%	6.3	($1,800,000)	$34,100,000
		200,000	($158,400,000)	($141,400,000)	$174,500,000	$33,100,000	20%	15%	4.8	$47,000,000	$118,800,000
Increase Revenue by 25%	**7**	3,772	($14,600,000)	($3,000,000)	$4,100,000	$1,100,000	4%	2%	13.3	($7,800,000)	($5,400,000)
		5,000	($17,300,000)	($4,000,000)	$5,500,000	$1,500,000	5%	3%	11.5	($8,200,000)	($5,000,000)
		10,000	($26,300,000)	($8,000,000)	$10,900,000	$2,900,000	9%	6%	9.1	($8,100,000)	($1,700,000)
		20,000	($39,800,000)	($15,900,000)	$21,800,000	$5,900,000	13%	9%	6.7	($3,400,000)	$9,300,000
		100,000	($104,500,000)	($79,700,000)	$109,100,000	$29,400,000	28%	22%	3.6	$77,400,000	$141,000,000
		200,000	($158,400,000)	($159,400,000)	$218,100,000	$58,700,000	37%	30%	2.7	$205,400,000	$332,600,000
Peak REE Prices (2011 - per USGS 2016 report)	**8**	3,772	($14,600,000)	($3,000,000)	$5,600,000	$2,600,000	17%	12%	5.6	$1,400,000	$48,100,000
		5,000	($17,300,000)	($4,000,000)	$7,400,000	$3,400,000	19%	14%	5.1	$4,000,000	$65,800,000
		10,000	($26,300,000)	($8,000,000)	$14,800,000	$6,900,000	26%	20%	3.8	$16,300,000	$140,100,000
		20,000	($39,800,000)	($15,900,000)	$29,700,000	$13,700,000	34%	28%	2.9	$45,300,000	$292,800,000
		100,000	($104,500,000)	($79,700,000)	$148,400,000	$68,700,000	66%	57%	1.5	$321,200,000	$1,558,600,000
		200,000	($158,400,000)	($159,400,000)	$296,800,000	$137,400,000	87%	77%	1.2	$692,900,000	$3,167,800,000

6.3 Commercialization Options

The work detailed in this dissertation has focused on the extraction and partial concentration of REEs from North Dakota lignite and lignite-related feedstocks. The technology is believed to be novel and warrants continued evaluation, scale-up, and if successful, eventual commercialization. The TEA completed in this study and described in this Chapter focused on what is essentially considered a large demonstration-scale first-of-a-kind commercial installation. While the REE/activated carbon/steam plant configuration has been shown to have very attractive economics, it is certainly not the only configuration possible for the REE extraction technology developed in this study. The below sections discuss some of the initial concepts for alternate commercialization approaches. However, these are also not to be considered inclusive of every possibility.

From a mining standpoint, it is important to recognize that the ideal scenario for this technology would be integration within an existing mine, so as to avoid mine startup costs and delays. However, the information detailed in Chapter 4 of this dissertation identified the Harmon-Hansen coal zone as a location with particularly elevated REE levels. Because the Harmon-Hansen coal zone has no active mines, it would be necessary to build an economically viable case to open a new mine, which may take several years and a large investment. Scenarios for both an existing and new mine are discussed below.

- Selective mining from an existing mine, combined with REE extraction and activated carbon production to produce a mine-mouth source of powdered activated carbon for mercury control at the adjacent power plant or other plants/facilities operating in the region. North Dakota lignite power plants are built very near the mines so as to avoid shipping the high moisture lignite long distances. By co-locating REE extraction and activated carbon production either at the mine or the adjacent power plant, the cost of transporting activated carbon will be reduced, and thus will represent savings for the plant that already requires activated carbon for mercury control. Due to emissions regulations (Mercury and Air Toxics Standards), most coal-fired power plants require the use of activated carbon to control mercury.

- Opening a new mine with a combination of selective mining for REE extraction and bulk mining for a new power application. For example, this could be the location of a future next generation lignite-fired electric generation facility, such as the Allam Cycle or chemical looping combustion. The North Dakota Industrial Commission Lignite Energy Council has been investing significant research funding/effort into the Allam Cycle, in particular, and is looking at the next generation of lignite-fired systems that will sustain the industry long-term in a carbon constrained regulatory environment. The new mine could also serve as the regional coal supplier to power the next generation of North Dakota University System (NDUS) steam heating plants, which together could utilize an estimated 1 million tons annually of lignite.
- Leonardite (oxidized lignite) is another potential target. There are currently two active leonardite mines in ND, the Stony Creek Mine and the Page/Perkins Thompkins Mine, and the two together produce about 95,000 tons per year [105] of leonardite that is used as feedstock for humic acid production and in soil fertilizers and oilfield drilling fluids. Analysis presented in Chapter 4 identified leonardite as one of the REE-enriched coal-related resources in the State. Leonardite also has unique surface chemistry properties that make it particularly adsorptive and able to attract and retain cations such as REEs [87]. In the case of leonardite, a unique opportunity presents itself because the

REE extraction process preserves the organic content of the feed. Therefore, the REE extraction plant could essentially “borrow” the mined leonardite, remove the REEs and return the REE-depleted leonardite back to the resource owner, essentially losing little value and not affecting its downstream applications.

7 SUMMARY, CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE RESEARCH

This chapter provides a summary of the work performed in this study, as well as the key results and the conclusions drawn. Additionally, a section has also been included that details the personal opinions of this author in regards to recommendations for future research work and technology direction.

7.1 Summary of Work Performed

This study has investigated the potential of rare earth element recovery from North Dakota lignite and lignite-related coal resources. The work was broken down into three phases: i) sampling and characterization, ii) laboratory-scale extraction/concentration testing, and iii) technical and economic feasibility analysis.

The majority of sampling was performed at the Falkirk Mine and the Coal Creek Station power plant, both located near Underwood, North Dakota. Samples from the Mine included roof, floor and partings materials associated with the coal seams and the coal seams themselves. Sampling was focused on the Hagel Bed, consisting of the Hagel A, B Rider and Hagel B coals and associated sediments. Sampling from the Coal Creek Station included streams associated with Great River Energy's DryFining™ lignite drying system as well as bottom ash and fly ash from the combustor. Additional samples were also collected, including from an outcropping of the Harmon-Hansen coal zone in Slope County, the Freedom Mine, the Coyote Creek Mine, the Antelope Valley Station power plant, and the Milton R. Young Station plant. In total, 174 unique samples were collected during the project.

Characterization of the samples consisted of determining the bulk chemistry, including rare earths abundance, as well as determining the modes of REE occurrence in the various samples. ICP-MS was the primary analytical tool used in the project to determine REE content. Two methods were used to understand modes of REE occurrence: i) SEM-EDS and CCSEM for the roof/floor sediment samples, and ii) Chemical Fractionation for the coal samples.

Although some preliminary work investigated physical beneficiation techniques to concentrate REEs from the associated roof/floor sediments, these methods were quickly determined to be ineffective and not feasible. The bulk of work for the laboratory-scale extraction/concentration testing was focused on extraction of REEs directly from the raw lignite coals using a liquid solvent/leaching approach that was derived from the results of Chemical Fractionation testing. A dilute (0.1-1.0M) and low temperature (~40°C) acid leaching process was investigated for the following coals: i) Hagel A, ii) Hagel B, iii) Harmon-Hansen, and iv) Leonardite. Three acid types (HCl, H_2SO_4, H_3PO_4) were evaluated in two different concentrations each, and 0.5M H_2SO_4 was determined to have the best combination of REE extractability and selectivity, as well as economic and environmental factors. Subsequent tests were focused on the 0.5M H_2SO_4 leaching process.

Using 0.5M H_2SO_4 as the leaching solution, two series of tests were performed, the first being at very long contact time (48 hours) to determine ‘equilibrium’ extraction, and the second using a range of contact times to determine kinetics of REE extraction. In the first series of tests, the Hagel B and the Harmon-Hansen coals were tested and in addition to the extraction of the REEs, extraction of other important elements was also determined, including those elements that may be monetizable (i.e. germanium, cobalt), and those elements that are considered impurities (i.e. thorium, uranium, iron). Complete mass balances were calculated based on the analysis to identify the concentration of the REEs in the extract solution. Performance for Hagel B and Harmon-Hansen coals were compared. Leonardite was also evaluated with the 0.5M H_2SO_4 leaching process, but only REEs were measured.

Once the equilibrium extractions were established, a series of tests was performed with Hagel B coal with 1hr, 2hr, 4hr, 8hr, 14hr, and 24hr contact times to compare overall REE extraction to the 48hr equilibrium tests. Based on the results for Hagel B, additional tests for Harmon-Hanse at 2hr and 14hr were performed and compared to the 48hr equilibrium tests. For the Hagel B testing, only the REEs were measured, while for the Harmon-Hansen all of the identified monetizable and impurity elements were measured as well to determine kinetics of their extraction in addition to the REEs.

Based on the results of the laboratory-scale REE extraction tests, a third party Engineering and Architecture firm was contracted to perform a technical and economic feasibility analysis of the REE extraction process developed in this study. This author was heavily involved throughout the process to establish flow sheets, process conditions and mass and energy balances, while the engineering firm performed an independent economic analysis to establish capital and operating costs, revenues and economic metrics such as internal rate of return, return on investment and simple payback time. For the purposes of this analysis, the model plant was based on the concept for a combined activated carbon production and steam/electricity production plant for the new facility at Valley City State University in North Dakota, with the REE extraction being integrated with the activated carbon production process. As part of the study, this author determined market impacts as well as evaluated the economics of the stand-alone REE extraction process that is not integrated with a coal conversion process such as activated carbon production.

7.2 Summary of Results and Conclusions

The initial hypothesis was that the content of REEs would be highest in the margins and partings of the coal seams in the clay-rich sediments. While this was confirmed on a whole sample basis, an unexpected finding was that on an ash basis, the highest concentration of REEs exists in certain locations within certain coal seams, often times in significantly higher quantity than the associated sediments. For instance, in the Falkirk Mine, the concentrated REE zones in the coal seams typically ranged from about 300 to 600 ppm total REE on an ash basis, compared to about 150-200 ppm in the associated sediments. This was a very important finding and is the basis for the novel REE extraction technology developed in this work. However, the content of REEs in the stratigraphic column is not uniform, and thus to effectively mine the coals with highest REE content, it is expected that selective mining practices will be needed. In the Falkirk Mine, the Hagel B seam appeared to have the best combination of high REE content and uniform REE distribution, and is thus a target for continued work.

Bulk mining practices at Falkirk Mine that combine multiple coal seams and associated sediments in the feed coal to the Coal Creek Station, result in a diluted REE content at the plant. Further, the original hypothesis was that the DryFining™ process would be a concentrating step that would enrich the REEs into the mineral-rich reject stream leaving the air jig of the process. However, it was found that the reject stream, primarily containing the heavy mineral fraction (pyrite), is diluted in REEs, indicating that they are not associated with pyrites or the other heavy minerals that are separated into the reject stream. In fact, it appears that the DryFining™ process is concentrating the REEs in an opposite fashion as originally expected, with enrichment into the cleaned coal stream instead of the reject stream. However, because of the diluted feed coal, the overall content of REEs in the plant was fairly low for all samples analyzed, with the highest being the bottom ash at about 275 ppm on an ash basis.

The highest REE content in any samples evaluated in this work were with samples collected by the North Dakota Geological Survey at an outcropping of the Harmon-Hansen coal zone. These samples consisted of a coal sample and a clay-rich roof sample that were submitted to UND for analysis and testing. Both samples had highly elevated levels of REEs, with the coal at 560 ppm (dry whole coal basis) and 2200 ppm (ash basis), and the roof at 450 ppm (dry whole sample) and 595 ppm (ash).

Evaluation of the REE modes of occurrence in the coal samples, combined with literature and inferred evidence derived from data analysis techniques looking at the relative distribution of the REEs in organic-rich versus inorganic-rich fractions/samples has led to the conclusion that the majority of REEs in North Dakota lignites are organically associated. The primary mode of occurrence appears to be as organic coordination complexes, but some other associations are likely as well, such as cations on carboxylic acid groups in the organic matrix, acid-soluble mineral forms such as phosphates and carbonates, and as cations adsorbed to clay minerals in the coal. There also appears to be a small fraction of REEs associated with non-acid soluble mineral forms such as silicates, clays and sulfides.

Distribution of the individual REEs has shown that the organic-rich coal samples are enriched in the HREEs compared to the inorganic-rich associated sediments which are enriched in the LREEs. This, combined with data that shows that the roof sediments are depleted in the HREEs compared to the floor sediments, suggests that the deposition of REEs in the coals has occurred through surface water leaching processes that have preferentially mobilized the HREEs with subsequent adsorption/accumulation in the organic matter of the coal seams. The analysis also suggests that the REEs in North Dakota are of tuffaceous origin with zirconium and niobium associations identified in the roof/floor sediments.

The results of the sampling and characterization efforts, combined with data available in the USGS CoalQual database suggests that there are several REE-rich coal zones in North Dakota that would be targets for a commercial process.

Based on the results of Chemical Fractionation testing, which showed that a high majority of REEs (80-95%) from the raw lignites could be easily extracted by dilute acids, the laboratory-scale REE extraction/concentration testing was focused on a conceptual process involving leaching of REEs directly from the raw lignite coals, instead of most other processes being investigated in the literature that are looking at combustion ash or other coal byproducts. Sulfuric acid at 0.5M concentration was down-selected for additional testing after initially looking at multiple concentrations and acid types. The sulfuric acid was able to extract about 60-85% of REEs from the Hagel B, with a strong trend of increasing extraction with molecular weight. For the Harmon-Hansen, extraction was very high across the board, ranging from about 86 to 89% for all of the REEs. For both coals, extraction of scandium was lower at 52% for Hagel B and 82% for Harmon-Hansen.

The testing showed that extraction of other elements also occurred with the REEs, including both high value monetizable elements and impurities. Elements such as germanium, gallium and cobalt may significantly augment economics of REE recovery, but elements such as thorium, uranium, iron, alkali and alkaline earth elements are impurities that must be addressed in downstream purification processes. After the acid leaching, the content of REEs in the solution was about 0.23wt% for Hagel B and 0.8wt% for Harmon-Hansen, on a dry basis. These represent enrichment factors of 4 and 55 on an ash and coal basis, respectively for Hagel B, and 3.7 and 14 on an ash and coal basis, respectively for Harmon-Hansen. The dominant impurity forms for Hagel B were alkali and alkaline earth elements, and for Harmon-Hansen was iron. For both coals, the iron, alkali and alkaline earth elements combined represent more than 80% of the total mass of extracted elements, indicating that if measures can be included to effectively reject these elements that the concentration of REEs will be dramatically increased.

For the above results, testing was completed at close to equilibrium conditions using a very long leaching contact time. Kinetics testing with multiple contact times showed some very interesting results. For the Hagel B coal, the data showed a strong selectivity towards the HREE, especially at shorter contact times. 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 acid-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 for Hagel B, an optimal balance between contact time and REE extraction exists when considering economic factors such as equipment sizing and revenues for REEs. The differences between the HREE and LREE can likely be attributed to the smaller ionic radii of the HREE, which allows them to be more mobile within the coal matrix. This would also suggest that particle size of the coal (i.e. mass transfer limitations) will play a large role in determining leaching rates.

For the Harmon-Hansen coal, kinetics testing shows that extraction rates are significantly faster than with Hagel B coal. At two hours of contact time, over 70% total REE extraction is achieved, with very minimal increase through 14 hours. There is some selectivity towards HREE extraction at the shorter contact times, consistent with data for Hagel B. Also an important finding from this testing is looking at the relative kinetics of the REEs versus the other inorganic components in the coals. For example, the kinetics of extraction of the radioactive impurities Th and U, as well as the dominant impurity species Fe, were much slower than REEs, indicating that by controlling contact time, it may be possible to prevent a large degree of extraction without significantly limiting the REE recovery. For the two hour contact time with Harmon-Hansen, the concentration of REEs in the extract solution was 1.36wt%, compared with 0.79wt% for the 48hr equilibrium case, even with the lower overall extraction achieved at the shorter contact time. This represents concentration factors of 6.0 and 24 on an ash and coal basis, respectively. Overall, the kinetics testing suggests that a balance must be achieved between contact time (i.e. equipment size), REE recovery (revenues) and REE concentration (purification costs) to maximize process economics.

Based on the results of laboratory-scale REE extraction testing an overall four-step process has been conceptualized to achieve the target of two weight percent REEs in the concentrate product. To maximize REE concentration in the product, the following processing steps can be implemented: i) gravity concentration on the feed coal to separate heavy mineral/pyrite content that has been shown to be depleted in REEs and of which significant impurity in the form of iron is extracted with REEs during leaching, ii) pre-leaching of the concentrated coal feed using an ion-exchange solution such as ammonium acetate to target removal of the alkali and alkaline earth content in the coal, at the expense of a ~5wt% loss in REEs, iii) acid leaching to target extraction of the REEs and other high-value elements, and iv) selective precipitation of impurities from the REE extract solution using methods such as pH adjustment and forced air oxidation. Testing on steps ii and iii was accomplished in this work, with steps i and iv being investigated through literature. When implementing the above approach at the equilibrium contact time of 48 hours, the concentration of REEs in solution is 2.3 to 5.5 wt% for Harmon-Hansen and 0.4 to 0.7 wt% for Hagel B, depending on the efficiency of alkali, alkaline earth elements rejection in the ion-exchange leaching and the removal of iron in either the gravity concentration step or the selective precipitation step. Additional testing will be needed to finalize the flowsheet and determine overall mass balances for each feedstock.

The process developed in this work has recently been submitted for patenting (Application number 15/462,164 – Rare Earth Element Extraction from Coal). There are several benefits and advantages of this technology that are summarized in the following discussion.

The REEs in North Dakota lignite (and likely other low-rank coals) are weakly bound within the organic matrix. In comparison, the REEs in high-rank coals are primarily bound in minerals such as monazite and xenotime in much stronger associations, making their extraction more technically difficult and expensive. The weak bonding in lignite presents a unique opportunity that allows for extremely simple, highly efficient and lower cost extraction than with other types of coals or with coal byproducts, such as combustion ash. A major benefit is that no (or limited) physical beneficiation of the feed is required prior to REE extraction. For example, traditional mineral ores and other forms of coal-related feedstocks such as higher rank coals or combustion fly ash require extremely complex, expensive and often inefficient physical beneficiation steps. In particular, the physical beneficiation of coal-related feedstocks is a huge technical/ economic challenge because the REE minerals are typically 10 microns or smaller and separation processes in this size range are limited, questionably effective, and costly. One of the major advantages of the ion-adsorbed clay deposits in China is that these processes are not needed. Instead the REE extraction is performed on the as-mined or more recently on the in-situ ore. The technology developed in this study is envisioned to take a similar approach once fully optimized.

A very dilute leaching process at low temperature is utilized to extract REEs. In comparison, extraction processes for mineral-bound REEs in traditional ore resources, combustion ash or high rank coals requires the use of highly concentrated acids or caustics at very high temperatures to “crack” or dissolve the entire REE-bearing mineral into solution. These processes are both expensive and environmentally challenging. The mild leaching process employed in this technology also offers the possibility for a more REE-selective extraction than the aggressive conditions used for other materials, as it can prevent dissolution of unwanted elements/minerals that are present in stronger bonding forms through control of the chemistry and process conditions.

Another very important benefit, and one of the primary differentiators of this technology is that the feedstock is the raw lignite coal. In essence, this technology has “flipped” the conventional notion of REE recovery from coal and coal byproducts being investigated by others. Conventionally, the REE feedstock is a byproduct of another coal process that has little/negative value. This technology uses the raw coal as the feedstock and preserves its organic content, and thus allows ability to dictate the value-added use of the high value coal byproduct to augment economics and maximize efficiency and synergies. Additionally, the REE extraction process can be considered a coal beneficiation process. Ash content is reduced by 10 to 75% and nearly all of the alkali is removed during REE extraction. This improves the purity/value of carbon-based products derived from the coal byproduct (i.e. activated carbon or metallurgical coke) and also has several important benefits if the coal is to be used for combustion fuel, such as higher heating value and reduced fouling and slagging and burden on particulate control devices. It can also improve the marketability of combustion fly ash through removal of some hazardous species prior to combustion.

With the information derived from sampling, characterization and laboratory-scale extraction testing a third party Engineering and Architecture firm performed an economic evaluation of the process as described above. A facility was modeled that combined REE extraction with activated carbon and steam production, with a coal throughput of 5,000 lb/hr as-received. With the Harmon-Hansen coal as the feedstock, this represents approximately 12 tons/year of REE production on a pure oxide basis. Three revenue streams are generated via this concept and include the REE concentrate product, activated carbon, and fuel gases generated during the activated carbon production. With these revenue streams and capital and operating costs of $28.3 Million and $4.7 Million annually, respectively, the economic metrics for the plant are highly attractive, at IRR ranging from 32 to 35% and ROI ranging from 21 to 28% for 10 and 20 year plant cycles, respectively. The simple payback was estimated at 2.9 years, with a net present value of between $18.6 and $32.6 Million for a 10 and 20 year plant cycle, respectively. The analysis identified that revenues for the activated carbon were about three times higher than the REE concentrate product, indicating the important added benefit of the coal byproduct produced by the technology. The individual elements in the REE concentrate product with highest revenues were scandium, germanium and cobalt.

In addition to evaluation of the economics associated with the combined REE/activated carbon/steam plant, the stand-alone economics of REE recovery alone were also determined. This analysis showed that although the economic merit is significantly reduced without value-added use of the coal byproduct, that the technology can still be profitable with larger processing volumes and/or future increases in REE sales prices, such as those that have been observed in the recent past (2010-2011).

7.3 Recommendations for Future Research

The 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 the State have been identified with elevated levels of REEs 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 that has been developed in this work. The technology is simpler than those being investigated in literature and provides many additional benefits.
- Although this work has developed the above information, significant additional work is needed to fully optimize the process, perform scaled-up demonstrations, more broadly identify target coal seams and regions for selective mining, and to better understand the geochemistry of REEs in North Dakota lignites. These items are the focus of recommended future research and are described in more detail in the sections below.

While the technology testing to date has proven effective in extracting REEs, significant optimization and parametric evaluation is yet needed prior to being ready for commercial operation. Specifically, by optimizing the acid leaching step with a combination of parameters including acid type, acid concentration, coal particle size, contact time and solution temperature, it is likely that significant improvements in the limitation of impurities extraction with the REEs can be achieved, and potentially allowing the elimination of one or more processing steps.

To date, only three acid types have been evaluated in the process, but it is likely that a significant number of other leach solution compositions would prove effective, and maybe more so than sulfuric acid. This includes alkaline or caustic leaching solutions as well, which merit investigation. Further, it may be beneficial to investigate multi-component leach solutions. For example, HCl proved to be the most effective at REE extraction, but came at the expense of large impurity extraction, while H_2SO_4 extracted a lower quantity of the REEs, but was significantly more selective. A combination of these two acids may prove to be optimal.

Further, the leaching kinetics testing has showed a very strong trend of faster kinetics for the HREE versus the LREE. It may be possible through a series of staged leaching steps to achieve some degree of REE speciation (i.e. extract solutions that are enriched in specific molecular weight groupings), which will tremendously simplify downstream separation processing. This type of approach may be accomplished through control of any of the previously listed leaching parameters. For example, higher temperature, smaller particle size and higher acid concentration would all be expected to improve extraction rates. Since the kinetics appear dependent upon molecular weight (or more likely ionic radius), each stage of the leaching could be set up to specifically target a grouping of the elements based on their known extraction rates. While it is not likely to achieve complete or even a moderate degree of speciation using this type of approach, any enrichment by molecular weight will mean greatly reduced costs of downstream separation. This could be another truly novel and differentiating benefit of the technology and something that is almost certainly not possible using other types of feedstocks.

To complement the above optimization efforts related to the REE extraction, it would be beneficial to gain a more thorough understanding of the geochemistry of North Dakota lignites as it relates to REEs, target monetizable elements and impurities that could be extracted. For example, this could be accomplished through a more comprehensive sequential extraction procedure detailed by Dai and others (2004) [106], and summarized in Figure 86. By truly understanding how the REEs are associated in the coals, more effective/tailored chemistries can be developed to target specific associations, thus improving REE-selectivity, process simplicity and ultimately economics.

Another method to better the understanding of the modes of REE occurrence in the lignites is to utilize the Stanford Synchrotron Radiation Lightsource [107], which produces extremely bright x-rays to study the samples being evaluated at an atomic or molecular level. This equipment could help to determine the electronic structure of the REE bonds in the lignites. For instance, the U.S. DOE NETL as part of its efforts in investigating REE recovery from coal and coal byproducts has successfully utilized this technology to verify molecular-level association of REEs in sulfates, oxides and phosphates in samples [108]. Because the association of REEs in lignite appear to be primarily within the organic matrix, the extremely powerful x-ray measurements may allow detection of the REEs in their organically associated states, whereas standard SEM-EDS techniques could not. Discussions with NETL have indicated that access to beam time may be a possibility in future work.

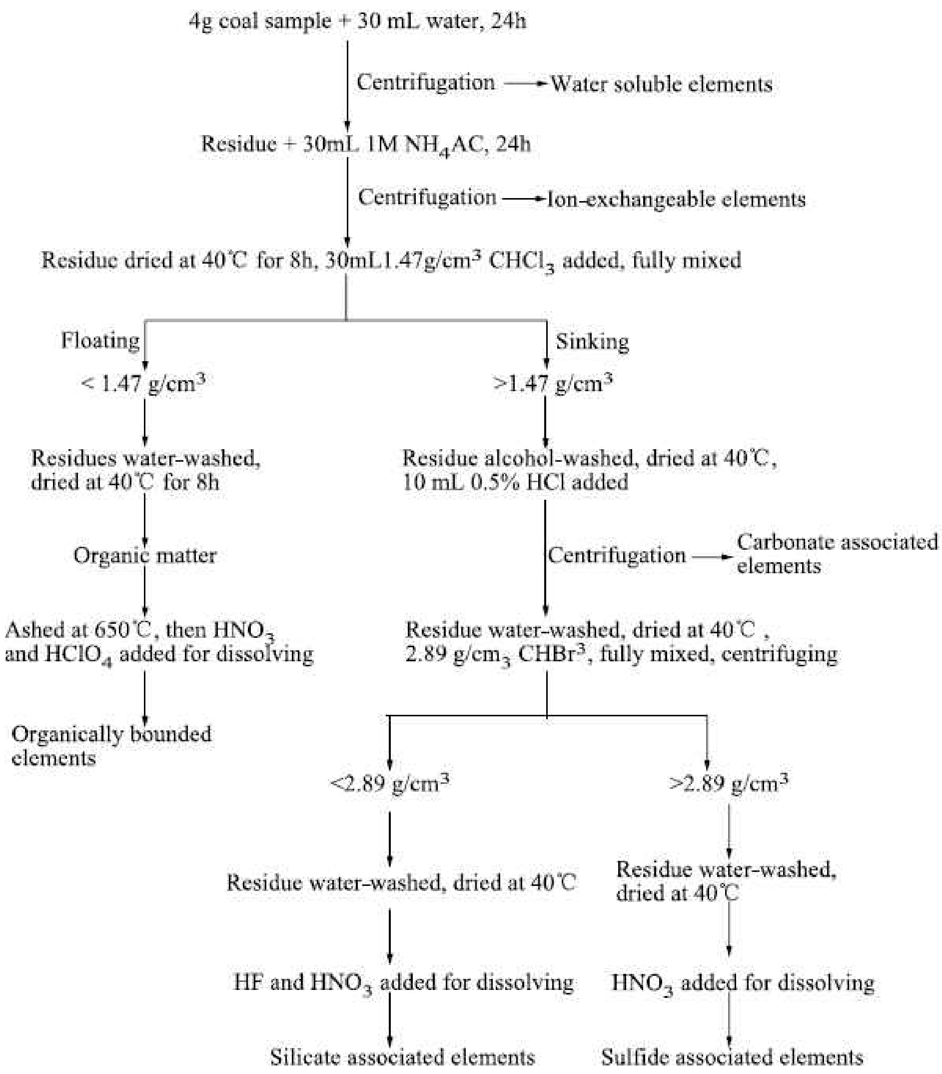


Figure 86. Chemical extraction prodedure by Dai and others (2012) [106]

In the opinion of this author, one of the primary risks to achieving successful commercial implementation of this technology is being able to identify a source of high REE-content lignite in sufficient and mineable quantity to be commercially feasible. While the sampling and analysis work conducted in this project has identified some target seams and areas, significant exploratory sampling work is yet needed to fully define the REE distribution in North Dakota, as well as in the existing mines. Even in the Falkirk Mine, which was the most heavily sampled under this project, there exists room for more detailed and precise sampling efforts. For instance, it would be beneficial to acquire drill cores representing the entire stratigraphic sequence and in multiple locations to reasonably represent the entire geographical area available for the mine. By analyzing specific vertical fractions of each drill core (i.e. foot-by-foot or other dimension), and plotting the REE content both vertically within each core and horizontally among multiple cores, a 3D map of the REE content and distribution can be created. This type of map would be immensely beneficial for a selective mining operation. Additionally, this work and work ongoing by the North Dakota Geological Survey [48], has identified the Harmon-Hansen coal zone as a potential hot spot for REEs. However, this study only evaluated two samples from one outcropping. Significantly more sampling of this coal zone is required, especially since the Harmon-Hansen has no active mines. Thus, to be able to justify the opening of a new mine, the distribution and content of REE-rich zones must be elucidated and proven to be an exceptional resource beyond that in the currently active mines.

Another approach that may be of significant benefit to REE-rich coal mining is to establish low-cost, expedient and accurate field analysis and sorting methods. To this end, UND and this author have recently partnered on a U.S. DOE Small Business Innovation Research proposal with Microbeam Technologies, Incorporated of Grand Forks, North Dakota under DOE funding opportunity DE-FOA-0001619. The goal of this proposal was to develop field deployable sensors and predictive algorithms along with real-time sorting technology to be able to identify REE-rich coal zones for selective mining and then sort and stockpile the coal with highest REE content. Although ICP-MS has become the standard method for REE analysis in solid samples, it is both time and cost intensive. Thus, it is desirable to develop lower cost and more expedient methods of analysis that can accurately predict REE content within a mine or field setting using marker elements. Previous work by Bryan and others (2015) [109] were successful in making correlations with bulk element species in the coal that could be used to develop algorithms to predict REE content without direct measurement of the REEs. This type of work will enable lower-cost and more effective selective mining, and ultimately improve the prospects of REE recovery from coal. It may also allow the possibility of REE distribution mapping using available historical core and sample databases, such as the USGS CoalQual database or resource owners' databases.

The work presented in this dissertation has focused on North Dakota lignites. However, it is likely that the technology will work effectively for other types of lignites and subbituminous coals. This assertion is confirmed by work done by Finkelman and others (1990) [110] looking at the leaching characteristics of trace elements from a range of coal types, including a North Dakota lignite, a Texas lignite, and Wyoming subbituminous and a series of higher rank eastern bituminous coal. Although sulfuric acid was not used in their testing, a similar procedure to the UND Chemical Fractionation procedure was used. Their results are summarized as follows for leaching extraction of REEs by HCl:

- 70-84% for North Dakota lignite
- 39-65% for Texas lignite
- 50-74% for Wyoming subbituminous
- ~10-30% for all bituminous coals

The authors concluded that the REE leaching characteristics of the three low-rank coals were significantly different than the higher rank coals, and was attributed to the likely association in organic coordination complexes. For the bituminous coals, the REE associations were non-acid soluble mineral forms primarily, which resulted in very low REE extraction by HCl. It would appear that the leachability of REEs by dilute acids is a function of their 'age' and degree (or absence) of secondary mineralization processes that would have transformed the organically adsorbed REEs into mineral forms during transitions from lignite to subbituminous to higher rank coals. This represents a tremendous advantage for these lower-rank coals. Therefore, it is recommended that the scope of this technology be extended to other lignite coals and subbituminous coals.

Upon completion of small-scale optimization studies, the technology will require scale-up to demonstration-scale levels prior to being ready for commercialization. This could be accomplished at one of the NDUS facilities, such as Valley City State University that will offer the infrastructure and existing coal conversion facility to lower costs of demonstration. If successful, these large-scale demonstration projects would de-risk the technology to a point where it could attract commercial licensing opportunities.

The work detailed in this dissertation was derived from the completion of Phase I work under a U.S. DOE-funded project. At the time of this writing, the UND team is preparing an application to continue into a subsequent Phase II project, during which much of the above work can be accomplished. However, not all of it will be possible, and thus additional funding opportunities should be sought out, especially as it relates to the fundamental research needed on the extraction chemistry and the coal geochemistry.

Lastly, the work detailed in this dissertation has only focused on two aspects of the REE value chain – mining and extraction/initial concentration. There still exists an incredible array of research opportunities associated with deep concentration, separation, purification, metal reduction and REE-based product manufacturing. These most valuable portions of the REE value chain are almost exclusively in China at current. By having a low (or lowest) cost REE concentrate produced by this technology in the U.S., significant opportunity will present itself to develop the entire value chain in North Dakota and domestically. For the good of U.S. national and economic security, it is recommended that significant funding be appropriated for REE-related research. Solvent extraction is an example of one area that needs improvement, as it can be considered a hold-over from the previous era of REE-production in the United States. While some technologies such as ion exchange resins are gaining traction, the separation and purification processes to produce salable REEs need to be improved both for economic and environmental reasons. It is the hope of this author to establish a center for research within the University of North Dakota focused on REE-based technology development.

8 REFERENCES

[1] V. K. Pecharsky and K. A. Gschneidner, "Rare-earth element," Encyclopaedia Britannica, 14 March 2014. [Online]. Available: https://www.britannica.com/science/rare-earth-element. [Accessed 10 March 2017].

[2] T. Bank, E. Roth, B. Howard and E. Granite, "U.S. Department of Energy National Energy Technology Laboratory: Geology of Rare Earth Deposits," 2016. [Online]. Available: https://www.netl.doe.gov/research/coal/rare-earth-elements/publications. [Accessed 10 March 2017].

[3] B. Mason and C. B. Moore, Principles of geochemistry, 4th ed., New York: Wiley, 1982.

[4] W. D. Jackson and G. Christiansen, "International Strategic Minerals Inventory summary report - Rare earth oxides," *U.S. Geological Survey Circular 930-N,* p. 68, 1993.

[5] J. L. Sabot and P. Maestro, Lanthanides, in Kroschwitz, J.I., and Grant, M.H., eds., Kirk-Othmer encyclopedia of chemical technology, 4th ed., New York: John Wiley, 1995.

[6] K. H. Wedepohl, "The composition of the continental crust," *Geochimica et Cosmochimica Acta,* vol. 59, no. 7, pp. 1217-1232, 1995.

[7] D. R. Lide, "Abundance of elements in the earth's crust and sea," in *CRC handbook of physics and chemistry, 78th edition*, Boca Raton, Florida, CRC Press, 1997, p. 14.

[8] I. McGill, "Rare earth metals," in *Habashi, F., ed., Handbook of extractive metallurgy*, Weinheim, New York, Wiley-VCH, 1997, pp. 1695-1741.

[9] Tutor Circle, "Lanthanide Contraction," 2017. [Online]. Available: http://chemistry.tutorcircle.com/inorganic-chemistry/lanthanide-contraction.html. [Accessed 11 March 2017].

[10] J. C. However, E. J. Granite, D. B. Mayfield and R. B. Finkelman, "Notes on Contributions to the Science of Rare Earth Element Enrichment in Coal and Coal Combustion Byproducts," *Minerals,* vol. 6, no. 2, p. 32, 2016.

[11] Economics & Statistics Department - American Chemistry Council, "The Economic Benefits of the North American Rare Earths Industry," Rare Earth Technology Alliance, 2014.

[12] "U.S. Department of Energy National Energy Technology Laboratory," 10 March 2017. [Online]. Available: https://www.netl.doe.gov/research/coal/rare-earth-elements/overview.

[13] D. Wise, "Security and supply chains and the role of rare earth elements," The Cipher, 17 April 2017. [Online]. Available: https://www.thecipherbrief.com/column/expert-view/security-and-supply-chains-role-rare-earth-elements-1091?utm_source=Aggregators&utm_campaign=facc7d4a3a-

EMAIL_CAMPAIGN_2017_04_09&utm_medium=email&utm_term=0_b02a5f1344-facc7d4a3a-122460921.

[14] Lynas Corporation Ltd., "Will there be sufficient rare earths to meed demand from clean energy technology," in *International Minor Metals Conference*, London, 2010.

[15] McDowell Group, "Bokan Mountain Rare Earth Element Mine Economic Impact Study," McDowell Group, 2013.

[16] P. Henderson, J. Gluyas, G. Gunn, F. Wall, A. Woolley, A. Finlay and N. Bilham, "Rare Earth Elements. A briefing note by the Geological Society of London," Geological Society of London, 2011.

[17] B. Seal, P. Verplanck, B. Van Gosen and A. Grosz, *Geologic and Environmental Characteristics of Rare Earth Element Deposit Types Found in the United States,* United States Geological Survey, 2012.

[18] R. L. Linnen, I. M. Samson, A. E. Williams-Jones and A. R. Chakhmouradian, "Geochemistry of the Rare-Earth Element , Nb, Ta, Hf, and Zr Deposits," Elsevier Ltd., 2014.

[19] Y. Kanazawa and M. Kamitani, "Rare Earth Minerals and Resources in the World," *Journal of Alloys and Compounds,* Vols. 408-412, pp. 1339-1343, 2005.

[20] K. R. Long, B. S. Van Gosen, N. K. Foley and D. Cordier, "The Prinicipal Rare Earth Elements Deposits of the United States - A Summary of Domestic

Deposits and a Global Perspective," U.S. Geological Survey Scientific Investigations Report 2010-5220, 96 p., 2010.

[21] A. Golev, M. Scott, P. D. Erskine, S. H. Ali and G. R. Ballantyne, "Rare earths supply chains: Current status, constraints and opportunities," *Resources Policy,* vol. 41, pp. 52-59, 2014.

[22] A. Jordens, Y. P. Cheng and K. E. Walters, "A review of the beneficiation of rare earth element bearing minerals," *Mineral Engineering,* vol. 41, pp. 97-114, 2013.

[23] C. K. Gupta and N. Krishnamurthy, Extractive Metallurgy of Rare Earths, CRC Press, 2005.

[24] H. Royen and U. Fortkamp, "Rare earth elements - Purification, separation and recycling," IVL Swedish Environmental Research Institute, Stockholm, Sweden, 2016.

[25] G. Hatch, "The rare-earth supply chain: an update," in *Magnetics 2015*, Orlando, Floriday, USA, 2015.

[26] S. B. Castor and J. B. Hendrick, "Rare earth elements," in *Kogel, J.E., Trivedi, N.C., Barker, J.M., and Krukowski, S.T., eds., Industrial minerals 7 rocks - Commodities, markets, and uses (7th ed)*, Littleton, Colo, Society for Mining, Metallurgy, and Exploration, Inc. (SME), 2006, pp. 769-792.

[27] N. Verbaan, K. Bradley, J. Brown and S. Mackie, "A review of hydrometallurgical flowsheets considered in current REE projects," in

Symposium on Strategic and Critical Materials, Victoria, British Columbia, 2015.

[28] National Resource Council, "Minerals, critical minerals, and the U.S. Economy," National Academies Press, Washinton D.C., 2008.

[29] U.S. Department of Energy, "Critical Materials Strategy," U.S. Department of Energy, 2011.

[30] Under Secretary of Defense for Acquisition, Technology and Logistics, "Strategic and Critical Materials Report on Stockpile Requirements," U.S. Department of Defense, 2015.

[31] D. Kingsnorth, "An Overview of the Rare Earth Market," IMCOA, 2009. [Online]. Available: http://www.ggg.gl/userfiles/file/Reports/GGG%20-Annual%20Report/202009.pdf.

[32] V. Seredin, "A new method for primary evaluation of the outlook for rare earth element ores," *Geology of Ore Deposits,* vol. 52, pp. 428-433, 2010.

[33] U.S. Department of the Interior; U.S. Geological Survey, "Mineral Commodity Summaries 2017," USGS, 2017.

[34] V. G. Papanglakis and G. Moldoveanu, "Recovery of rare earth elements from clay minerals," in *ERES2014: 1st European Rare Earth Resources Conference*, Milos, 2014.

[35] "REE - Rare earth elements and their uses," Geoscience News and Information - Geology.com, 2017. [Online]. Available: http://geology.com/articles/rare-earth-elements/.

[36] R. Kiggings, The political economy of rare earth elements, New York: Palgrave MacMillan, 2015.

[37] G. Barakos, H. Mischo and J. Gutzmer, "The AusIMM Bulletin - An outlook on the rare earth elements mining industry," April 2016. [Online]. Available: https://www.ausimmbulletin.com/feature/an-outlook-on-the-rare-earth-elements-mining-industry/.

[38] X. J. Yang, A. Lin, L. Xiao-Liang, Y. Wu, W. Zhou and Z. Chen, "China's ion-adsroption rare earth resources, mining consequences and preservation," *Environmental Development,* vol. 8, pp. 131-136, 2013.

[39] C. C. Pavel, C. Thiel, S. Degreif and E. Tzimas, "Role of substituion in mitigating the supply pressure of rare earths in electric road transport applications," *Sustainable Materials and Technologies,* 2017.

[40] N. Foley, "Rare earth element accumulation processes resulting in high-value metal enrichments in regolith," United States Geological Survey, December 2016. [Online]. Available: https://minerals.usgs.gov/science/residual/index.html.

[41] V. Zepf, A new approach to the nexus of supply, demand and use: exemplified along the use of neodymium in permanent magents, Berlin: Springer-Verlag, 2013.

[42] "Bear Lodge Project," Rare Element Resources, 2017. [Online]. Available: http://www.rareelementresources.com/bear-lodge-project/bear-lodge-project#.WM7UPaJOmUk.

[43] UCORE Rare Metals, "Bokan Mountain Key Features," [Online]. Available: http://ucore.com/projects/bokan-mountain-alaska/bokan-mountain-alaska-key-features. [Accessed 13 March 2017].

[44] "U.S. Department of Energy - Office of Fossil Energy. DE-FOA-0001202," 26 June 2016. [Online]. Available: https://www.fedconnect.net/FedConnect/default.aspx?ReturnUrl=%2fFedConnect%2f%3fdoc%3dDE-FOA-0001202%26agency%3dDOE&doc=DE-FOA-0001202&agency=DOE.

[45] F. R. Karner, S. A. Benson, H. H. Schobert and R. G. Roaldson, "Geochemical varioation of inorganic constituents in a North Dakota lignite," in *In The Chemistry of Low-Rank Coals; Schobert, H.H., (Ed); American Chemical Society Symposium Series 264*, 1984.

[46] F. R. Karner, H. H. Schobert, S. K. Falcone and S. A. Benson, "Elemental distribution and association with inorganic and organic components in North Dakota lignites," in *In Mineral Matter and Ash in Coal; Vorres, Karl S. (Ed); ACS Symposium Series 301*, 1986.

[47] E. Murphy, "Mineral Resources of North Dakota: COAL," North Dakota Geological Survey, [Online]. Available: https://www.dmr.nd.gov/ndgs/mineral/nd_coalnew.asp.

[48] N. W. Kruger and North Dakota Department of Mineral Resources, "Rare Earths in Coal," January 2017. [Online]. Available:

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

[49] N. Kruger and North Dakota Department of Mineral Resources, "A "Rare Opportunity"," January 2016. [Online]. Available: https://www.dmr.nd.gov/ndgs/documents/newsletter/Winter%202015/A%20Rare%20Opportunity.pdf.

[50] V. V. Seredin and R. B. Finkelman, "Metalliferous coals: A review of the main genetic and geochemical types," *International Journal of Coal Geology,* vol. 76, pp. 253-289, 2008.

[51] S. S. Crowley, R. W. Stanton and T. A. Ryer, "The effects of volcanic ash on the maceral and chemical composition of the C coal bed, Emery Coal Field, Utah," *Org. Geochem.,* vol. 14, pp. 315-331, 1989.

[52] V. V. Seredin and S. Dai, "Coal deposits as potential alternative sources for lanthanides and yttrium," *International Journal of Coal Geology,* vol. 94, pp. 67-93, 2012.

[53] K. H. Johanneson and X. Zhou, "Geochemistry of the rare earth element in natural terrestrial waters: a review of what is currently known," *Chinese Journal of Geochemistry,* vol. 16, pp. 20-42, 1997.

[54] V. V. Seredin and M. Y. Shpirt, "Rare earth elements in the humic substance of metalliferous coals," *Lithology and Mineral Resources,* vol. 52, pp. 428-433, 1999.

[55] V. Seredin, "Major regularities of the REE distribution in coal," *Doklady Earth Sciences,* vol. 377, pp. 250-253, 2001.

[56] S. I. Arbuzov and V. V. Ershov, Geochemistry of rare elements in coals of Siberia, Tomsk: D-Print, 2007.

[57] S. I. Arbruzov, V. V. Potseluev and L. P. Rikhvanov, Rare elements in coals of the Kuznetsk Basin, Kemerovo, 2000.

[58] S. Dai, D. Li, C. -L. Chou, L. Zhao, Y. Zhang, D. Ren, Y. Ma and Y. Sun, "Mineralogy and geochemistry of boehmite-rich coals: new insights from the Haerwusu Surface Mine, Jungar Coalfield, Inner Mongolia, China," *International Journal of COal Geology,* vol. 74, pp. 185-202, 2008.

[59] S. Dai, X. Wang, W. Chen, D. Li, C. -L. Chou, Y. Zhou, C. Zhu, H. Li, X. Zhu, Y. Xing, W. Zhang and J. Zou, "A high-pyrite semianthracite of Late Permian age in the Songzao Coalfield, southwestern China: mineralogical and geochemical relations with underlying mafic tuffs," *International Journal of Coal Geology,* vol. 8, pp. 430-445, 2010.

[60] S. Dai, J. Zou, Y. Jiang, C. R. Ward, X. Wang, T. Li, W. Xue, S. Liu, H. Tian, X. Sun and D. Zhou, "Mineralogical and geochemical compositions of the Pennsylvanian coal in the Adaohai Mine, Daqingshan Coalfield, Inner Mongolia, China: modes of occurrence and origin of diaspore, gorceixite, and ammonium illite," *International Journal of Coal Geology,* vol. doi: 10.1016/j.coal.2011.06.010, 2011.

[61] H. G. Dill, "The geology of aluminum phosphates and sulphates of teh alunite group minerals: a review," *Earth-Science Reviews,* vol. 53, pp. 35-93, 2001.

[62] V. Ershov, "Rare earth elements in the coals of Kizelovsk basin," *Geochimia,* vol. 3, pp. 274-276, 1961.

[63] G. M. Eskenazy, "Rare earth elements and yttrium in lithotypes of Bulgarian coals," *Organic Geochemistry,* vol. 11, pp. 83-89, 1987.

[64] G. Eskenazy, "Geochemistry of rare earth elements in Bulgarian Coals," *Ann. de L' Univ. de Sofia 'St. Kl. Ohridski', Livre - 1,* vol. 88, pp. 39-65, 1995.

[65] R. Finkelman, "Trace and minor elements in coal," in *Engel, M.H., Macko, S.A. (Eds), Organic Geochemistry*, Plenum, New York, 1993, pp. 593-607.

[66] J. C. Hower, L. F. Rupper and C. F. Eble, "Lanthanide, yttrium, and zirconium anomalies in the Fire Clay coal bed, Eastern Kentucky," *International Journal of Coal Geology,* vol. 39, pp. 141-153, 1999.

[67] V. Seredin, "Rare earth element-bearing coals from the Russian Far East deposits," *Internation Journal of Coal Geology,* vol. 30, pp. 101-129, 1996.

[68] V. Seredin, "Metalliferous coals: formation conditions and outlooks for development," in *Resources of Russia, vol. VI*, Moscow, Geoinformmark, 2004, pp. 452-519.

[69] V. V. Seredin and M. Y. Shpirt, "REE contents and distribution in humic matter of REE-rich coals," in *Stanley, C.J., et al (Eds.), Mineral Deposits: Processes to Processing*, Balkema, Rotterdam, Brookfield, 1999, pp. 267-269.

[70] C. Ward, "Mineral matter in Australian bituminous coals," in *Austral-asian Institute of Mining and Mettallurgy 267*, 1978.

[71] P. Zubovic, T. Stadnichenko and N. Sheffey, "Geochemistry of minor elements in coals of the Northern Great Plains Coal Province.," *U.S. Geol. Surv. Bull., 1117-A,* p. 58, 1961.

[72] G. M. Eskenazy, "Aspects of teh geochemistry of rare earth elements in coal: an experimental approach," *International Journal of Coal Geology,* vol. 38, pp. 285-295, 1999.

[73] A. Szalay, "Cation exchange properties of humic acids and their importance in the geochemical enrichment of UO2 and other cations," *Geochimica et Cosmochimica Acta,* vol. 28, pp. 1605-1614, 1964.

[74] M. T. Aide and C. Aide, "Rare earth elements: Their importance in understanding soil genesis," *International Scholarly Research Network,* vol. doi:10.5402/2012/783876, 2012.

[75] M. Pedrot, A. Dai and M. Davranche, "Dynamic structure of humic substances: Rare earth elements as a fingerprint," *J. Colloid Interface Sci.,* vol. 345, pp. 206-213, 2010.

[76] M. Davranche, M. Grybos, G. Gruau, M. Pedrot, A. Dai and R. Marsac, "Rare earth element patterns: A tool for identifying trace metal sources during wetland soil reduction," *Chem. Geol.,* vol. 284, pp. 127-137, 2011.

[77] R. Finkelman, "The origin, occurrence, and distribution of the inorganic constituents in low-rank coals.," in *Basic Coal Science Workshop*, Houston, TX, USA, 1981.

[78] G. Eskenazy, "Rare earth elements in a sampled coal from the Pirin Deposit, Bulgaria," *International Journal of Coal Geology,* vol. 7, pp. 301-314, 1987.

[79] "Annual Coal Report," U.S. Energy Information Administration, 3 November 2016. [Online]. Available: https://www.eia.gov/coal/annual/.

[80] "Countries with the biggest coal reserves," mining-technology.com, 2013. [Online]. Available: http://www.mining-technology.com/features/feature-the-worlds-biggest-coal-reserves-by-country/.

[81] T. Ackman, J. Ekmann, C. Kirchner, E. Lopert and J. Pierre, "Rare earth elements in coal - the case for research and development into co-production with coal," Leonardo Technologies, Inc., 2012.

[82] R. Matthias and L. Ruppert, "COALQUAL Database," United States Geological Survey, 6 4 2017. [Online]. Available: https://ncrdspublic.er.usgs.gov/coalqual/.

[83] R. M. Flores, C. W. Keighin, A. M. Ochs, P. D. Warwick, L. R. Bader and E. C. Murphy, "Chapter WF - Framework Geology of Fort Union Coal in the Williston Basin," in *U.S. Geological Survey Professional Paper 1625-A*, United States Geological Survey, 1999.

[84] T. Bank, E. Roth, P. Tinker and E. Granite, "Analysis of rare earth elements in geologic samples using inductively couple plasma mass spectrometry," U.S. DOE Topical Report - DOE/NETL-2016/1794, 2016.

[85] "Certified Reference Materials," Natural Resources Canada, 2017. [Online]. Available: http://www.nrcan.gc.ca/mining-materials/certified-reference-materials/7827.

[86] S. A. Benson and P. L. Holm, "Comparison of inorganics in three low-rank coals," *Ind. Eng. Chem. Prod. Res. Dev.,* vol. 24, pp. 145-149, 1985.

[87] A. Ausavasukhi, C. Kampoosaen and O. Kengnok, "Adsorption characteristics of Congo red on carbonized leonardite," *Journal of Cleaner Production,* vol. doi: 10.1016/j.jclepro.2015.10.034, no. 2015.

[88] "Research - Coal - Rare Earth Elements. Project Information," U.S. Department of Energy National Energy Technology Laboratory, 2017. [Online]. Available: https://www.netl.doe.gov/research/coal/rare-earth-elements/project-information.

[89] P. F. Ziemkiewicz, "Recovery of REEs from Coal Mine Drainage," in *2016 NETL Crosscutting Technology Research Review Meeting*, Pittsburgh, PA, 2016.

[90] H. Hsu-Kim, M. Wiesner, D. Plata, J. C. Hower and Z. Hendren, "Novel membrane and electrodeposition-based separation and recovery of rare earth elements from coal combustion residues," in *2016 NETL Crosscutting Technology Research Review Meeting*, Pittsburgh, PA, 2016.

[91] R. Peterson, M. Heinrichs and A. Lane, "Recovery of rare earth elements from coal byproducts using Battelle's acid digestion process," in *2016 NETL Crosscutting Technology Research Review Meeting*, Pittsburg, PA, 2016.

[92] R. Q. Honaker, J. Groppo, R. -H. Yoon, A. Noble and J. Herbst, "Process evaluation and flowsheet development for the recovery of rare earth elements from coal and associated byproducts," in *Society for Mechanical Engineers Annual Meeting. Feb 19-22*, Denver, CO, 2017.

[93] M. Fan, H. Tian, M. Radosz, E. Williams, G. Gaustad and H. Adidharma, "A pollution-prevention and economically-viable technology for separation of rare earth elements from Powder River Basin coal ashes," in *2016 NETL Crosscutting Technology Research Review Meeting*, Pittsburgh, PA, 2016.

[94] J. E. Renew, K. Jeffers, K. Davis, R. Vera, V. Filatov and J. Buetler, "Plasma arc gasification based rare earth element recovery from coal fly ash," in *2016 NETL Crosscutting Technology Research Review Meeting*, Pittsburg, PA, 2016.

[95] D. Stull, G. Carlson, T. Lanyk, R. Kadunc, G. Khanna, G. Yates and K. J. Reddy, "Economically viable and environmentally benign high performance technology to recovery rare earth elements from coal byproducts," in *2016 NETL Crosscutting Technology Research Review Meeting*, Pittsburg, PA, 2016.

[96] P. Joshi, "High yield and economical production of rare earth elements from coal ash," in *2016 Crosscutting Technology Research Review Meeting*, Pittsburgh, PA, 2016.

[97] "Advanced Combustion Systems Projects & Performers," U.S. Department of Energy National Energy Technology Laboratory, 2017. [Online]. Available: https://www.netl.doe.gov/research/coal/energy-systems/advanced-combustion/project-portfolio/projects-performers.

[98] D. Dreisinger, N. Verbaan, M. Johnson and G. Andres, "The Search Minerals Direct Extraction technology for rare earth recovery," in *IMPC 2016: XXVIII International Mineral Processing Congress Proceedings - ISBN: 978-1-926872-29-2*, 2016.

[99] X. Dai, P. Zeng, Y. Li, M. Huang, M. Yang, G. Chen and G. Li, "Testing and application of iron precipitation as geothite (FEOOH) using a strong air flow," in *IMPC 2016: XXVIII International Mineral Processing Congress Proceedings - ISBN: 978-1-926872-29-2*, 2016.

[100] L. Yuran, Z. Jinting, Z. Tingyu and J. Pengfei, "Calcium sulfite oxidation and crystal growth in the process of calcium carbide residue to produce gypsum," *Waste and Biomass Valorization,* vol. 5, no. 1, pp. 125-31, February 2014.

[101] B. Morgan and O. Lahav, "The effect of pH on the kinetics of spontaneous Fe(II) oxidation by O2 in aqueous solution - basic principles and a simple heuristic description," *Chemosphere,* vol. 68, pp. 2080-2084, 2007.

[102] W. Stumm and F. Lee, "Oxygenation of ferrous iron," in *Industrial Engineering Chemistry. Division of Water and Waste Chemistry, 137th Meeting, ACS*, Cleveland, OH, 1960.

[103] M. D. Mann and S. A. Benson, "Advanced Power Systems Initiative: Lignite Feasibility Study," 29 May 2009. [Online]. Available: http://www.nd.gov/ndic/lrc/meeting090723/iv-b-proposal.pdf.

[104] "North Dakota Senate Bill 2196," North Dakota 2017-2018 65th Legislative Assembly, 10 April 2017. [Online]. Available: https://legiscan.com/ND/bill/2196/2017.

[105] "North Dakota Public Service Commission. Jurisdiction: Coal Mining," North Dakota State Government, 2017. [Online]. Available: http://www.psc.nd.gov/jurisdiction/coalmining/companies.php.

[106] S. Dai, D. Li, D. Ren, Y. Tang, L. Shao and H. Song, "Geochemistry of the late Permian No. 30 coal seam, Zhijin Coalfield of Southwest China: influence of a siliceous low-temperature hydrothermal fluid," *Applied Geochemistry,* vol. 19, pp. 1315-1330, 2004.

[107] SLAC National Accelerator Laboratory, "Stanford Synchrotron Radiation Lightsource," DOE Office of Science, 2017. [Online]. Available: http://www-ssrl.slac.stanford.edu/content/about-ssrl/about-stanford-synchrotron-radiation-lightsource.

[108] E. Granite, E. Roth, T. Bank, S. Benyahia, M. Summers and M. A. Alvin, "R&IC characterization and recovery of rare earths from coal and coal by-products," in *2017 NETL Crosscutting Technology Research Review Meeting*, Pittsburg, PA, 2017.

[109] R. C. Bryan, D. Richers, H. T. Andersen and T. Ackman, "Study on the utilization of portable hand-held XRF spectroscopy as a screening tool for rare earth elements in coal and coal waste products," Document No: 114-910178X-100-REP-R001-01, 2015.

[110] R. B. Finkelman, C. A. Palmer, M. R. Krasnow, P. J. Aruscavage and G. A. Sellers, "Combustion and leaching behavior of elements in the Argonne premium coal samples," *Energy & Fuels,* vol. 4, pp. 755-766, 1990.

[111] P. L. Verplanck, B. S. Van Gosen, R. R. Seal and A. E. McCafferty, "A Deposit Model for Carbonatite and Peralkaline Intrusion-Related Rare Earth Element Deposits," U.S. Geological Survey Scientific Investigations Report 2010-5070-J, 2010.

[112] J. Hendrick, "Rare earths," in *Minerals Yearbook, v.1, Metals and Minerals: U.S. Geological Survey*, pp. 60.1-60.15.

[113] D. M. Hoatson, S. Jaireth and Y. Miezitis, "The major rare earth element deposits of Australia: geological setting, exploration, and resources," Australian Government: Department of Resources, Energy and Tourism, Canberra, 2011.

[114] A. V. Anufrieva, O. S. Andrienko, A. S. Buynovskiy, Y. N. Makaseev, I. N. Mazov, R. A. Nefedov, V. I. Sachkov, O. B. Stepanova and A. V. Valkov, "Rare earth elements materials production from apatite ores," *IOP Conference Series: Materials Science and Engineering,* vol. 112, no. Conference 1, 2016.

[115] B. I. Palsson, O. Martinsson, C. Wanhainen and A. Fredriksson, "Unlocking rare earth elements from European apatite-iron ores," in *ERES2014: 1st European Rare Earth Resources Conference*, Milos, 2014.

[116] K. Palmer, P. Broad, P. Franklin, G. Arseneau and T. Maunula, "Preliminary Economic Assessment on the Thor Lake Rare Metals Project, NWT," Avalon Ventures Ltd., 2007.

[117] Quest Rare Minerals Ltd., "Strange Lake Project," 2017. [Online]. Available: http://www.questrareminerals.com/strange_lake.php. [Accessed 13 March 2017].

[118] P. Emsbo, P. I. McLaughlin, G. N. Breit, E. A. du Bray and A. E. Koenig, "Rare earth elements in sedimentary phosphate deposits: Solution to the global REE crisis?," *Gondwana Research,* vol. 27, pp. 776-785, 2015.

[119] Z. Bao and Z. Zhao, "Geochemistry of Mineralization with Exchangeable REY in the Weathering Crusts of Granitic Rocks in South China," *Ore Geology Reviews,* vol. 33, pp. 519-535, 2008.

[120] S. Peng, "Geological characteristics and the prospecting criteria of the granite-weathering crust ion-adsorption type REE deposits in Nanling ARea, South China," in *Materials Science Forum 33-42*, Switzerland, Trans Tech Publications, 1991.

[121] J. B. Hendrick, "The global rare earth cycle," *Journal of Alloys and Compounds,* vol. 225, pp. 609-618, 1995.

[122] M. H. Bradbury and B. Bayyens, "Sorption of Eu on Na- and Ca-montmorillonites: Experimantal investigations modeling with cation exchange and surface complexation," *Geochimica and Cosmochimica Acta,* vol. 66, pp. 3964-3979, 2002.

[123] W. Piasecky and D. A. Sverjensky, "Speciation of adsorbed Yttrium and rare earth elements on oxide surfaces," *Geochimica and Cosmochimica Acta,* vol. 72, pp. 2325-2334, 2008.

[124] R. Chi and J. Tian, Weathered crust elution-deposited rare earth ores, New York: Nova Science Publishers, 2008.

[125] K. Sanematsu, Y. Kon, A. Imai, K. Watanabe and Y. Watanabe, "Geochemical and mineralogical characteristics of ion-adsorption type REE mineralization in Phuket, Thailand," *Miner. Deposita,* vol. 48, pp. 437-451, 2013.

[126] E. Janots, "Ce(III) and Ce(IV) (re)distribution and fractionation in a laterite profile from Madagascar: insights from in situ XANES spectroscopy at the Ce LIII-edge," *Geochim. Cosmochim. Acta,* vol. 153, pp. 134-148, 2015.

[127] N. Foley, B. Hubbard, C. Bern and A. Shah, *Proceeding of the 13th Biennial Society for Geology Applied to Ore Deposits (SGA) Meeting, Vol. 2, 725-728,* Nancy, France, 2015.

[128] C. Xu, J. Kynicky, M. Smith, A. Kopriva, M. Brtnicky, T. Urubek, Y. Yang, Z. Zhao, C. He and W. Song, "Origin of heavy rare earth mineralization in South China," *Nature Communications,* vol. 8, 2017.

[129] "CYANEX 572 Solvent Extraction Reagent - Product Data Sheet," CYTEC, 2017. [Online]. Available: https://www.cytec.com/sites/default/files/files/CYTEC_CYANEX_572_FINAL.pdf.

9 APPENDICES

A. Supplemental Background Information on Rare Earth Elements

B. Sample Log

C. ICP-MS Raw Data

D. Technical and Economic Feasibility Analysis Report

E. Pro Forma – Valley City State University Activated Carbon Plant

APPENDIX A - BACKGROUND ON RARE EARTH ELEMENTS

The information contained in this appendix is meant to provide supplementary information for Chapter 1. Discussions on the uses of rare earth elements, the geology of rare earth elements and the production and purification processes for rare earth elements are provided in more detail than contained in Chapter 1.

A.1 Uses of Rare Earth Elements

The major market segments that utilize REEs are discussed in the following sections.

A.1.1 Magnets

Rare earth magnets represent the largest global application for REEs. Due to their unique magnetic properties, some of the lanthanides can be combined with other metals, such as Co or Fe to produce the strongest magnets available today. The rare earth magnets are used in a huge variety of applications (Table A-1) and due to their special properties and high performance, are replacing iron-based magnets (ferritic magnets) for many applications. Emerging technologies are also being developed at a rapid pace. The important REEs that make up this market are Sm and Nd, but others are used to varying extent as well. Samarium cobalt magnets have high magnetic energy, but also offer high temperature stability, allowing their use for compact systems and higher temperatures. Examples include motors and various sensors. Neodymium-iron-boron magnets are a fairly new class of permanent magnets, but are the strongest magnets known today, although do not have the temperature stability of Sm-Co magnets. Although the market for these materials are relatively small at current, demand for applications such as in wind turbines, motors for hybrid/electric vehicles and computer hard drives are growing quickly. These extremely strong magnets offer the ability to have small sized components with shape flexibility.

Table A-1. Applications for rare earth magnets [11]

- AC Compressors and Fans
- Aerospace Motors:
  - Controls
  - Rudder Motors
  - Tailfin Motors
- Appliance Motors
- Automotive Applications:
  - AC Compressor Motors
  - Electric Drives for EVs, PHEVs, and HEVs
  - Fuel Pump Motors
  - Fuel Valve Controls
  - Headlight Adjustment Motors
  - Passive Constraint/Air Bag Controls
  - Power Steering Sensor Motors
  - Seat Motors
  - Sensors
  - Window Lift Motors
- Bicycle Dynamos
- Brakes
- Ceiling Fan Motors
- CD/DVD Drives
- Defense:
  - Hybrid Electric Motors
  - Fin Motors
  - Laser Gun Sights
  - Navigation and Radar System Motors
  - Reference System Motors
- Direct Drive Motors
- Electric Bicycles
- Energy Storage Systems
- Fax Machines
- Gauges
- Generators
- Guitar Pickups
- Hand Power Tool Motors
- Hard Disk Drives
- Headphones
- HVAC Circulation Pumps
- Hysteresis Clutch
- Industrial Motors
- Loudspeakers
- Low-Voltage Motors
- Magnetic Refrigeration
- Magnetic Separation
- Microphones
- Microrelays
- Motors for Off-Highway Trucks, Machinery, etc.
- Motors for Mining and Construction Equipment
- MRI
- Optical Disk Drives
- Pipe Inspection
- Printers
- Refrigerator Motors
- Relays and Switches
- Reprographics
- Sensors
- Servers
- Spindle Drive Motors
- Switched Reluctance Motors
- Super High-Efficiency Motors
- Torque-Coupled Drives
- Torque-Coupled Drives
- Traction Drives
- Transducers
- Vacuum Cleaner Motors
- Vibration Motors
- Wind Turbine Generators

A.1.2 Catalysts

As mentioned previously in Chapter 1, catalysts represents the largest U.S. application for REEs, accounting for about 12-14% of the total catalyst industry [11]. La and Ce are the major elements used for this application, with Pr and Nd used in lesser volumes. A major catalyst application is for fluid catalytic cracking (FCC) for petroleum refining, in which the introduction of REE into the zeolite-based catalyst in proportions up to about

5% (La and Pr) results in increased yields of the gasoline fractions and improved energy efficiency. The primary use for La overall is FCC catalysts. Another large catalyst application is for automotive catalytic converters, in which Ce is used as the active component to clean the automotive exhaust, as well as a stabilizer for the alumina support ensuring its ability to withstand the high temperature environment. Other catalyst applications include combustion catalysts and emissions control, namely sulfur dioxide during regeneration of FCC catalysts and nitrogen oxide control, as well as polymerization catalysts and other chemical processes.

A.1.3 Metallurgical Additives

REEs have found wide use in a number of metallurgical applications, including ductile iron and graphite iron, high-strength low-alloy stainless and specialty steels, as an alloying element in aluminum and magnesium, superalloys, and as an additive in hot-dipped galvanizing processes [11]. Rare earths are often added to a variety of alloys to serve as sulfur, oxygen or gas scavengers to control the morphology of the alloy and can significantly improve alloy properties such as ductility, workability, strength, and corrosion performance. For example, superalloys are Ni or Co-based alloys that are used in high temperature, corrosive or abrasive environments, and addition of very small amounts (< 0.2%) of La, Y or Ce are added to improve temperature performance by controlling diffusion mechanisms and oxidation/corrosion resistance. There are numerous other alloy-based applications, another important one being for defense applications such as in magnesium and aluminum alloys used in military helicopters where addition of REEs greatly decreases weight and increases strength of the materials. Some other applications include niche aluminum alloy markets, such as in baseball/softball bats, a major use of Sc.

A.1.4 Polishing Powders

Glass applications, primarily glass polishing, are an older market for REEs. Ce, in particular, is used extensively in this market due to its superior performance over other glass polishes. Ce is used in the polishing of optical lenses, television and computer monitor plates, and mirrors. The major driver for this market is the production of large screen televisions. Optical glass usage is in decline due to increased popularity of non-glass lenses (polycarbonate).

A.1.5 Phosphors

Phosphors are optical transducers that provide luminescence. REEs are used heavily in this market for items such as color television screens, computer monitors, cellular phones, fluorescent lighting and medical imaging. This is the most important use for Eu. REEs are used in modern electronics components as activators for the phosphors that determine the emission spectra while and as hosts that convert absorbed energy into radiant energy. REEs used as activators include Eu, Tb, Ce, Tm, and Pr; hosts include Y, Gd, and La. Usage in medical imaging devices includes X-ray where the phosphor converts the photon into the visible light range. The REE used in these types of phosphors decreases the exposure time needed for producing the film images and reduces exposure time for operating personnel and patients.

A.1.6 Glass Additives

REEs are widely used in glass manufacturing, primarily in five areas: i) decolorizers, ii) color tint, iii) refractive index enhancers, iv) color filters, and iv) radiation and UV protection. Ce is the most commonly used for this applications, with La, Nd, Pr and Er also used [11]. Decolorization of glass is primarily needed to to presence of iron species impurity in the glass raw materials (sand, limestone). Addition of cerium oxide during production oxidizes the iron oxide to the ferric state to remove blue coloring, and also reduces requirement of other glass additives (i.e. selenium) to remove yellow coloring from the ferric iron. The cerium also promotes other enhancements, including improved ultraviolet resistance, reduced quantity of physical decolorizers and replacement of toxic species (i.e. arsenic). Color tinting through addition of various REE oxides occurs through selective absorption of specific visible light ranges. Artistic or technical glasses often utilize REEs such as Nd, Pr or Ce to produce violet, pink, green or yellow shades to the glass. La oxide is the primary REE used in high index of refraction applications such as cameras and some eye glasses. Color filtration is used in items such as safety lenses and containers, in which REEs are added to filter light through goggles for welding or glass blowing and in glass containers to decrease rate of deterioration of food or beverages. Nd and Ce are the primary REEs used in this sector, but Sm and Eu are also used. UV and radiation protection from high energy sources such as x-rays, gamma-rays and cathode rays is possible by addition of Ce compounds to the glass. These radiation sources cause color deterioration over time, but Ce traps the liberated electrons either preventing or slowing deterioration. Ce-stabilized glass is used in applications such as television screens, cathode ray tubes and in radiation shielding glass for nuclear power.

A.1.7 Ceramics

There are three primary areas of use in the ceramics sector that include: colorants in glazes, refractories, and electronic ceramics. For example Y-oxide is used in ceramics to increase the strength of the materials by allowing formation of certain crystal planes, as well as a thermal barrier in high temperature engine components. Coloring for glazes is accomplished by blending REEs with a range of other elements. For example, a yellow color is enabled through use of Pr mixed with zirconium silicate, while green can be achieved by blending the same yellow stain with a blue vanadium-based colorant. Refractory ceramics primarily include use of Y in yttrium-stabilized zirconium oxide ceramics (YSZ). YSZ ceramics are used in a number of extreme environments, such as in sensors for combustion exhaust and molten glass/steel, industrial control systems for nuclear reactors, geothermal power systems and several other high temperature or high pressure severe-service applications. Electronics uses include electro-optical applications like laser dopants or microwave agents. Some REEs are used in the manufacturing of various advanced capacitors, resistors and thermistors. There are a very wide variety of uses in this sector.

A.1.8 Others

Two other significant REE applications are batteries and lasers. The battery application consists mainly of lanthanum and REE mixtures in nickel-metal hydride (NiMH) secondary batteries, which have largely supplanted nickel-cadmium formulations. The REE containing batteries eliminate use of cadmium, a toxic element, resulting in a more environmentally friendly consumer product. One of the common uses of these batteries is laptop computers. Laser applications include the most commonly used communications laser Nd:YAG, that consists of neodymium substituted yttrium aluminum garnet composition in the light tube. Nd lasers are often used due to their optimal selection and absorption of emitting wavelengths, with typical applications including material processing, drilling, spot welding and marking, and medical devices. There are many additional smaller or niche applications, some of which include: garnets, nuclear applications, carbon arc electrodes, drying agents in paints, and textiles specialties.

A.2 Geology of Rare Earth Elements

The following sections provide discussions on the geology of the various classifications of REE mineral deposits.

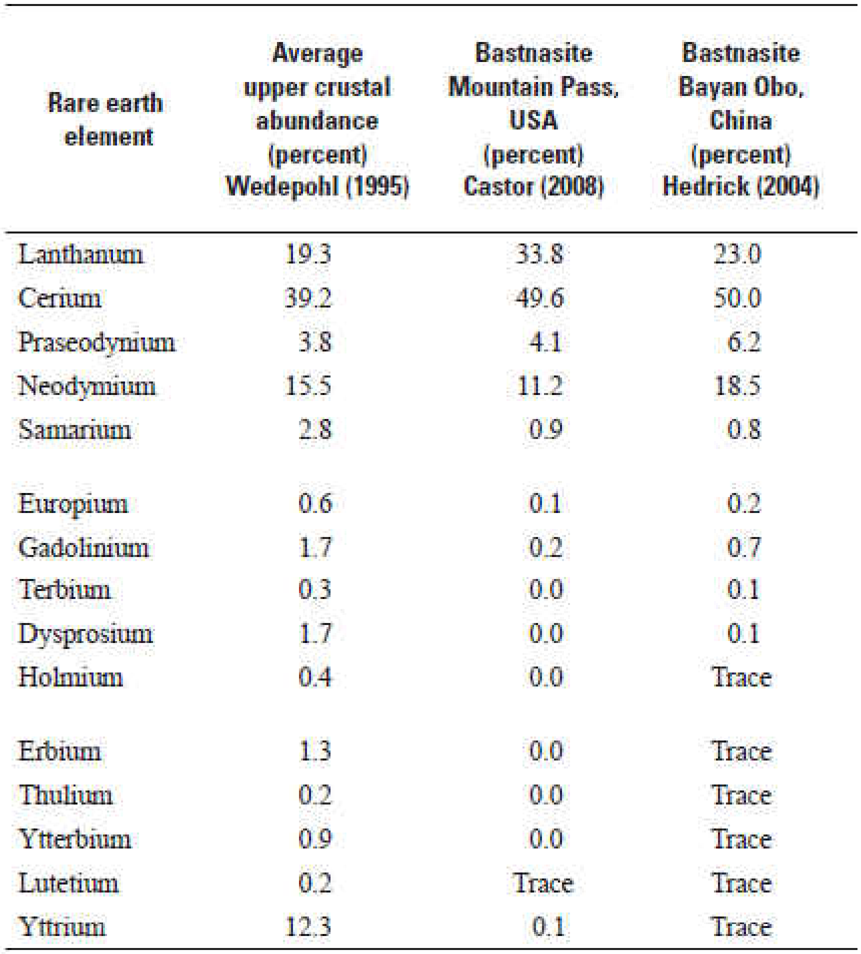
A.2.1 Carbonatite Rare Earth Element Deposits

A form of alkaline igneous rock (i.e. enriched in Na_2O and K_2O relative to SiO_2), carbonatite deposits are a type of intrusive or extrusive igneous rock that has composition of at least 50% carbonate minerals (i.e. calcite, dolomite and ankerite). They are rare deposits with only about 330 known locations on earth and almost exclusively form in continental rift zones most likely by partial melting of crustal rocks, fractional crystallization or mantle degassing [2, 18]. Carbonatites are enriched in incompatible elements, such as REE and Cs, Rb and Bs, while being depleted in compatible elements such as Hf, Zr and Ti. Incompatible elements are classified as elements that are preferentially retained (i.e. within the carbonate magma) because they do not partition readily into common rock-forming minerals. Due to their easy weathering, carbonatite deposits have not been well preserved in earth's geologic record (leads to their scarcity), but their weathering products are the source of other REE-containing resources (i.e. secondary sources). Some additional important characteristics of carbonatite deposits are summarized below [111]:

- Tend to be enriched in high field strength elements, such as REEs, Nb, Zr, Ta, Th and U
- REE-rich carbonatites tend to be light REE-enriched
- Can contain a variety of ore minerals, particularly carbonates, phosphates or florates
- Significant REE ore minerals include bastnasite, monazite and xenotime
- The origin is from magmatic processes, but overlaying hydrothermal processes may redistribute or enrich REEs
- Of the major REE-bearing carbonatite minerals, bastnasite is the most important and has a total rare earth oxides (REO) content of about 70-74 wt% of the mineral, with the majority being the lightest REEs La and Ce.

Examples of the REE distribution within two of the largest REE-bearing carbonatite deposits known are provided in Table A-2 [6, 26, 112] and compared to average crustal distribution. The data shows that both deposits, which are primarily bastnasite, are highly enriched in the LREE, mainly La and Ce, but are relatively depleted in the other REEs. The Mountain Pass ore (California, U.S.) contains about 8 to 12wt% REO, while the Bayan Obo ore (China) contains about 6% REO.

Table A-2. Distribution of rare earth elements in two large carbonatite deposits (bastnasite) compared to crustal averages (percent of total REE) [6, 26, 112]



Rare earth element	Average upper crustal abundance (percent) Wedepohl (1995)	Bastnasite Mountain Pass, USA (percent) Castor (2008)	Bastnasite Bayan Obo, China (percent) Hedrick (2004)
Lanthanum	19.3	33.8	23.0
Cerium	39.2	49.6	50.0
Praseodymium	3.8	4.1	6.2
Neodymium	15.5	11.2	18.5
Samarium	2.8	0.9	0.8
Europium	0.6	0.1	0.2
Gadolinium	1.7	0.2	0.7
Terbium	0.3	0.0	0.1
Dysprosium	1.7	0.0	0.1
Holmium	0.4	0.0	Trace
Erbium	1.3	0.0	Trace
Thulium	0.2	0.0	Trace
Ytterbium	0.9	0.0	Trace
Lutetium	0.2	Trace	Trace
Yttrium	12.3	0.1	Trace

A.2.2 Peralkaline Rare Earth Element Deposits

Peralkaline rocks are igneous rocks that are oversaturated with Na_2O and K_2O with respect to Al_2O_3, with the following requirement:

$$Al_2O_3 < (Na_2O + K_2O)$$

They are typically formed in island arc and mountain building regions, and are related to carbonatite deposits in that they are both thought to be deposited through partial melting of the mantle with transportation of the magma to the crust. Figure A-1 displays a genetic sequence of events that are thought to occur during formation of both peralkaline and carbonatite deposits. Here the REE-enriched deposits are produced by partial melting of the metasomatised subcontinental lithospheric mantle (SCLM) with transportation of the REE from the mantle into the crust. Because the REE are incompatible elements, they become progressively concentrated in the melt as rock-forming processes occur. Granites are produced from partial melting of the crust material and are less enriched in REE compared to the peralkaline/carbonatite materials [113]. One thing to note is that the relative content of REE in peralkaline materials is typically slightly less that carbonatites (1650 vs. 2900 ppm according to this reference), but the content of the HREE is significantly higher in the peralkaline deposits (LREE/HREE of 7 vs. 46 for carbonatite) [113].

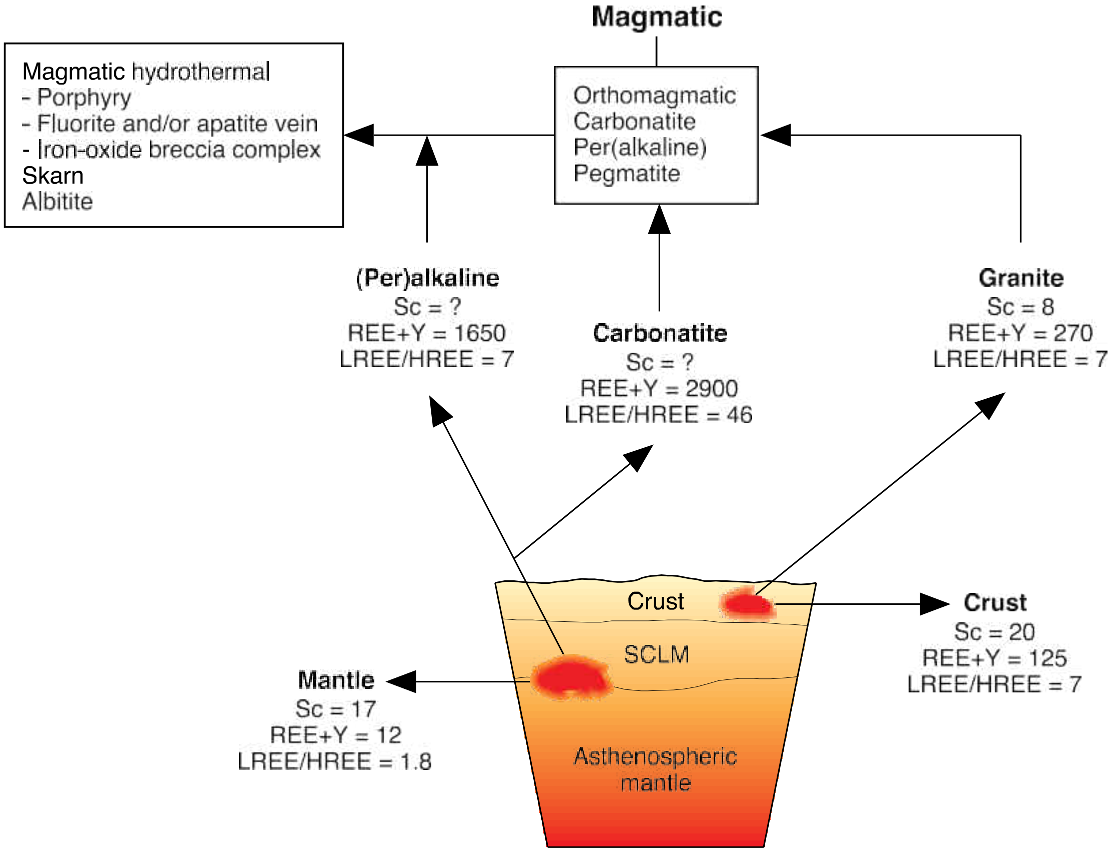


Figure A-1. Mantle-crust-surface geochemical cycle for rare earth elements (REE concentrations are in ppm) [113].

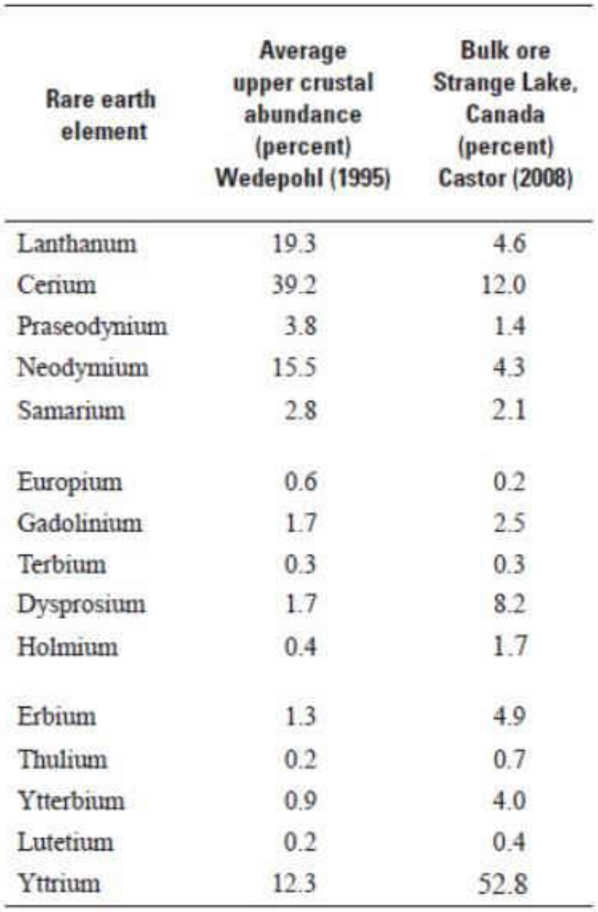
The primary REE-bearing minerals include apatite, xenotime, monazite and to a lesser extent bastnasite. Apatite is a somewhat different geochemistry, in that the REEs present substitute for a portion of the calcium and are present in much lower quantity than xenotime, monazite or bastnasite. The mineral formula and REO content for each of these minerals is shown below:

- Apatite – $[(Ca,REE,Sr,Na,K)_3Ca_2(PO_4)_3(F,OH)]$; 0.1-0.8 wt% REO [114, 115]
- Xenotime – YPO_4; 52-67 wt% REO [20]
- Monazite – $(Ce,La,Nd,Th)PO_4$; 35-71 wt% REO [20]

Two of the known North American peralkaline REE deposits are Bokan Mountain (Alaska) and Thor Lake (Canadian Northwest Territories). Although ore grade (total REO content) is relatively lower (typically less than 1 wt% REO) than the carbonatite deposits discussed previously, both of these deposits contain a higher content of the HREE [15, 43, 116]. Another example is the Strange Lake (Quebec, Canada) deposit that has an overall REE distribution as shown in Table A-3 and compared to crustal averages. This deposit is reported to contain an average of 0.93 wt% REO [117], and is particularly enriched in yttrium. It also has a significantly higher content of HREE compared to carbonatite type deposits.

Pegmatitic deposits of REEs are typically peralkaline in form, and thus can be included in this category. Pegmatites are coarse-grained felsic intrusive rocks that are rich in incompatible elements, including REE. They are commonly enriched in the mineral apatite. The pegmatites are extreme igneous rocks that form during the final stage of magma crystallization. They are classified as extreme because of the very large crystal size with a diameter of at least one centimeter. In the early stages of crystallization, the ions that form high-temperature minerals are depleted from the melt, and so the incompatible elements become concentrated in the melt and remain during the final crystallization. Although concentrated in the REE, pegmatitic deposits typically occur at the periphery of large granitic intrusions, and are generally small in comparison.

Table A-3. Rare earth element distribution at the peralkaline deposit at Strange Lake, Canada
[6, 26]



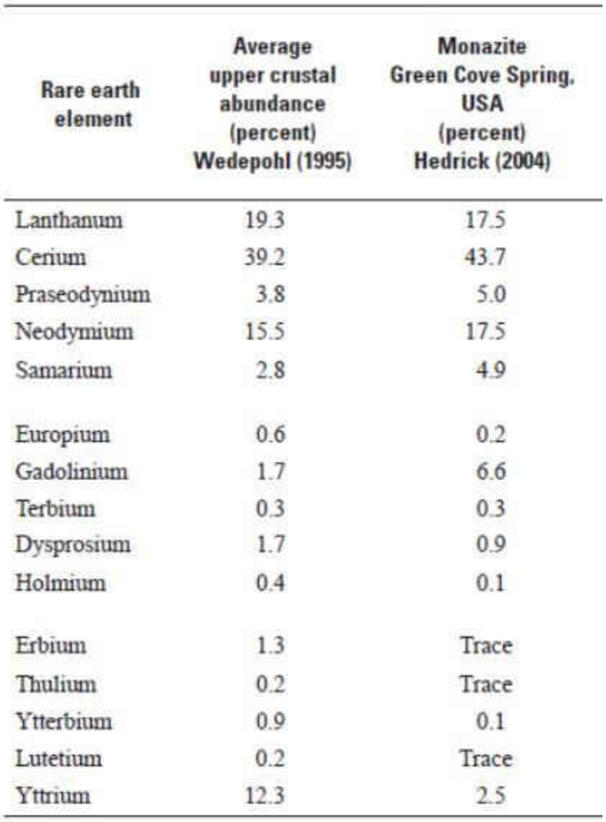
Rare earth element	Average upper crustal abundance (percent) Wedepohl (1995)	Bulk ore Strange Lake, Canada (percent) Castor (2008)
Lanthanum	19.3	4.6
Cerium	39.2	12.0
Praseodymium	3.8	1.4
Neodymium	15.5	4.3
Samarium	2.8	2.1
Europium	0.6	0.2
Gadolinium	1.7	2.5
Terbium	0.3	0.3
Dysprosium	1.7	8.2
Holmium	0.4	1.7
Erbium	1.3	4.9
Thulium	0.2	0.7
Ytterbium	0.9	4.0
Lutetium	0.2	0.4
Yttrium	12.3	52.8

A.2.3 Placer Rare Earth Element Deposits

Weathering of all types of rocks yields sediments that are deposited in a wide variety of environments, such as streams and rivers, shorelines, alluvial fans, and deltas. The process of erosion concentrates denser minerals, most notably gold, into deposits known as placers. Depending on the source of the erosion products, certain REE-bearing minerals, such as monazite and xenotime, can be concentrated along with other heavy minerals. The sources can be, for example, weathered carbonatite or peralkaline materials. However, many common igneous, metamorphic or older sedimentary rocks contain sufficient monazite to form a monazite-bearing placer [20].

An example of a placer REE deposit in the U.S. is Florida beach sands (Garden Cove Spring), which has been mined primarily for titanium compounds ilmenite and rutile, but also contains large quantities of monazite. The estimated distribution of REEs in the Garden Cove Spring deposit are shown in Table A-4 compared to crustal averages. Estimated monazite content in this deposit is roughly 1 wt%, which contains about 50-60 wt% REO [20]. Another example is the paleoplacer deposits at Elliot Lake, Ontario Canada. Here the source rock is some of the oldest on Earth, the Canadian Shield, which resulted in the placer deposit through intense weathering of this granite [2]. In this deposit, which has been mined mainly for uranium and gold, the REEs are associated with uranium minerals such as uraninite, brannerite and uranothorite, with monazite also being present. The HREE are more concentrated than the LREE and the overall average REO content is about 0.16 wt%.

Table A-4. Rare earth element distribution in the Florida beach sands placer deposit [6, 112]



Rare earth element	Average upper crustal abundance (percent) Wedepohl (1995)	Monazite Green Cove Spring, USA (percent) Hedrick (2004)
Lanthanum	19.3	17.5
Cerium	39.2	43.7
Praseodynium	3.8	5.0
Neodymium	15.5	17.5
Samarium	2.8	4.9
Europium	0.6	0.2
Gadolinium	1.7	6.6
Terbium	0.3	0.3
Dysprosium	1.7	0.9
Holmium	0.4	0.1
Erbium	1.3	Trace
Thulium	0.2	Trace
Ytterbium	0.9	0.1
Lutetium	0.2	Trace
Yttrium	12.3	2.5

A.2.4 Phosphorite Rare Earth Element Deposits

Phosphorite deposits form as chemical precipitates on continental shelves due to temperature dependent solubility of carbonate and phosphate components. Upwelling of cold, phosphate rich waters causes warming and decreased solubility causing precipitation at the shallower sea depth. A schematic of this process is shown in Figure A-2 [2]. Phosphorite deposits have traditionally been used as the feedstock for phosphate-based fertilizers produced through a dilute sulfuric acid dissolution process. According to recent work [118] evaluating U.S. phosphorite deposits for REE recovery, the REE are entirely contained in the mineral francolite, in which the REE substitutes for Ca. Francolite has the following mineral form: $(Ca,Mg,Sr,Na)_{10}(PO_4,SO_4,CO_4)_6F_{2\text{-}3}$. The deposits are abnormally enriched in HREE. Total REE as high as 1.8 wt% has been measured in certain deposits, with an overall average of about 0.1 wt%. The homogeneity of the REE content is quite uniform within a given geologic age, surprisingly even among vastly different geologic settings. Although intensely debated, some authors attribute this geologic age homogeneity to secular variations in ocean water chemistry, rather than geologic processes [118]. For example, Upper Devonian and Mississippian phosphorites have been shown to have the highest REE content, but samples from other geologic eras have shown three orders of magnitude or more difference.

An example of the REE distribution within a phosphorite REE deposit is presented in Table A-5 for the Love Hollow formation in Arkansas, U.S., and compared to crustal averages. Their combination of high HREE enrichment and easy dissolution in dilute acid makes phosphorite REE deposits an attractive target.

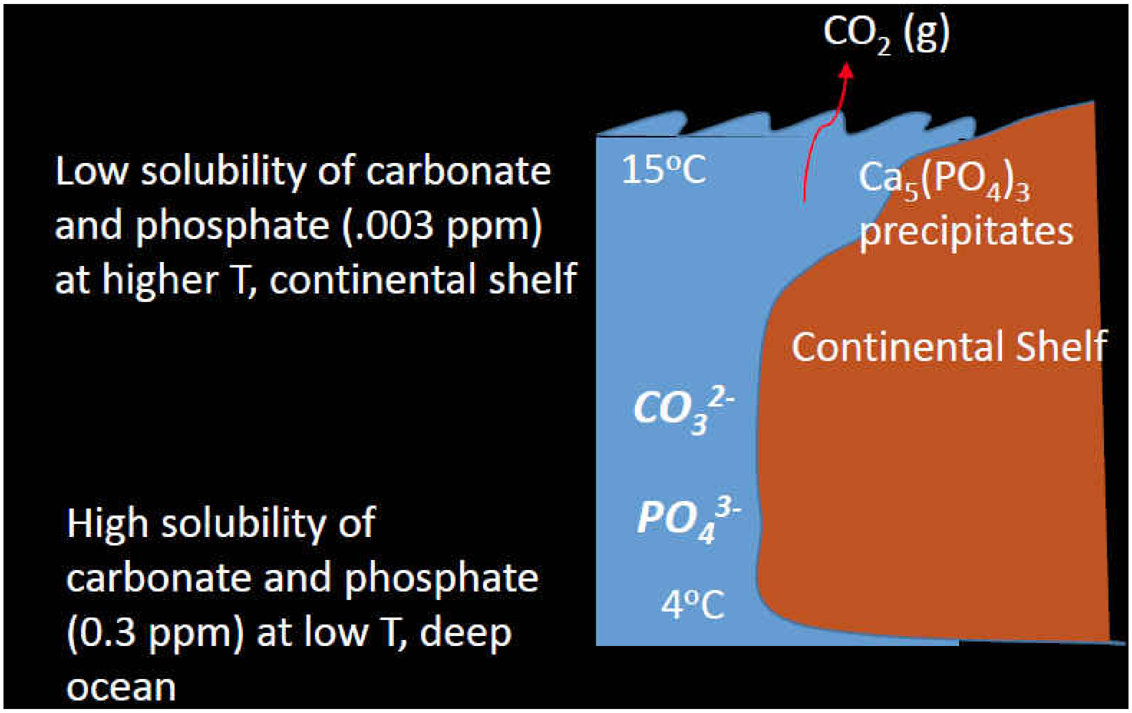


Figure A-2. Process of phosphorite precipitation on continental shelves [2]

Table A-5. Rare earth element distribution of a U.S. phosphorite deposit [6, 118]

Element	Average upper crustal abundance (percent) Wedepohl (1995)	Love Hollow Phosphorite (Arkansas) (percent) Emsbo (2015)
Lanthanum	19.3	15.8
Cerium	39.2	34.9
Praseodymium	3.8	3.2
Neodymium	15.5	14.3
Samarium	2.8	2.9
Europium	0.6	0.7
Gadolinium	1.7	3.3
Terbium	0.3	0.4
Dysprosium	1.7	2.6
Holmium	0.4	0.5
Erbium	1.3	1.3
Thulium	0.2	0.2
Ytterbium	0.9	0.8
Lutetium	0.2	0.1
Yttrium	12.3	19.1

A.2.5 Lateritic Rare Earth Element Deposits (Ion-adsorbed Clays)

Laterite deposits are a general class of sedimentary materials that formed due to intense weathering of a source rock in tropical or subtropical regions with a humid climate, typically under mildly acidic, strongly oxidizing and leaching conditions [1]. Laterites are characterized by complete breakdown of primary mineral assemblages, largely to a mixture of Fe-Mn oxyhydroxides (i.e. hematite, goethite, ramsdellite), barite and various phosphate minerals [18]. Also known as weathered crust elution-deposited material, a unique type of laterite deposit is the ion-adsorbed clays, the best understood of which are found in Southern China. The clays were formed as a result of deep weathering of granitic source rocks that over time lead to the formation of aluminosilicate clays, mainly kaolinite, illite and smectite. During the weathering process, the REEs contained in the source granite leached out and were ionically bound to the clay materials. Bao and Zhao

[119] have estimated that the weathered crusts are up to 30 m deep and can be divided into four layers:

1. Upper humic layer of quartz, organic matter and soil: 0-2 m thick, with very low/nil REE content
2. A strongly weathered layer enriched in REE: 5-10 m thick with kaolinite, halloysite, quartz and mica
3. A semi-weathered layer: 3-5 m thick with kaolinite and sericite
4. A weakly weathered bottom layer with the same mineral compositions as the host rock.

80-90% of the adsorbed REE report to the strongly weathered layer (2), with most of the remainder being present in the semi-weathered layer (3). Peng [120] and Hendrick [121] have detailed the metallogenic mechanism of formation for the weathered REE deposits, as shown in Figure A-3.

Clay materials, very often, undergo isomorphous substitution of one cation with another of similar size, but lesser charge, such as Al^{3+} for Si^{4+} or Mg^{2+} for Al^{3+}. This leads to a charge imbalance in silicate clays, which accounts for the permanent negative charge on clay particles, that allows them to attract cations such as REEs to their surface.

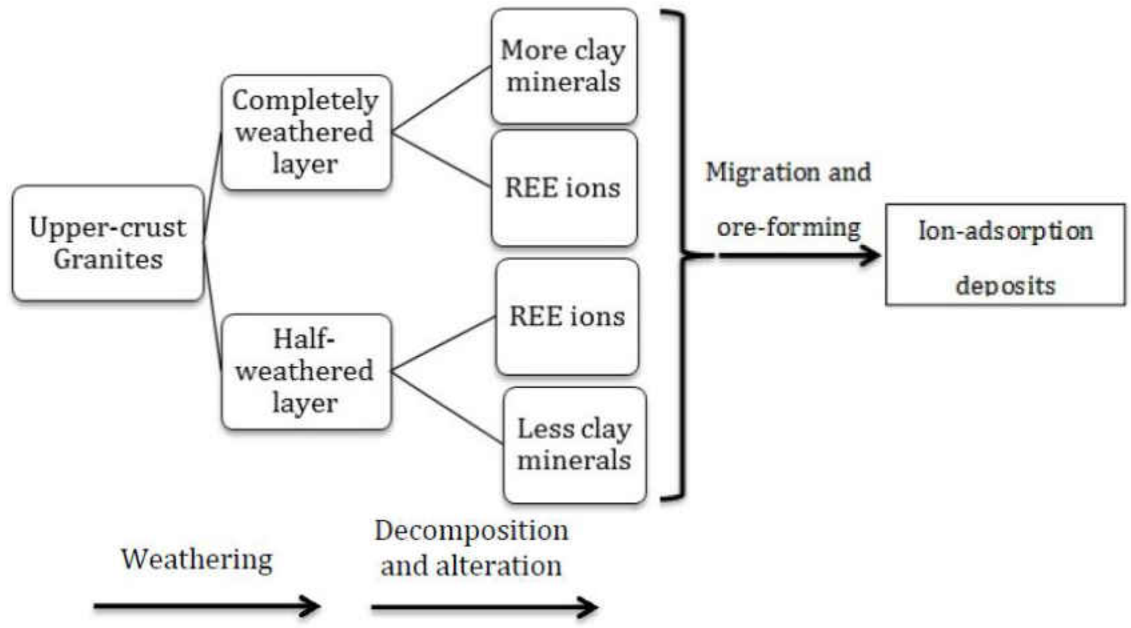


Figure A-3. Metallogenic mechanism of formation for REE-rich adsorption-type ores (adapted from [120, 121])

Some authors [122, 123] have claimed that under slightly acidic conditions, most REEs in these materials are associated as simple or hydrated cations derived from a physisorption process of simple cation-exchange at the negative sites in the silicate clays, while under slightly basic conditions, the dominant form is a hydrolyzed species formed through chemisorption by permanent complexation reactions at the surface hydroxyl groups or soluble carbonate/ bicarbonate complexes [124].

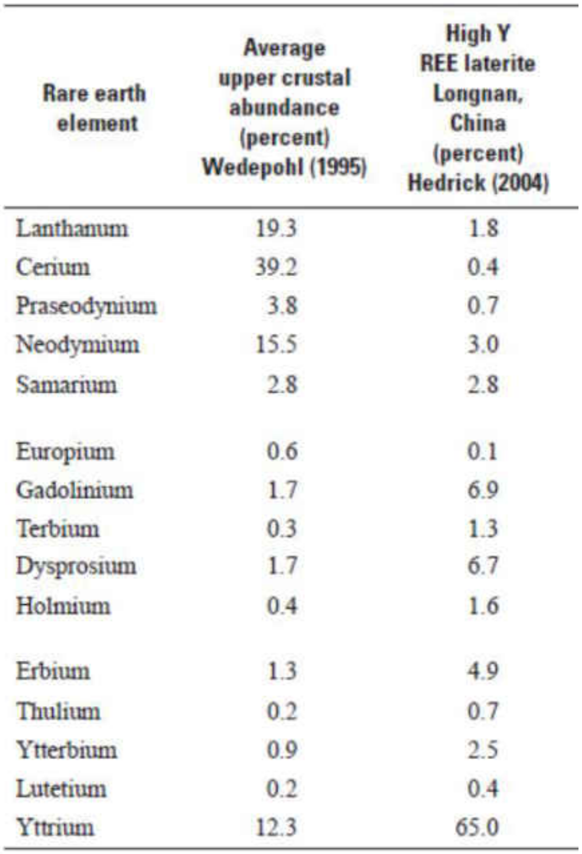
Depending on weathering conditions – nature of the host rocks, water and soil pH, temperature, pressure, redox conditions – there are three main categories of REE present in ion-adsorption clays [124]:

1. <u>Colloid Phase</u>: REE deposited as insoluble oxides or hydroxides or as part of colloidal polymeric organometallic compounds. These species have low occurrence in ores at the slightly acidic conditions.

2. Exchangeable Phase: REE occur as soluble free cations/hydrated cations or part of positively-charged complexes in solution adsorbed species on clays. These account for about 60-90% of the total REE
3. Mineral Phase: REE part of solid fine particles with same mineral matrix as the host rocks.

One of the unique aspects of the Chinese ion-adsorbed clays is their abnormal distribution of REEs, which is heavily skewed to the HREE, particularly Y, unlike most other deposits which contain mainly LREE. However, their total REE content is considerably lower than other deposits, such as carbonatites, at about 0.05 to 0.5wt%. An example from the Longnan clay in Southern China is provided in Table A-6 and compared to crustal averages. The clays also typically show the “negative cerium anomaly”, in which the content of Ce is lower that would be expected. Because the REEs are adsorbed as 3+ cations, the relatively easy oxidation of Ce^{3+} to its higher valence state Ce^{4+} results in the formation/precipitation of cerianite (CeO_2), and speciation of Ce from the adsorbed lanthanides [34]. The Chinese clays also have low content of radioactive elements Th and U compared to other deposit types containing monazite or bastnasite as the REE-bearing minerals. Because it is the best developed, the Chinese resource is also the best understood. However, because the source granite is intensely weathered, the explanation for the high HREE enrichment is not obvious, an in fact, appears to be an isolated phenomenon, as recently discovered lateritic clays enriched in REEs have been found in other parts of the world (Southeast Asia [125], Madagascar [126], and the Southeastern United States [2, 127]), but do not exhibit the same HREE enrichment. In recent work, Xu and others [128] attempted to determine the cause of the abnormal HREE enrichment, and concluded that highly oxidized, REE-rich fluids, derived from external, isotopically depleted sources, metasomatized the source granites, which resulted in Ce depletion as Ce^{4+} and enrichment of the remaining REE, especially the HREE.

Table A-6. REE distribution in the Chinese ion-adsorbed clays compared to crustal averages
[6, 112]



Rare earth element	Average upper crustal abundance (percent) Wedepohl (1995)	High Y REE laterite Longnan, China (percent) Hedrick (2004)
Lanthanum	19.3	1.8
Cerium	39.2	0.4
Praseodynium	3.8	0.7
Neodymium	15.5	3.0
Samarium	2.8	2.8
Europium	0.6	0.1
Gadolinium	1.7	6.9
Terbium	0.3	1.3
Dysprosium	1.7	6.7
Holmium	0.4	1.6
Erbium	1.3	4.9
Thulium	0.2	0.7
Ytterbium	0.9	2.5
Lutetium	0.2	0.4
Yttrium	12.3	65.0

A.3 Production and Purification Processes for Rare Earth Elements

For the hard rock ores, physical beneficiation processes are typically employed to achieve some degree of concentration prior to chemical extraction of the REEs. In most cases, grinding/milling of the ore to achieve liberation of the REE-bearing minerals from the gangue is the first step, which can be followed by a series of beneficiation techniques that may include sortation (i.e. X-ray), gravity concentration, magnetics or flotation. Flotation is typically the backbone of the physical beneficiation plant, but gravity concentration or magnetic separation can be used to upgrade the flotation concentrate. The goal of the physical beneficiation steps is to concentrate a low-grade ore with minimal REE losses to the tailings, however the efficiency of these steps is largely dependent on the degree of REE-mineral liberation that is achieved in the grinding steps, resulting in a tradeoff between energy consumption (grinding) and concentrate grade/recovery. Typical upgrade factors (concentrate REO grade over ore REO grade) range from 2 to as high as 30, depending on the ore type and the methods used [27].

Following physical beneficiation steps, chemical extraction is typically used with a wide variety of methods with the goal of preferentially dissolving (i.e. cracking) the REE-bearing minerals into solution. Most methods use hot concentrated acid (i.e. 200-600°C) baking, typically sulfuric or hydrochloric acids. Caustic cracking is also commonly used, in which hot sodium hydroxide or other caustic cracks the REE into hydroxide forms. In either case, the dissolved REE-bearing mineral solution now contains the REEs along with impurities derived from dissolution of the minerals.

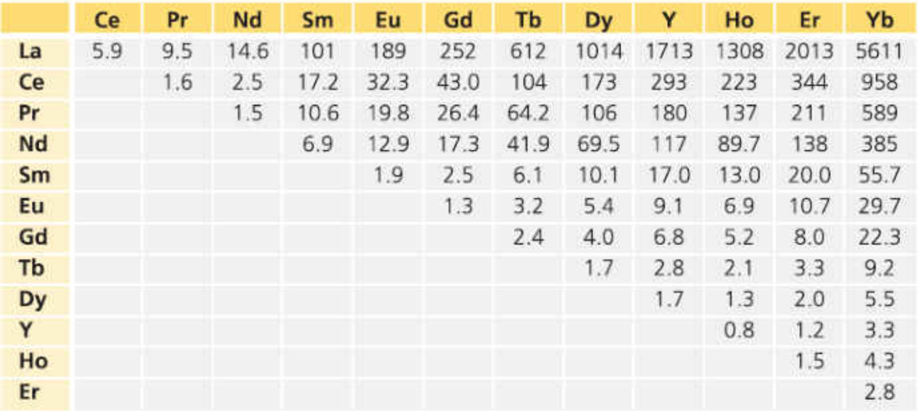
Impurity removal from the solution or selective precipitation of the REE from the solution can take many forms. One method is pH neutralization (i.e. base addition) to selectively precipitate elements such as Th, Fe, P and Al. In other cases, the mixed REE may be precipitated as a variety of compounds (i.e. oxalates from precipitation with oxalic acid reagent) depending on the precipitating reagents used. Once precipitated, the mixed REE is often then selectively re-dissolved into a more concentrated solution to simplify downstream processes. This secondary dissolution step is often another means of impurity removal (i.e. secondary impurity removal). Finally, once the REEs have been purified in solution to the required extent, another precipitation step followed by calcination is used to produce a pure mixed REO product. Reagent regeneration is used where feasible to reduce consumption at the expense of added capital/operational complexity.

In the case of the ion-adsorbed clays and similar deposits, no physical beneficiation processes are used. Instead chemical extraction of the raw ore is the first step which occurs by an ion exchange solution leaching, typically using a concentrated monovalent inorganic salt solution (i.e. ammonium sulfate). In the case of the Chinese clays, approximately 60-90% of the REE are associated as ion-exchangeable cations, and are easily extracted via the leaching process being transferred into the solution as soluble sulfates or chlorides (depending on the reagent used) following a 3:1 stoichiometry (Equation 1 as shown for the sulfate solution method).

$$2\ \text{Clay-REE} + 3M_2SO_4 \rightarrow 2\ \text{Clay-}M_3 + REE_2(SO_4)_3 \qquad (1)$$

Solubilized REE are then usually selectively precipitated with oxalic acid and then calcined to produce a pure mixed REO product. One of the major advantages of these clay deposits is their simple extraction process compared to hard rock ores. Adding to the simplicity, is that in recent years, mining of the clays is not even done, rather the leaching is done in-situ, where injection and production wells are drilled into the deposit. The leaching solution is injected under pressure and the porosity of the clays allows contacting in-situ, with the REE-concentrated leach solution then collected and processed through the production wells.

For both hard rock and ion-adsorbed clay-type deposits, once a pure mixed REO product is produced, separation of the individual REOs is typically done through a solvent extraction method, although some other methods, namely ion exchange, are used for limited applications. Solvent extraction (i.e. liquid-liquid extraction) is carried out in a multi-stage process of repetitive fractionation in a group of mixer-settlers. The REE-containing solution is first mixed with an organic phase containing an organic solvation agent that forms complexes with the REE ions. The ions are then extracted from the REE-enriched organic phase by moving it into contact with an aqueous solution where the ions of specific REE or groups of REE have higher solubility, a step called stripping. This is repeated until a desired purity is reached. Because REE are chemically very similar, their separation is very difficult, and the stripping step must be repeated many times to reach purity levels required (i.e. 99.99%). REE specific solvents have been developed, such as CYANEX® 572 [129]. Separation factors have been established that determine the number of stripping steps required to reach a desired purity, depending on the separation being attempted. The closer the elements are in molecular weight the more steps will be required (i.e. smaller separation factor). For instance, the published separation factors for CYANEX® 572 are shown in Figure A-4.



	Ce	**Pr**	**Nd**	**Sm**	**Eu**	**Gd**	**Tb**	**Dy**	**Y**	**Ho**	**Er**	**Yb**
La	5.9	9.5	14.6	101	189	252	612	1014	1713	1308	2013	5611
Ce		1.6	2.5	17.2	32.3	43.0	104	173	293	223	344	958
Pr			1.5	10.6	19.8	26.4	64.2	106	180	137	211	589
Nd				6.9	12.9	17.3	41.9	69.5	117	89.7	138	385
Sm					1.9	2.5	6.1	10.1	17.0	13.0	20.0	55.7
Eu						1.3	3.2	5.4	9.1	6.9	10.7	29.7
Gd							2.4	4.0	6.8	5.2	8.0	22.3
Tb								1.7	2.8	2.1	3.3	9.2
Dy									1.7	1.3	2.0	5.5
Y										0.8	1.2	3.3
Ho											1.5	4.3
Er												2.8

Figure A-4. Separation factors for CYANEX® 572 solvent extraction reagent [129].

Once the individual REOs are separated in this method, individual precipitation (i.e. oxalic acid) and carbonation steps are typically used to produce the dry pure individual REOs. Conceptual solvent extraction flow diagrams for REE from bastnasite and monazite and REE from Chinese clays are provided in Figure A-5 and Figure A-6, respectively. The figures show that the first separations are into groups of mixed REEs, with progressive separations into individual elements.

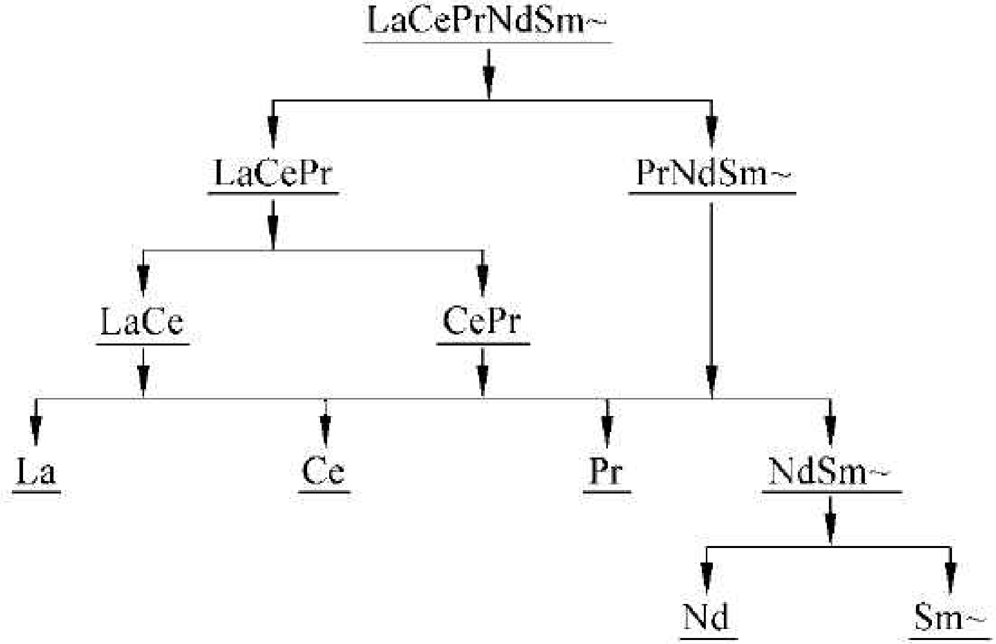


Figure A-5. Conceptual flowsheet for solvent extraction-based separation of mixed REO from hard rock ores [24]

Finally, once separated into individual pure REO, the REO must undergo refining into pure REE metals or specific REE-compounds to be of use for product manufacturing. This is typically done by molten salt electrolysis and by metallothermic reduction methods. Metallothermic reduction is the most widely used method, and occurs by reductants reacting in a furnace with oxidants (i.e. oxygen, sulfide, carbonate) to separate and free metal. These processes are technically complicated are require large amounts of energy. Refining plants and technical know-how are almost exclusively centered in China, and represents one of the primary challenges associated with development of the complete REE value chain in other parts of the world.

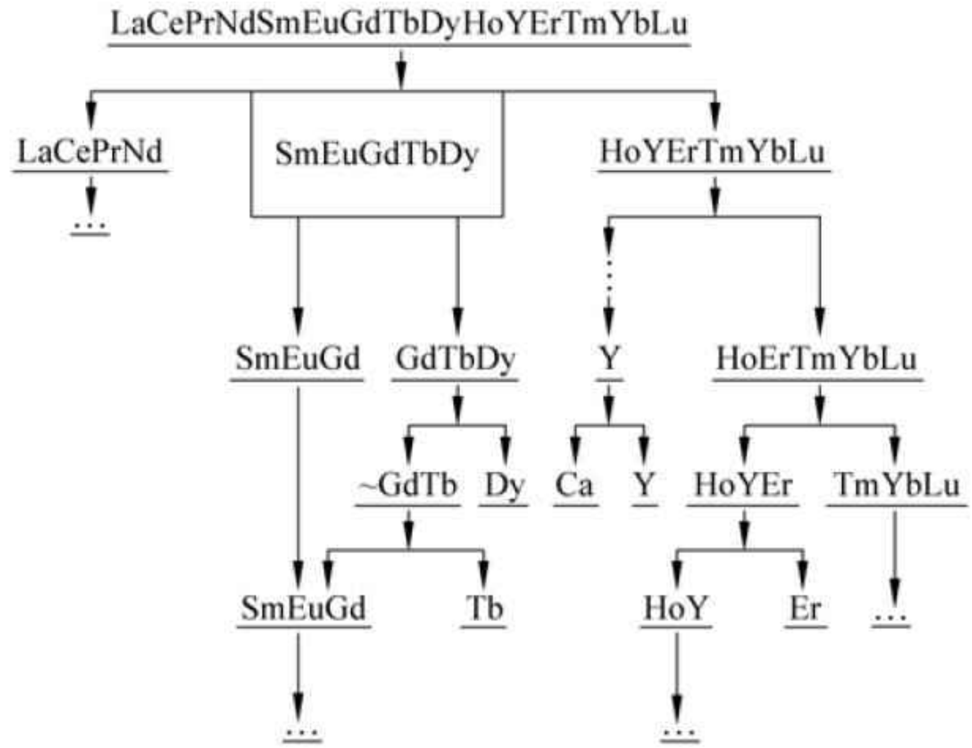


Figure A-6. Conceptual flowsheet for solvent extraction-based separation of mixed REO from ion-adsorbed clays [24]

APPENDIX B – SAMPLE LOG

This section contains the entire list of samples collected during this study, as shown in Table B-1

Table B-1. Listing and description of all samples collected

Sample ID		Sampling Location	Seam/Plant	Footage/Date	Description
IES	16004	Coal dryer fabric filter	Coal Creek Station	old samples	fly ash fines
IES	16005	Air jig rejects (2016)	Coal Creek Station	old samples	Air Jig Reject
IES	16006	Air jig rejects composite (2016)	Coal Creek Station	old samples	Air Jig Reject
IES	16007	Air jig rejects (2016)	Coal Creek Station	old samples	Air Jig Reject
IES	16008	FA14001C	Hagel A coal	0.75-9.25	coal
IES	16009	FA14001C	Hagel B coal	3.55-6.85	coal
IES	16010	FA14002C	Hagel A coal	0.25-9.55	coal
IES	16011	FA14002C	Hagel B coal	0.45-4.2	coal
IES	16012	RD15001C	Hagel A coal	0.7-8.2	coal
IES	16013	RD15002C	Tavis coal	2.0-11.3	coal
IES	16014	RD15002C	Tavis Rider	0.6-2.0	coal
IES	16015	FA14001C	Hagel A Roof 1	0-0.75	sediment
IES	16016	FA14001C	Hagel A Floor 1	9.25-10.0	sediment
IES	16017	FA14001C	Hagel B Floor 1	6.85-8.0	sediment
IES	16018	FA14002C	Hagel A Roof 2	0-0.25	sediment
IES	16019	FA14002C	Hagel A Floor 2	9.55-9.75	sediment
IES	16020	FA14002C	Hagel B Roof 1	0-0.45	sediment
IES	16021	FA14002C	Hagel B Floor 2	4.2-5.5	sediment
IES	16022	RD15001C	Hagel A Roof 3	0-0.7	sediment
IES	16023	RD15001C	Hagel A Floor 3	n/a	sediment
IES	16024	RD15002C	Tavis Roof	0-0.6	sediment
IES	16025	RD15002C	Tavis Floor	11.3-12.1	sediment
IES	16026	South Point	Hagel A Roof	1	sediment
IES	16027	South Point	Hagel A coal	0-1	coal
IES	16028	South Point	Hagel A coal	1-2	coal
IES	16029	South Point	Hagel A coal	2-3	coal
IES	16030	South Point	Hagel A coal	3-4	coal
IES	16031	South Point	Hagel A coal	4-5	coal
IES	16032	South Point	Hagel A coal	5-6	coal
IES	16033	South Point	Hagel A coal	6-7	coal
IES	16034	South Point	Hagel A Floor	0-1	sediment
IES	16035	South Point	Hagel A Floor	1-2	sediment

Table B-1. Listing and description of all samples collected

Sample ID		Sampling Location	Seam/Plant	Footage/Date	Description
IES	16036	East Point 1	Hagel A Roof	2	sediment
IES	16037	East Point 1	Hagel A Roof	1	sediment
IES	16038	East Point 1	Hagel A coal	0-1	coal
IES	16039	East Point 1	Hagel A coal	1-2	coal
IES	16040	East Point 1	Hagel A coal	2-3	coal
IES	16041	East Point 1	Hagel A coal	3-4	coal
IES	16042	East Point 1	Hagel A coal	4-5	coal
IES	16043	East Point 1	Hagel A coal	5-6	coal
IES	16044	East Point 1	Hagel A Floor	0-1	sediment
IES	16045	East Point 1	Hagel A Floor	1-2	sediment
IES	16046	East Point 2	Hagel B Roof	3	sediment
IES	16047	East Point 2	Hagel B Roof	2	sediment
IES	16048	East Point 2	Hagel B Roof	1	sediment
IES	16049	East Point 2	Hagel B Coal	0-1	coal
IES	16050	East Point 2	Hagel B Coal	1-2	coal
IES	16051	East Point 2	Hagel B Coal	2-3	coal
IES	16052	East Point 2	Hagel B Coal	3-4	coal
IES	16053	East Point 2	Hagel B Floor	0-1	sediment
IES	16054	East Point 2	Hagel B Floor	1-2	sediment
IES	16055	East Point 2	Hagel B Floor	2-3	sediment
IES	16056	East Point 3	B rider Roof	1	sediment
IES	16057	East Point 3	B rider coal	from pile	coal
IES	16058	East Point 3	B rider floor	from pile	sediment
IES	16059	East Point 3	Hagel B Roof	1	sediment
IES	16060	East Point 3	Hagel B Coal	from pile	coal
IES	16061	East Point 3	Hagel B Floor	from pile	sediment
IES	16062	air jig rejects	Coal Creek Station	4/9/2016	DryFining
IES	16063	air jig rejects	Coal Creek Station	5-5-16 & 5-6-16	DryFining
IES	16064	air jig rejects	Coal Creek Station	5/3/2016	DryFining
IES	16065	air jig rejects	Coal Creek Station	5/2/2016	DryFining
IES	16066	Coal dryer fabric filter	Coal Creek Station	5-5-16&5-6-16	DryFining
IES	16067	Coal dryer fabric filter	Coal Creek Station	5-3-16 am & pm	DryFining
IES	16068	Coal dryer fabric filter	Coal Creek Station	5-2-16 am pm	DryFining
IES	16069	air jig rejects	Coal Creek Station	4/29/2016	DryFining
IES	16070	air jig rejects	Coal Creek Station	4/27/2016	DryFining
IES	16071	air jig rejects	Coal Creek Station	4/25&26/2016	DryFining
IES	16072	Coal dryer fabric filter	Coal Creek Station	4/25&26/2016	DryFining
IES	16073	Coal dryer fabric filter	Coal Creek Station	4/27/2016	DryFining

Table B-1. Listing and description of all samples collected

Sample ID		**Sampling Location**	**Seam/Plant**	**Footage/Date**	**Description**
IES	16074	Coal dryer fabric filter	Coal Creek Station	4-28&4-29-2016	DryFining
IES	16075	Coal dryer fabric filter	Coal Creek Station	7/28/2015	DryFining
IES	16076	Coal to pulverizer	Coal Creek Station	4/25/2016 6:00	DryFining
IES	16077	Coal to pulverizer	Coal Creek Station	4/25/2016 18:00	DryFining
IES	16078	Coal to pulverizer	Coal Creek Station	4/26/2016 6:30	DryFining
IES	16079	Coal to pulverizer	Coal Creek Station	4/26/2016 18:30	DryFining
IES	16080	Coal to pulverizer	Coal Creek Station	4/27/2016 6:30	DryFining
IES	16081	Coal to pulverizer	Coal Creek Station	4/27/2016 18:00	DryFining
IES	16082	Coal to pulverizer	Coal Creek Station	4/28/2016 7:00	DryFining
IES	16083	Coal to pulverizer	Coal Creek Station	4/28/2016 18:00	DryFining
IES	16084	Raw coal	Coal Creek Station	4/25/2016	DryFining
IES	16085	Raw coal	Coal Creek Station	4/25/2016	DryFining
IES	16086	Raw coal	Coal Creek Station	4/26/2016	DryFining
IES	16087	Raw coal	Coal Creek Station	4/26/2016	DryFining
IES	16088	Raw coal	Coal Creek Station	4/27/2016	DryFining
IES	16089	Raw coal	Coal Creek Station	4/27/2016	DryFining
IES	16090	Raw coal	Coal Creek Station	4/28/2016	DryFining
IES	16091	Raw coal	Coal Creek Station	4/28/2016	DryFining
IES	16092	Raw coal	Coal Creek Station	4/29/2016	DryFining
IES	16093	Raw coal	Coal Creek Station	4/29/2016	DryFining
IES	16094	Coal dryer rejects to air jig	Coal Creek Station	4/25/2016 18:00	DryFining
IES	16095	Coal dryer rejects to air jig	Coal Creek Station	4/26/2016 18:00	DryFining
IES	16096	Coal dryer rejects to air jig	Coal Creek Station	4/27/2016 6:30	DryFining
IES	16097	Coal dryer rejects to air jig	Coal Creek Station	4/27/2016 18:00	DryFining
IES	16098	Coal dryer rejects to air jig	Coal Creek Station	4/28/2016 7:00	DryFining
IES	16099	Coal dryer rejects to air jig	Coal Creek Station	4/28/2016 18:00	DryFining
IES	16100	Air jig clean coal	Coal Creek Station	4/25/2016 18:00	DryFining
IES	16101	Air jig clean coal	Coal Creek Station	4/26/2016 6:30	DryFining
IES	16102	Air jig clean coal	Coal Creek Station	4/26/2016 18:00	DryFining
IES	16103	Air jig clean coal	Coal Creek Station	4/27/2016 6:30	DryFining
IES	16104	Air jig clean coal	Coal Creek Station	4/27/2016 18:00	DryFining
IES	16105	Air jig clean coal	Coal Creek Station	4/28/2016 7:00	DryFining
IES	16106	Air jig clean coal	Coal Creek Station	4/29/2016 18:00	DryFining
IES	16107	Coal to pulverizer	Coal Creek Station	5/2/2016 7:30	DryFining
IES	16108	Coal to pulverizer	Coal Creek Station	5/2/2016 18:00	DryFining
IES	16109	Coal to pulverizer	Coal Creek Station	5/3/2016 6:15	DryFining

Table B-1. Listing and description of all samples collected

Sample ID		**Sampling Location**	**Seam/Plant**	**Footage/Date**	**Description**
IES	16110	Coal to pulverizer	Coal Creek Station	5/3/2016 18:00	DryFining
IES	16111	Coal to pulverizer	Coal Creek Station	5/4/2016 7:00	DryFining
IES	16112	Coal to pulverizer	Coal Creek Station	5/4/2016 18:00	DryFining
IES	16113	Coal to pulverizer	Coal Creek Station	5/5/2016 7:00	DryFining
IES	16114	Coal to pulverizer	Coal Creek Station	5/5/2016 18:00	DryFining
IES	16115	Coal dryer rejects to air jig	Coal Creek Station	5/2/2016 7:30	DryFining
IES	16116	Coal dryer rejects to air jig	Coal Creek Station	5/2/2016 18:00	DryFining
IES	16117	Coal dryer rejects to air jig	Coal Creek Station	5/3/2016 6:15	DryFining
IES	16118	Coal dryer rejects to air jig	Coal Creek Station	5/3/2016 18:00	DryFining
IES	16119	Coal dryer rejects to air jig	Coal Creek Station	5/4/2016 7:00	DryFining
IES	16120	Coal dryer rejects to air jig	Coal Creek Station	5/4/2016 18:00	DryFining
IES	16121	Coal dryer rejects to air jig	Coal Creek Station	5/5/2016 7:00	DryFining
IES	16122	Coal dryer rejects to air jig	Coal Creek Station	5/5/2016 18:00	DryFining
IES	16123	Raw coal	Coal Creek Station	5/2/2016	DryFining
IES	16124	Raw coal	Coal Creek Station	5/3/2016	DryFining
IES	16125	Raw coal	Coal Creek Station	5/3/2016	DryFining
IES	16126	Raw coal	Coal Creek Station	5/4/2016	DryFining
IES	16127	Raw coal	Coal Creek Station	5/4/2016	DryFining
IES	16128	Raw coal	Coal Creek Station	5/5/2016	DryFining
IES	16129	Raw coal	Coal Creek Station	5/5/2016	DryFining
IES	16130	Air jig clean coal	Coal Creek Station	5/2/2016 7:30	DryFining
IES	16131	Air jig clean coal	Coal Creek Station	5/2/2016 18:00	DryFining
IES	16132	Air jig clean coal	Coal Creek Station	5/3/2016 6:15	DryFining
IES	16133	Air jig clean coal	Coal Creek Station	5/3/2016 18:00	DryFining
IES	16134	Air jig clean coal	Coal Creek Station	5/4/2016 7:00	DryFining
IES	16135	Air jig clean coal	Coal Creek Station	5/4/2016 18:00	DryFining
IES	16136	Air jig clean coal	Coal Creek Station	5/5/2016 7:00	DryFining
IES	16138	Freedom Mine coal	Freedom Mine	n/a	From pile
IES	16139	Freedom Mine roof	Freedom Mine	n/a	From pile
IES	16140	Freedom Mine floor	Freedom Mine	n/a	From pile
IES	16141	Coyote Creek roof	Coyote Creek Mine	n/a	From pile
IES	16142	Coyote Creek floor	Coyote Creek Mine	n/a	From pile
IES	16143	Coyote Creek Ubeu Coal	Coyote Creek Mine	n/a	From pile
IES	16144	Coyote Creek Blackjack Coal	Coyote Creek Mine	n/a	From pile

Table B-1. Listing and description of all samples collected

Sample ID		Sampling Location	Seam/Plant	Footage/Date	Description
IES	16145	Fly Ash	Antelope Valley Station	6/21/2016	Combustion byproduct
IES	16146	Bottom Ash	Antelope Valley Station	6/22/2016	Combustion byproduct
IES	16147	Fly ash	Coal Creek Station	7/7/2016	Combustion byproduct
IES	16148	Bottom ash	Coal Creek Station	7/7/2016	Combustion byproduct
IES	16149	Pulverizer rejects	Coal Creek Station	7/7/2016	DryFining
IES	16150	FGD scrubber solids	Coal Creek Station	7/7/2016	Combustion byproduct
IES	16151	Cyclone slag	Milton R. Young Station	n/a	Combustion byproduct
IES	16152	Cyclone slag	Milton R. Young Station	n/a	Combustion byproduct
IES	16153	Cyclone slag	Milton R. Young Station	n/a	Combustion byproduct
IES	16154	Cyclone slag	Milton R. Young Station	n/a	Combustion byproduct
IES	16155	Cyclone slag	Milton R. Young Station	n/a	Combustion byproduct
IES	16156	Cyclone slag	Milton R. Young Station	n/a	Combustion byproduct
IES	16157	Cyclone slag	Milton R. Young Station	n/a	Combustion byproduct
IES	16158	Cyclone slag	Milton R. Young Station	n/a	Combustion byproduct
IES	16159	Cyclone slag	Milton R. Young Station	n/a	Combustion byproduct
IES	16160	Cyclone slag	Milton R. Young Station	n/a	Combustion byproduct
IES	16161	Cyclone slag	Milton R. Young Station	n/a	Combustion byproduct
IES	16162	Cyclone slag	Milton R. Young Station	n/a	Combustion byproduct
IES	16163	Composite Fly ash	Coal Creek Station	7/27-7/28	Combustion byproduct
IES	16164	Composite Fly ash	Coal Creek Station	7/29-8/1	Combustion byproduct
IES	16165	Composite Fly ash	Coal Creek Station	8/1-8/3	Combustion byproduct
IES	16166	Composite Fly ash	Coal Creek Station	8/3-8/4	Combustion byproduct
IES	16167	Composite Fly ash	Coal Creek Station	8/9-8/11	Combustion byproduct
ND15RE-6A		Harmon-Hansen Coal	Slope County, ND		Provided by NDGS
ND15RE-6A-1		Harmon-Hansen Roof	Slope County, ND		Provided by NDGS
Leonardite Coarse		Leonardite (oxidized lignite)	Leonardite Products LLC		> 11 mesh
Leonardite 11		Leonardite (oxidized lignite)	Leonardite Products LLC		< 11 mesh
Leonardite Fine		Leonardite (oxidized lignite)	Leonardite Products LLC		62% < 270 mesh

Table B-1. Listing and description of all samples collected

Sample ID	Sampling Location	Seam/Plant	Footage/Date	Description
E2-B seam-1	East Point 2	Hagel B coal	9/6/16	~100 lb split # 1
E2-B seam-2	East Point 2	Hagel B coal	9/6/16	~100 lb split # 2
E2-B seam-3	East Point 2	Hagel B coal	9/6/16	~100 lb split # 3
E2-B seam-4	East Point 2	Hagel B coal	9/6/16	~100 lb split # 4
E2-B seam-5	East Point 2	Hagel B coal	9/6/16	~100 lb split # 5
E3-B seam-1	East Point 3	Hagel B coal	9/6/16	~100 lb split #1
E3-B seam-2	East Point 3	Hagel B coal	9/6/16	~100 lb split #2

APPENDIX C – ICP-MS DATA

This section contains all of the raw ICP-MS data for each of the samples analyzed in this study, as shown in Table C-1.

Table C-1. ICP-MS raw data for all samples analyzed

Sample ID	Ash %	Concentration (Dry Whole Sample Basis), ppm																
		Sc	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Total
E2-B seam-1	6.2	1.7	10.5	6.6	8.8	1.0	3.7	0.9	0.3	1.1	0.2	1.2	0.3	0.8	0.1	0.7	0.1	38.0
E2-B seam-1	7.0	2.0	11.8	7.3	9.7	1.0	4.1	1.0	0.3	1.2	0.2	1.3	0.3	0.9	0.1	0.8	0.1	42.0
E2-B seam-2	7.4	1.6	9.6	3.4	6.6	0.8	3.4	0.8	0.2	1.2	0.2	1.2	0.3	0.8	0.1	0.7	0.1	31.1
E2-B seam-3	6.3	1.7	10.5	5.0	7.8	0.9	3.8	0.9	0.3	1.2	0.2	1.3	0.3	0.9	0.1	0.7	0.1	35.6
E2-B seam-4	6.7	1.7	11.0	5.8	8.7	1.0	4.0	1.0	0.3	1.2	0.2	1.3	0.3	0.9	0.1	0.8	0.1	38.4
E2-B seam-5	7.2	1.7	11.0	6.5	9.4	1.0	4.1	1.0	0.3	1.2	0.2	1.3	0.3	0.9	0.1	0.8	0.1	40.0
E3-B seam-1	8.8	3.0	12.6	4.0	8.1	1.0	4.2	1.0	0.3	1.4	0.2	1.7	0.4	1.2	0.2	1.1	0.2	40.5
E3-B seam-2	8.4	2.5	10.2	3.2	6.5	0.8	3.4	0.8	0.2	1.1	0.2	1.3	0.3	1.0	0.1	0.9	0.1	32.6
H-H Roof	75.5	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
IES16004	40.1		4.8	6.9	13.0	1.5	5.5	1.0	0.2	0.9	0.1	0.8	0.2	0.5	0.1	0.5	0.1	36.1
IES16004	40.2		4.8	6.7	12.5	1.4	5.3	1.0	0.2	0.9	0.1	0.8	0.2	0.5	0.1	0.5	0.1	35.2
IES16005	21.2		4.8	4.4	8.5	1.0	3.8	0.8	0.2	0.8	0.1	0.7	0.2	0.5	0.1	0.4	0.1	26.3
IES16005	21.2		4.8	5.6	10.2	1.2	4.3	0.8	0.2	0.8	0.1	0.8	0.2	0.5	0.1	0.4	0.1	30.0
IES16006	37.0		7.8	10.2	19.0	2.3	8.5	1.6	0.4	1.5	0.2	1.3	0.3	0.9	0.1	0.8	0.1	54.9
IES16006	37.3		7.4	9.5	18.3	2.2	8.2	1.6	0.4	1.4	0.2	1.3	0.3	0.8	0.1	0.8	0.1	52.4
IES16007	24.2		4.4	4.3	8.3	1.0	3.7	0.8	0.2	0.7	0.1	0.7	0.1	0.4	0.1	0.4	0.1	25.3
IES16007	24.3		4.8	4.7	9.0	1.1	4.0	0.8	0.2	0.8	0.1	0.8	0.2	0.5	0.1	0.5	0.1	27.5
IES16008	8.8		5.2	4.6	8.4	1.0	3.6	0.7	0.2	0.7	0.1	0.7	0.2	0.5	0.1	0.4	0.1	26.4
IES16009	9.2		10.7	5.6	10.1	1.2	4.6	1.0	0.3	1.3	0.2	1.4	0.3	0.9	0.1	0.8	0.1	38.7
IES16010	23.2		7.3	8.4	15.5	1.9	7.3	1.4	0.3	1.3	0.2	1.2	0.3	0.8	0.1	0.7	0.1	46.8
IES16010	23.4		8.9	10.0	18.6	2.3	8.6	1.7	0.4	1.6	0.2	1.5	0.3	0.9	0.1	0.9	0.1	56.1
IES16011	13.7		8.9	7.4	12.9	1.5	5.8	1.3	0.3	1.4	0.2	1.4	0.3	0.9	0.1	0.8	0.1	43.1
IES16011	13.7		9.0	7.5	13.1	1.5	5.9	1.3	0.3	1.4	0.2	1.4	0.3	0.9	0.1	0.8	0.1	43.8
IES16012	9.0		4.8	2.4	4.4	0.5	2.1	0.5	0.1	0.5	0.1	0.6	0.1	0.5	0.1	0.4	0.1	17.3
IES16012	9.0		4.8	2.2	3.9	0.5	1.9	0.4	0.1	0.5	0.1	0.6	0.1	0.4	0.1	0.4	0.1	15.9
IES16013	7.5		2.9	1.9	3.4	0.4	1.6	0.3	0.1	0.4	0.1	0.4	0.1	0.2	0.0	0.2	0.0	12.1
IES16014	11.1		8.3	3.6	6.9	0.9	3.5	0.8	0.2	1.0	0.2	1.2	0.3	0.8	0.1	0.8	0.1	28.7
IES16015	91.2		19.2	31.5	61.7	7.4	27.7	5.4	1.2	4.6	0.7	3.9	0.8	2.2	0.3	2.1	0.3	169.0
IES16015	91.2		18.9	32.2	62.7	7.5	28.2	5.5	1.2	4.8	0.7	3.9	0.8	2.3	0.3	2.1	0.3	171.4
IES16015	90.6		17.4	28.9	56.3	6.7	25.6	5.0	1.1	4.3	0.6	3.6	0.7	2.1	0.3	2.0	0.3	154.9
IES16016	86.2		15.7	23.3	44.2	5.0	17.8	3.1	0.6	2.6	0.4	2.7	0.6	1.9	0.3	2.0	0.3	120.7
IES16016	86.2		16.1	23.8	43.7	5.0	18.1	3.2	0.7	2.7	0.4	2.8	0.6	2.0	0.3	2.2	0.3	121.9

Table C-1. ICP-MS raw data for all samples analyzed

Sample ID	Ash %	Concentration (Dry Whole Sample Basis), ppm																
		Sc	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Total
IES16016	82.3		15.0	21.7	40.2	4.6	16.7	2.9	0.6	2.6	0.4	2.6	0.6	1.9	0.3	2.1	0.3	112.5
IES16017	91.6		20.9	30.4	58.7	7.2	27.0	5.2	1.0	4.4	0.7	3.9	0.8	2.4	0.3	2.2	0.4	165.5
IES16017	91.6		21.5	29.3	57.8	7.1	26.8	5.1	1.0	4.5	0.7	4.0	0.8	2.4	0.4	2.4	0.4	164.0
IES16017	86.9		19.9	27.6	54.4	6.6	25.0	4.8	1.0	4.3	0.6	3.7	0.8	2.3	0.3	2.2	0.3	153.9
IES16018	72.1		16.6	23.8	46.3	5.5	20.8	4.1	0.9	3.7	0.5	3.2	0.6	1.9	0.3	1.8	0.3	130.4
IES16018	72.1		15.2	22.3	43.4	5.2	19.5	3.8	0.9	3.3	0.5	3.0	0.6	1.8	0.3	1.7	0.3	121.7
IES16018	63.2		11.9	17.1	32.9	4.0	14.8	2.8	0.7	2.6	0.4	2.3	0.5	1.4	0.2	1.3	0.2	93.1
IES16019	67.3		16.8	23.9	45.2	5.4	19.7	3.7	0.7	3.1	0.5	2.9	0.6	1.9	0.3	1.9	0.3	126.9
IES16019	67.3		20.2	28.7	54.3	6.5	23.9	4.4	0.9	3.8	0.6	3.5	0.7	2.3	0.3	2.3	0.4	152.7
IES16019	54.2		18.4	21.3	40.1	4.8	17.6	3.3	0.7	3.1	0.5	3.0	0.7	2.1	0.3	2.0	0.3	118.1
IES16020	87.1		16.6	20.2	39.9	4.9	18.9	3.8	0.8	3.4	0.5	3.1	0.6	1.9	0.3	1.9	0.3	117.2
IES16020	87.1		18.0	21.9	43.3	5.3	20.3	4.0	0.8	3.6	0.6	3.4	0.7	2.0	0.3	1.9	0.3	126.5
IES16020	86.4		20.8	25.2	48.8	6.0	23.1	4.6	1.0	4.2	0.7	4.0	0.8	2.4	0.3	2.3	0.4	144.5
IES16020	86.3		20.5	24.8	48.3	6.0	22.6	4.6	0.9	4.2	0.6	3.9	0.8	2.4	0.3	2.3	0.3	142.6
IES16021	86.5		21.4	25.0	48.7	6.0	23.0	4.5	0.9	4.1	0.6	3.8	0.8	2.3	0.3	2.2	0.3	144.1
IES16021	86.5		19.0	23.1	44.9	5.6	21.2	4.2	0.9	3.8	0.6	3.4	0.7	2.0	0.3	2.0	0.3	131.8
IES16021	85.2		21.1	24.4	47.2	5.8	22.2	4.4	0.9	4.1	0.6	3.7	0.8	2.3	0.3	2.2	0.3	140.4
IES16022	96.2		16.4	26.7	50.7	6.1	23.1	4.5	1.0	4.0	0.6	3.3	0.7	1.9	0.3	1.8	0.3	141.4
IES16022	96.2		16.0	25.2	48.5	5.8	22.1	4.4	1.0	3.9	0.6	3.3	0.7	1.9	0.3	1.8	0.3	135.6
IES16023	89.9		18.8	25.7	50.6	6.1	23.5	4.7	1.0	4.3	0.6	3.7	0.8	2.2	0.3	2.1	0.3	144.7
IES16024	92.8		17.7	28.7	57.7	6.9	26.5	5.2	1.2	4.6	0.7	3.7	0.7	2.1	0.3	1.9	0.3	158.2
IES16025	88.5		20.0	32.9	63.5	7.7	28.5	5.3	1.1	4.5	0.7	3.9	0.8	2.4	0.3	2.3	0.3	174.2
IES16026	94.8		23.8	32.2	65.2	7.9	30.5	6.1	1.4	5.7	0.9	5.0	1.0	2.9	0.4	2.6	0.4	186.0
IES16027	9.3		7.5	2.2	4.5	0.6	2.5	0.6	0.2	0.8	0.1	1.0	0.2	0.7	0.1	0.7	0.1	21.9
IES16027	9.0		7.4	2.2	4.5	0.6	2.5	0.6	0.2	0.8	0.1	1.0	0.2	0.7	0.1	0.7	0.1	21.8
IES16028	7.9		4.2	4.3	5.6	0.6	2.1	0.4	0.1	0.5	0.1	0.5	0.1	0.4	0.1	0.3	0.1	19.4
IES16029	6.1		2.0	2.4	3.4	0.4	1.4	0.3	0.1	0.3	0.0	0.2	0.1	0.1	0.0	0.1	0.0	10.7
IES16030	7.0		1.7	2.0	3.6	0.4	1.5	0.3	0.1	0.3	0.0	0.2	0.1	0.2	0.0	0.1	0.0	10.5
IES16031	6.7		1.3	1.5	2.8	0.3	1.3	0.2	0.1	0.2	0.0	0.2	0.0	0.1	0.0	0.1	0.0	8.3
IES16032	5.7		2.7	4.3	6.5	0.7	2.4	0.4	0.1	0.4	0.1	0.3	0.1	0.2	0.0	0.2	0.0	18.3
IES16033	33.7		12.8	13.8	27.1	3.3	12.7	2.4	0.5	2.4	0.4	2.2	0.5	1.4	0.2	1.3	0.2	81.1
IES16033	33.1		12.6	13.7	27.0	3.3	12.6	2.4	0.5	2.4	0.4	2.2	0.5	1.4	0.2	1.3	0.2	80.8
IES16034	89.6		22.6	35.1	66.8	8.1	30.2	5.7	1.1	5.0	0.8	4.4	0.9	2.6	0.4	2.5	0.4	186.6
IES16034	88.2	13.7	24.8	37.0	72.5	8.7	32.8	6.1	1.2	5.5	0.8	4.7	1.0	2.8	0.4	2.7	0.4	215.0
IES16034	87.7	27.3	25.1	37.4	74.0	8.9	33.4	6.3	1.3	5.6	0.8	4.9	1.0	2.9	0.4	2.8	0.4	232.3
IES16034	88.1	14.4	24.0	36.5	72.2	8.6	32.8	6.2	1.2	5.5	0.8	4.8	1.0	2.8	0.4	2.7	0.4	214.2
IES16035	88.8		24.0	33.6	64.7	7.8	29.7	5.7	1.1	5.2	0.8	4.6	0.9	2.8	0.4	2.7	0.4	184.6
IES16036	91.5		19.8	31.7	61.9	7.4	28.3	5.6	1.3	5.0	0.7	4.1	0.8	2.3	0.3	2.1	0.3	171.6

Table C-1. ICP-MS raw data for all samples analyzed

Sample ID	Ash %	Concentration (Dry Whole Sample Basis), ppm															
		Sc	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Total
IES16037	90.9		17.1	28.0	55.1	6.6	25.0	4.8	1.1	4.2	0.6	3.5	0.7	2.0	0.3	1.9	0.3	151.1
IES16038	8.0		2.7	2.5	4.3	0.5	2.0	0.4	0.1	0.4	0.1	0.4	0.1	0.2	0.0	0.2	0.0	13.9
IES16039	7.1		1.4	1.9	3.2	0.4	1.5	0.3	0.1	0.3	0.0	0.2	0.0	0.1	0.0	0.1	0.0	9.5
IES16040	11.0		8.7	16.1	21.2	2.0	6.7	1.3	0.3	1.4	0.2	1.3	0.3	0.8	0.1	0.7	0.1	61.2
IES16041	15.5		5.0	6.9	13.1	1.5	5.7	1.0	0.2	0.9	0.1	0.9	0.2	0.5	0.1	0.5	0.1	36.9
IES16042	9.1		5.7	4.0	7.8	1.0	4.0	0.8	0.2	0.9	0.1	0.8	0.2	0.5	0.1	0.4	0.1	26.6
IES16043	8.7		8.4	2.6	5.1	0.7	2.9	0.8	0.2	1.0	0.2	1.2	0.3	0.9	0.1	0.8	0.1	25.3
IES16044	59.3		17.8	21.3	41.3	4.9	18.6	3.5	0.8	3.3	0.5	3.3	0.7	2.2	0.3	2.2	0.3	121.0
IES16045	83.4		15.3	25.2	47.9	5.5	20.5	3.6	0.7	3.1	0.5	2.9	0.6	2.0	0.3	2.1	0.3	130.6
IES16046	84.8		21.0	25.9	50.2	6.0	23.1	4.6	1.1	4.2	0.6	3.9	0.8	2.5	0.4	2.4	0.4	147.0
IES16047	92.9		22.1	29.1	57.1	6.9	26.3	5.3	1.2	4.9	0.7	4.4	0.9	2.6	0.4	2.3	0.4	164.4
IES16048	90.0		17.6	28.1	53.1	6.5	24.7	4.9	1.1	4.3	0.6	3.6	0.7	2.1	0.3	1.9	0.3	149.7
IES16049	18.2		9.4	5.7	11.2	1.4	5.8	1.3	0.3	1.4	0.2	1.5	0.3	1.0	0.1	0.9	0.2	41.0
IES16049	14.9		9.0	5.1	9.4	1.2	4.9	1.2	0.3	1.3	0.2	1.4	0.3	1.0	0.1	0.9	0.1	36.5
IES16049	15.0		7.8	4.4	8.0	1.0	4.2	1.0	0.3	1.1	0.2	1.2	0.3	0.8	0.1	0.8	0.1	31.3
IES16050	11.0		8.4	15.5	20.4	1.9	6.5	1.3	0.3	1.4	0.2	1.3	0.3	0.8	0.1	0.7	0.1	59.1
IES16050	11.2		8.5	15.6	20.6	1.9	6.5	1.3	0.3	1.4	0.2	1.3	0.3	0.8	0.1	0.7	0.1	59.5
IES16051	13.1		7.5	12.7	19.2	1.9	6.4	1.1	0.3	1.2	0.2	1.0	0.2	0.6	0.1	0.5	0.1	53.0
IES16052	8.1		9.5	3.0	5.5	0.7	3.1	0.8	0.2	1.0	0.2	1.3	0.3	0.9	0.1	0.8	0.1	27.5
IES16053	78.8		21.1	26.4	52.0	6.4	24.7	4.7	1.0	4.3	0.7	4.0	0.8	2.5	0.4	2.4	0.4	151.7
IES16054	86.4		20.8	27.2	52.6	6.4	24.6	4.9	1.0	4.4	0.7	4.0	0.8	2.4	0.3	2.3	0.4	152.8
IES16055	86.0		18.1	24.9	49.1	6.0	22.8	4.5	0.9	4.0	0.6	3.6	0.7	2.2	0.3	2.1	0.3	140.1
IES16056	89.5		27.0	34.5	68.2	8.3	31.7	6.5	1.4	5.9	0.9	5.2	1.0	3.1	0.4	2.9	0.5	197.5
IES16056	90.1		23.6	30.0	58.8	7.2	27.7	5.6	1.2	5.2	0.8	4.6	0.9	2.7	0.4	2.6	0.4	171.7
IES16056	91.4		24.0	31.5	61.9	7.5	29.0	5.8	1.3	5.5	0.8	4.8	1.0	2.8	0.4	2.6	0.4	179.1
IES16056	91.5		23.4	35.3	62.6	7.6	29.4	5.9	1.3	5.7	0.8	4.9	1.0	2.9	0.4	2.7	0.4	184.3
IES16056	91.5		22.7	30.4	60.1	7.3	28.3	5.8	1.3	5.5	0.8	4.8	1.0	2.8	0.4	2.6	0.4	174.0
IES16056	91.5		25.0	33.9	67.5	8.2	31.9	6.5	1.4	6.1	0.9	5.3	1.1	3.1	0.4	2.9	0.4	194.8
IES16057	4.3		6.6	1.3	2.5	0.3	1.5	0.4	0.1	0.6	0.1	0.9	0.2	0.8	0.1	0.8	0.1	16.5
IES16058	67.2		17.8	21.9	42.0	5.2	19.9	4.0	1.0	3.6	0.5	3.3	0.7	2.1	0.3	2.1	0.3	124.8
IES16058	65.1		19.1	23.2	44.0	5.5	21.3	4.3	1.0	4.0	0.6	3.8	0.8	2.4	0.4	2.4	0.4	133.3
IES16058	73.3		18.0	25.5	49.3	6.1	23.5	4.7	1.1	4.3	0.6	3.7	0.8	2.3	0.3	2.2	0.3	142.8
IES16058	73.2		18.1	25.4	49.0	6.0	23.5	4.7	1.1	4.3	0.6	3.7	0.8	2.3	0.3	2.2	0.3	142.4
IES16058	73.3		18.5	26.2	50.5	6.2	24.2	4.8	1.1	4.4	0.6	3.8	0.8	2.4	0.3	2.3	0.4	146.7
IES16058	73.3		18.7	26.3	50.7	6.3	24.3	4.8	1.1	4.4	0.6	3.8	0.8	2.4	0.4	2.3	0.3	147.3
IES16059	78.3		16.8	19.3	36.9	4.6	17.7	3.5	0.9	3.2	0.5	3.1	0.6	2.0	0.3	2.0	0.3	111.8
IES16060	10.4		14.5	4.2	8.9	1.2	5.0	1.3	0.4	1.7	0.3	2.2	0.5	1.6	0.2	1.5	0.2	43.8
IES16061	94.7		19.1	28.8	56.3	6.7	24.9	4.7	0.9	4.0	0.6	3.6	0.7	2.3	0.3	2.3	0.4	155.5

Table C-1. ICP-MS raw data for all samples analyzed

Sample ID	Ash %	Concentration (Dry Whole Sample Basis), ppm																
		Sc	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Total
IES16061	91.9		18.0	28.1	54.0	6.4	24.0	4.4	0.8	3.7	0.6	3.3	0.7	2.1	0.3	2.1	0.3	149.0
IES16062	32.9		7.4	8.2	15.8	1.9	7.3	1.4	0.3	1.4	0.2	1.3	0.3	0.8	0.1	0.8	0.1	47.3
IES16063	40.5		7.9	9.0	17.6	2.0	7.8	1.5	0.3	1.4	0.2	1.3	0.3	0.8	0.1	0.8	0.1	51.4
IES16063	40.5		7.8	9.4	17.5	2.0	7.8	1.5	0.3	1.4	0.2	1.3	0.3	0.8	0.1	0.8	0.1	51.3
IES16064	30.1		5.8	4.9	9.4	1.1	4.5	0.9	0.2	0.9	0.1	0.9	0.2	0.6	0.1	0.6	0.1	30.4
IES16065	26.3		11.1	7.4	14.1	1.7	6.7	1.4	0.4	1.5	0.3	1.6	0.4	1.1	0.2	1.0	0.2	49.0
IES16066	31.3		10.9	11.4	22.1	2.6	10.1	2.0	0.5	1.9	0.3	1.9	0.4	1.2	0.2	1.1	0.2	66.7
IES16067	29.5		10.7	10.8	21.0	2.5	9.6	1.9	0.4	1.8	0.3	1.8	0.4	1.2	0.2	1.1	0.2	63.8
IES16067	30.0		10.7	10.8	21.1	2.5	9.7	1.9	0.5	1.8	0.3	1.8	0.4	1.2	0.2	1.1	0.2	64.1
IES16068	32.0		11.1	11.6	22.4	2.7	10.3	2.0	0.5	1.9	0.3	1.9	0.4	1.2	0.2	1.2	0.2	67.8
IES16069	27.9		4.9	5.1	9.5	1.1	4.4	0.9	0.2	0.9	0.1	0.8	0.2	0.5	0.1	0.5	0.1	29.2
IES16070	28.0		4.6	4.7	9.7	1.0	3.9	0.8	0.2	0.8	0.1	0.7	0.2	0.5	0.1	0.5	0.1	27.8
IES16071	26.2		4.0	4.2	7.5	0.9	3.5	0.7	0.2	0.7	0.1	0.6	0.1	0.4	0.1	0.4	0.1	23.4
IES16072	27.0		9.3	11.0	21.1	2.5	9.6	1.8	0.4	1.8	0.3	1.7	0.3	1.0	0.2	1.0	0.2	62.3
IES16073	26.2		8.4	9.5	17.7	2.1	8.1	1.6	0.4	1.5	0.2	1.4	0.3	0.9	0.1	0.9	0.1	53.3
IES16074	30.7		8.8	10.7	20.3	2.4	9.1	1.7	0.4	1.6	0.2	1.5	0.3	1.0	0.2	1.0	0.2	59.4
IES16075	37.8		11.8	15.7	30.6	3.6	13.8	2.6	0.6	2.4	0.4	2.2	0.5	1.4	0.2	1.3	0.2	87.1
IES16100	9.1	1.4	3.9	3.4	7.4	0.7	2.8	0.6	0.1	0.6	0.1	0.6	0.1	0.4	0.1	0.4	0.1	22.7
IES16100	9.0	1.2	3.8	3.3	7.2	0.7	2.7	0.6	0.1	0.6	0.1	0.6	0.1	0.4	0.1	0.4	0.1	21.9
IES16100	9.1	1.6	4.1	3.5	7.5	0.7	2.8	0.6	0.1	0.6	0.1	0.6	0.1	0.4	0.1	0.4	0.1	23.3
IES16100	9.0	1.5	4.0	3.3	7.2	0.7	2.7	0.6	0.1	0.6	0.1	0.6	0.1	0.4	0.1	0.4	0.1	22.4
IES16101	6.7	0.8	3.0	2.5	4.8	0.5	2.0	0.4	0.1	0.5	0.1	0.5	0.1	0.3	0.0	0.3	0.0	15.9
IES16101	6.7	1.1	3.2	2.6	4.9	0.5	2.0	0.4	0.1	0.5	0.1	0.5	0.1	0.3	0.0	0.3	0.0	16.6
IES16102	9.8	1.1	3.7	3.0	5.9	0.7	2.7	0.6	0.1	0.6	0.1	0.6	0.1	0.4	0.1	0.4	0.1	20.1
IES16102	9.8	1.5	4.0	3.2	6.0	0.7	2.7	0.5	0.1	0.6	0.1	0.6	0.1	0.4	0.1	0.4	0.1	20.9
IES16103	10.2	1.4	5.1	3.7	6.9	0.8	3.3	0.7	0.2	0.8	0.1	0.8	0.2	0.5	0.1	0.5	0.1	25.1
IES16103	10.2	1.9	5.5	3.8	6.9	0.8	3.2	0.7	0.2	0.7	0.1	0.8	0.2	0.5	0.1	0.5	0.1	26.0
IES16104	15.4	2.1	6.6	5.4	10.0	1.2	4.7	1.0	0.3	1.0	0.2	1.0	0.2	0.7	0.1	0.6	0.1	35.1
IES16104	15.4	2.8	6.9	5.5	10.1	1.2	4.6	1.0	0.2	1.0	0.2	1.0	0.2	0.7	0.1	0.6	0.1	36.3
IES16105	7.9	0.9	2.9	2.3	4.4	0.5	2.0	0.4	0.1	0.5	0.1	0.5	0.1	0.3	0.0	0.3	0.0	15.2
IES16105	7.9	1.1	3.1	2.4	4.4	0.5	2.0	0.4	0.1	0.4	0.1	0.4	0.1	0.3	0.0	0.3	0.0	15.7
IES16106	12.6	1.7	5.7	4.5	8.4	1.0	3.9	0.8	0.2	0.9	0.1	0.9	0.2	0.6	0.1	0.6	0.1	29.6
IES16106	12.6	2.3	6.1	4.6	8.4	1.0	3.9	0.8	0.2	0.8	0.1	0.9	0.2	0.6	0.1	0.5	0.1	30.7
IES16130	10.4	1.4	5.4	3.5	6.5	0.8	3.2	0.7	0.2	0.8	0.1	0.8	0.2	0.6	0.1	0.5	0.1	24.6
IES16130	10.4	1.9	5.8	3.6	6.6	0.8	3.1	0.7	0.2	0.7	0.1	0.8	0.2	0.5	0.1	0.5	0.1	25.7
IES16131	11.2	1.6	6.5	3.7	7.0	0.9	3.4	0.7	0.2	0.9	0.1	1.0	0.2	0.7	0.1	0.6	0.1	27.6
IES16131	11.2	2.2	7.0	3.8	7.2	0.9	3.5	0.8	0.2	0.8	0.1	0.9	0.2	0.6	0.1	0.6	0.1	29.0
IES16132	9.3	1.4	6.2	3.0	5.8	0.7	2.9	0.7	0.2	0.8	0.1	0.9	0.2	0.6	0.1	0.6	0.1	24.3

Table C-1. ICP-MS raw data for all samples analyzed

Sample ID	Ash %	Concentration (Dry Whole Sample Basis), ppm																
		Sc	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Total
IES16132	9.3	1.9	6.8	3.1	5.9	0.7	2.9	0.7	0.2	0.8	0.1	0.9	0.2	0.6	0.1	0.6	0.1	25.5
IES16133	11.1	1.5	6.1	3.5	6.7	0.8	3.3	0.7	0.2	0.8	0.1	0.9	0.2	0.6	0.1	0.6	0.1	26.2
IES16133	11.1	2.1	6.6	3.6	6.7	0.8	3.3	0.7	0.2	0.8	0.1	0.9	0.2	0.6	0.1	0.6	0.1	27.3
IES16134	12.6	1.8	7.1	4.2	8.3	1.0	4.0	0.9	0.2	1.0	0.2	1.1	0.2	0.7	0.1	0.7	0.1	31.6
IES16134	12.6	2.5	7.6	4.4	8.4	1.0	4.0	0.9	0.2	0.9	0.2	1.0	0.2	0.7	0.1	0.7	0.1	33.0
IES16135	9.9	1.4	6.2	3.1	6.0	0.7	3.0	0.7	0.2	0.8	0.1	0.9	0.2	0.6	0.1	0.6	0.1	24.5
IES16135	9.9	1.9	6.6	3.2	6.1	0.7	3.0	0.7	0.2	0.8	0.1	0.9	0.2	0.6	0.1	0.5	0.1	25.6
IES16136	10.0	1.4	5.6	3.3	6.5	0.8	3.2	0.7	0.2	0.8	0.1	0.8	0.2	0.6	0.1	0.5	0.1	24.8
IES16136	10.2	1.5	5.8	3.4	6.6	0.8	3.2	0.7	0.2	0.8	0.1	0.9	0.2	0.6	0.1	0.5	0.1	25.4
IES16136	10.0	2.0	6.0	3.4	6.5	0.8	3.1	0.7	0.2	0.7	0.1	0.8	0.2	0.6	0.1	0.5	0.1	25.9
IES16136	10.2	2.0	6.1	3.5	6.7	0.8	3.2	0.7	0.2	0.8	0.1	0.8	0.2	0.6	0.1	0.5	0.1	26.4
IES16138	14.3		10.8	4.5	8.2	1.0	3.9	0.9	0.3	1.2	0.2	1.4	0.3	1.0	0.1	0.9	0.1	34.9
IES16139	92.3		20.4	30.3	59.8	7.2	28.2	5.6	1.2	5.1	0.8	4.3	0.9	2.5	0.4	2.4	0.4	169.2
IES16140	94.6		24.9	36.3	73.9	9.0	35.1	6.8	1.4	6.2	0.9	5.2	1.0	3.0	0.4	2.9	0.4	207.7
IES16141	90.5		22.9	27.8	54.8	6.7	26.2	5.3	1.2	5.1	0.8	4.6	0.9	2.8	0.4	2.7	0.4	162.7
IES16142	92.3		19.6	29.6	58.6	7.1	27.4	5.3	1.2	4.8	0.7	4.1	0.8	2.4	0.4	2.3	0.3	164.7
IES16143	17.1		5.7	4.8	9.3	1.1	4.1	0.9	0.2	0.9	0.2	1.0	0.2	0.6	0.1	0.6	0.1	29.6
IES16143	16.8		5.7	5.0	9.5	1.1	4.3	0.9	0.2	1.0	0.2	1.0	0.2	0.6	0.1	0.6	0.1	30.4
IES16144	57.9		17.8	26.8	53.9	6.2	23.5	4.5	1.0	4.1	0.6	3.6	0.7	2.2	0.3	2.1	0.3	147.6
IES16145	92.9		19.2	19.6	36.7	4.3	16.4	3.2	0.9	3.3	0.5	3.2	0.7	2.0	0.3	1.9	0.3	112.6
IES16146	100.0		29.2	30.7	58.0	6.8	25.8	5.1	1.4	5.1	0.8	5.0	1.1	3.2	0.5	3.0	0.5	176.1
IES16147	100.0	15.5	44.1	39.9	75.1	8.9	34.4	6.9	1.8	7.1	1.1	6.9	1.5	4.4	0.6	4.1	0.6	252.8
IES16148	99.5	16.2	48.9	41.7	77.1	9.1	35.2	7.2	1.8	7.6	1.2	7.5	1.6	4.9	0.7	4.6	0.7	265.9
IES16149	39.7	8.6	4.9	5.7	10.3	1.2	4.7	0.9	0.2	0.9	0.1	0.8	0.2	0.5	0.1	0.5	0.1	39.8
IES16150	94.9	5.1	1.2	1.3	1.9	0.2	0.9	0.2	0.0	0.2	0.0	0.2	0.0	0.1	0.0	0.1	0.0	11.4
IES16150	94.9	0.4	1.5	1.3	2.2	0.3	1.1	0.2	0.0	0.2	0.0	0.2	0.0	0.1	0.0	0.1	0.0	7.8
IES16151	99.7	0.4	25.1	27.1	52.0	6.1	23.1	4.4	1.1	4.3	0.7	4.1	0.9	2.7	0.4	2.7	0.4	155.3
IES16152	99.0	12.2	27.5	22.6	43.5	5.2	20.0	4.0	1.0	4.1	0.6	4.2	0.9	2.9	0.4	2.8	0.4	152.4
IES16153	99.6	16.1	31.7	25.8	49.3	5.9	22.7	4.6	1.2	4.7	0.8	4.8	1.1	3.3	0.5	3.3	0.5	176.2
IES16154	99.6	14.2	35.4	27.1	51.3	6.1	24.0	4.9	1.3	5.1	0.8	5.3	1.2	3.6	0.5	3.6	0.5	185.0
IES16155	99.8	18.3	32.8	26.9	51.0	6.1	23.5	4.8	1.2	4.9	0.8	5.0	1.1	3.4	0.5	3.4	0.5	184.3
IES16156	99.6	13.6	28.0	23.9	45.7	5.4	21.0	4.2	1.1	4.3	0.7	4.3	1.0	3.0	0.4	3.0	0.4	159.9
IES16156	99.5	17.5	29.8	25.0	48.2	5.7	22.0	4.4	1.1	4.5	0.7	4.6	1.0	3.1	0.5	3.1	0.5	171.8
IES16157	99.8	16.7	32.4	28.7	53.1	6.3	24.4	4.8	1.2	4.9	0.8	4.9	1.1	3.4	0.5	3.3	0.5	187.2
IES16158	99.8	17.5	35.8	28.8	55.2	6.6	25.3	5.1	1.3	5.3	0.8	5.4	1.2	3.7	0.5	3.6	0.6	196.7
IES16159	99.8	13.2	29.4	23.9	45.3	5.4	21.0	4.2	1.1	4.3	0.7	4.3	1.0	2.9	0.4	2.8	0.4	160.5
IES16160	99.9	14.4	33.9	26.4	49.8	5.9	23.0	4.6	1.2	4.9	0.7	4.9	1.1	3.3	0.5	3.2	0.5	178.5
IES16161	99.9	13.8	31.6	25.0	47.0	5.6	21.7	4.4	1.2	4.6	0.7	4.6	1.0	3.1	0.5	3.1	0.5	168.3

Table C-1. ICP-MS raw data for all samples analyzed

Sample ID	Ash %	Concentration (Dry Whole Sample Basis), ppm																
		Sc	**Y**	**La**	**Ce**	**Pr**	**Nd**	**Sm**	**Eu**	**Gd**	**Tb**	**Dy**	**Ho**	**Er**	**Tm**	**Yb**	**Lu**	**Total**
IES16162	99.9	12.8	30.1	24.4	44.7	5.4	20.7	4.2	1.1	4.3	0.7	4.4	1.0	3.0	0.4	2.8	0.4	160.4
IES16162	99.9	14.1	32.5	25.6	47.7	5.8	22.3	4.5	1.2	4.7	0.7	4.8	1.1	3.2	0.5	3.1	0.5	172.1
IES16163	99.8	17.5	41.3	38.4	86.2	8.2	31.8	6.1	1.6	6.3	1.0	6.2	1.4	4.1	0.6	3.8	0.6	255.2
IES16163	99.8	17.2	42.2	39.0	87.7	8.4	32.1	6.3	1.7	6.4	1.0	6.3	1.4	4.1	0.6	3.9	0.6	258.8
IES16164	99.8	15.4	39.2	35.3	72.1	7.9	30.2	5.9	1.6	6.0	1.0	5.9	1.3	3.9	0.6	3.7	0.6	230.4
IES16165	99.8	15.7	39.4	35.6	66.2	8.0	30.7	6.0	1.6	6.0	1.0	6.0	1.3	3.9	0.6	3.7	0.6	226.3
IES16166	99.8	14.5	39.1	34.5	66.0	7.7	29.5	5.8	1.5	5.8	0.9	5.9	1.3	3.8	0.6	3.6	0.6	221.1
IES16167	99.8	14.8	44.6	39.1	72.3	8.8	33.4	6.7	1.8	6.8	1.1	6.8	1.5	4.5	0.7	4.1	0.7	247.6
Leonardite - 11 mesh	19.7	4.0	10.1	8.9	17.6	2.2	8.6	1.9	0.5	1.9	0.3	1.7	0.4	1.0	0.1	1.0	0.2	60.4
Leonardite - course	23.9	3.6	11.1	9.4	17.7	2.2	8.6	1.9	0.5	1.9	0.3	1.8	0.4	1.1	0.2	1.0	0.2	61.9
Leonardite - course	23.9	3.8	11.0	9.2	17.5	2.2	8.5	1.8	0.5	1.9	0.3	1.8	0.4	1.1	0.2	1.0	0.2	61.2
Leonardite - fine	18.7	6.0	15.2	14.9	27.5	3.3	13.0	2.8	0.8	2.9	0.4	2.6	0.5	1.5	0.2	1.3	0.2	93.1
ND15RE-6A	20.1	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
ND15RE-6A	20.1	38.1	45.9	63.6	180.3	26.3	119.6	28.9	6.4	21.9	2.9	14.6	2.5	6.2	0.8	5.3	0.7	563.9
ND15RE-6A	20.2	35.0	43.0	60.0	172.1	25.2	114.7	27.8	6.2	21.3	2.8	14.1	2.4	6.1	0.8	5.1	0.7	537.2
ND15RE-6A	20.1	34.1	42.3	63.0	175.5	26.5	120.5	28.7	6.4	21.9	2.9	14.6	2.5	6.2	0.8	5.4	0.7	551.9
ND15RE-6A	20.1	34.1	43.2	63.4	176.7	26.4	119.5	28.5	6.3	21.6	2.8	14.3	2.4	6.1	0.8	5.3	0.7	552.2
ND15RE-6A	20.2	32.7	41.3	61.4	171.1	25.7	116.9	28.1	6.3	21.3	2.8	14.2	2.4	6.1	0.8	5.3	0.7	537.1

APPENDIX D – TECHNICAL AND ECONOMIC FEASIBILITY ANALYSIS REPORT

The following document is the report prepared by Barr Engineering detailing the technical and economic feasibility analysis performed. The report contains the formatting used by Barr Engineering which is not consistent with the rest of this dissertation. It is to be taken as a stand-alone document.

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

Technical and Economic Feasibility Study

Prepared for
The University of North Dakota - Institute for Energy Studies

February 15, 2017

3128 14th Avenue E
Hibbing, MN 55746
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Acronyms

Acronym	Description
AACE	Association for the Advancement of Cost Engineering International
AOI	Area of Interest
Barr	Barr Engineering Co.
CAPEX	Capital Expenses
DOE	Department of Energy
FOA	Funding Opportunity Announcement
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
SX/EW	Solvent Extraction/Electro-Winning
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) and Pacific Northwest National Laboratory (PNNL) 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 being conducted with the support of cost-share partners North American Coal Corporation, Great River Energy, and the North Dakota Industrial Commission/Lignite Energy Council. The North Dakota Geological Survey is also providing technical support regarding lignite geology and selection of areas for sampling.

The work described in this report identifies parameters for an economically viable and environmentally benign process to produce a two-weight-percent REE concentrate. The effort includes feedstock identification, separation and concentration methods development and testing, preliminary design of concentrating methods, 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:

Feedstock	**Harmon-Hanson Lignite Coal**[1]
Plant Size	3,772 lb/hr (Dry coal feed rate)
Lignite Feedstock REE concentration	• 560 ppm REE+Y, (dry coal basis), 2300 ppm REE+Y, (ash basis)
Process and Concentrating Sequence	• **Pulverizing** (to -200 mesh) • **Leaching** (0.5 M H_2SO_4) • **Separate** – Residual Un-leached coal for Activated Carbon Processing • **Remove Fe Impurity** – Forced Oxidation • **Transport** mineral concentrate to processor/buyer
Concentration Results (dry elemental basis, not incl. solution)	**6.07% wt% REE**[2] **1.94% wt% REE**[3]
Environmental Considerations	• Low temperature and mild leaching solution w/ zero acid discharge methodology • Byproducts processed to create saleable syngas and activated carbon • Waste heat used to reduce energy.

1 Selectively mined coal from the Harmon-Hansen seam in ND.
2 90% Fe Removal, w preleach (Dry Basis)
3 72% Fe Removal, w/o preleach (Dry Basis)

Section 3.0 - Process Design and PFDs: Exhibit A 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 (details in Exhibit C and Exhibit D). Section 5.0 discusses the technical and economic evaluation results (details in Exhibit B and Exhibit E). These Class 5 estimate results are based on mining and minerals processing industries and are summarized below:

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
$28,300,000	$4,700,000	$9,800,000	2.9	21%	28%	32%	35%	$18,600,000	$32,600,000

1 assumes over a 10- and 20-year plant life

Economic Metric	Value
CAPEX/annual dry ton feed	$1,800
OPEX/annual dry ton feed	$300
Net Revenue/annual dry ton feed	$620

The data presented in this document can reasonably be assumed as the likely or average scenario, accounting for conservative assumptions based on limited process definition to date. Best-case scenarios would involve: (i) simplifying the processing scheme or to significantly increase the concentration of REEs in the product, (ii) identification of an improved feedstock with either higher total REE content, higher critical or heavy REE content, more stable impurity forms or lower cost mining, (iii) increases in REE/target element sales prices, and (iv) scaling up the technology beyond the first implementation at VCSU. Worst-case scenarios would involve: (i) increased process complexity to achieve 2-wt% REE concentration, (ii) less desirable feedstock, and (iii) lower REE/target element and activated carbon sales prices.

The best-case scenario could be estimated as the following combined sensitivity case:

- Decrease in CAPEX/OPEX, including REE/target element purification costs by 10%
- Increase in REE/target element sales price by 10%
- Increase in activated carbon sales price by 10%

When combining the above, best-case economic metrics are as follows:

- 20 year IRR: 46%
- 20 year ROI: 38%
- Simple Payback: 2.2 years
- 20 year NPV (15% discount rate): $46,700,000

The worst-case scenario could be estimated as the following combined sensitivity case:

- Increase in CAPEX by 50%
- Increase in OPEX, including REE/target element purification costs by 10%
- Decrease in REE/target element sales price by 10%
- Decrease in activated carbon sales price by 10%

When combining the above, worst-case economic metrics are as follows:

- 20 year IRR: 18%

- 20 year ROI: 13%
- Simple Payback: 5.3 years
- 20 year NPV (15% discount rate): $6,900,000

1.0 Introduction

Background of Funding Opportunity Announcement DE-FOA-0001202

This project address 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 objectives for this FOA are as follows:

- Develop high performance, economically viable, and environmentally benign concentrating technologies for coal-related feedstocks to a target of two weight percent REE concentration

The specific objectives of this Phase I Project included: feedstock identification, concentrating methods development/testing, technical and economic evaluation of the concentrating process, and design of a bench-scale test system to be constructed and tested in a subsequent Phase II project.

Project Team

The University of North Dakota Institute for Energy Studies (UND IES) has teamed with Barr Engineering Co. (Barr) and Pacific Northwest National Laboratory (PNNL) 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, and the North Dakota Industrial Commission/Lignite Energy Council. The North Dakota Geological Survey is also providing technical support regarding lignite geology and selection of areas for sampling REE-rich feedstocks.

1.1 Purpose

The overall goal of the project was to develop a high performance, economically viable, and environmentally benign technology to recover rare earth elements from North Dakota lignite coal and related feedstocks.

In order to meet the goal, the following are specific objectives in Phase 1:

- Develop sampling protocols and obtain statistically representative samples of lignite, associated roof and floor materials, and coal drying reject stream
- Determine the abundance and modes of occurrence of rare earth elements and relevant material properties
- Determine the potential to concentrate REEs through mineral processing methods that include gravity separation, fine coal cleaning technologies and novel separation technologies
- Identify the optimum methods to economically separate and concentrate REEs to 2 percent by weight
- Perform a technical and economic analysis of the optimum methods to concentrate REEs

- Develop a design of a bench scale system (5 to 10 kg/hour feedstock throughput) to concentrate the REEs

1.2 Scope and Technical Basis

The scope and basis for the technical and economic feasibility analysis is derived from the results of the work conducted in this project. An extensive sampling and analysis campaign was conducted on a range of coals and associated sediments (byproducts) from multiple seams in North Dakota and found that on an ash basis, the REE are more concentrated in certain locations and certain coal seams than in the associated roof/floor sediments. Detailed analysis results also 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 large majority of REE forms are weakly bonded and are extractable using a mild acid leaching process.

The UND REE extraction process involves a mild acid leach at ambient temperature of the raw coal (not the coal ash) that produces very high recovery of the REE, Y and Sc. The mild leach is made possible by the 'loose' association of the REE within the lignite coals. The resulting residual coal has lower ash content and higher heating value and can be utilized in other processes such as activated carbon manufacturing.

The overall concept for commercial implementation of this REE recovery process is to combine the REE recovery with activated carbon production co-located at a combined heat and power plant. 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 is currently constructing a new steam generation plant. This is a concept that has very favorable economics and has generated tremendous support within the State of North Dakota. Allocation of funding through a revenue bond or other funding scenarios to build the integrated plant just unanimously passed in the ND State Senate appropriations committee, with final approval by the State House remaining before moving forward on the project. 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 are attached as Exhibit F to 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. For this TEA, the scope of economic modeling is shown in Figure 1-1. Major assumptions include:

- Selectively mined coal from the Harmon-Hansen seam is purchased (additional locations for selective mining have been identified, but the Harmon-Hansen seam is used as the base case in this evaluation)
- Concentrated REE solution is sold to a commercial processor for final purification (*see attached letter of support in Exhibit F from a potential buyer of the concentrate*)
- 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

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 germanium, gallium, copper, cobalt, manganese and zinc.
- The REE extraction process significantly 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 (i.e., University of North Dakota (UND) and North Dakota State University (NDSU), both of which require new facilities in the near future) that offer significant scale-up opportunities.
- Technical, environmental and economic benefits of the REE extraction/concentration process include: (i) no physical beneficiation required, (ii) low temperature and mild leaching of the raw coal, and (iii) simple, highly effective and industrially proven processing steps. Additional details are located in Section 2.4.

This study evaluates integration of REE recovery with the activated carbon and steam production plant at VCSU; 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.

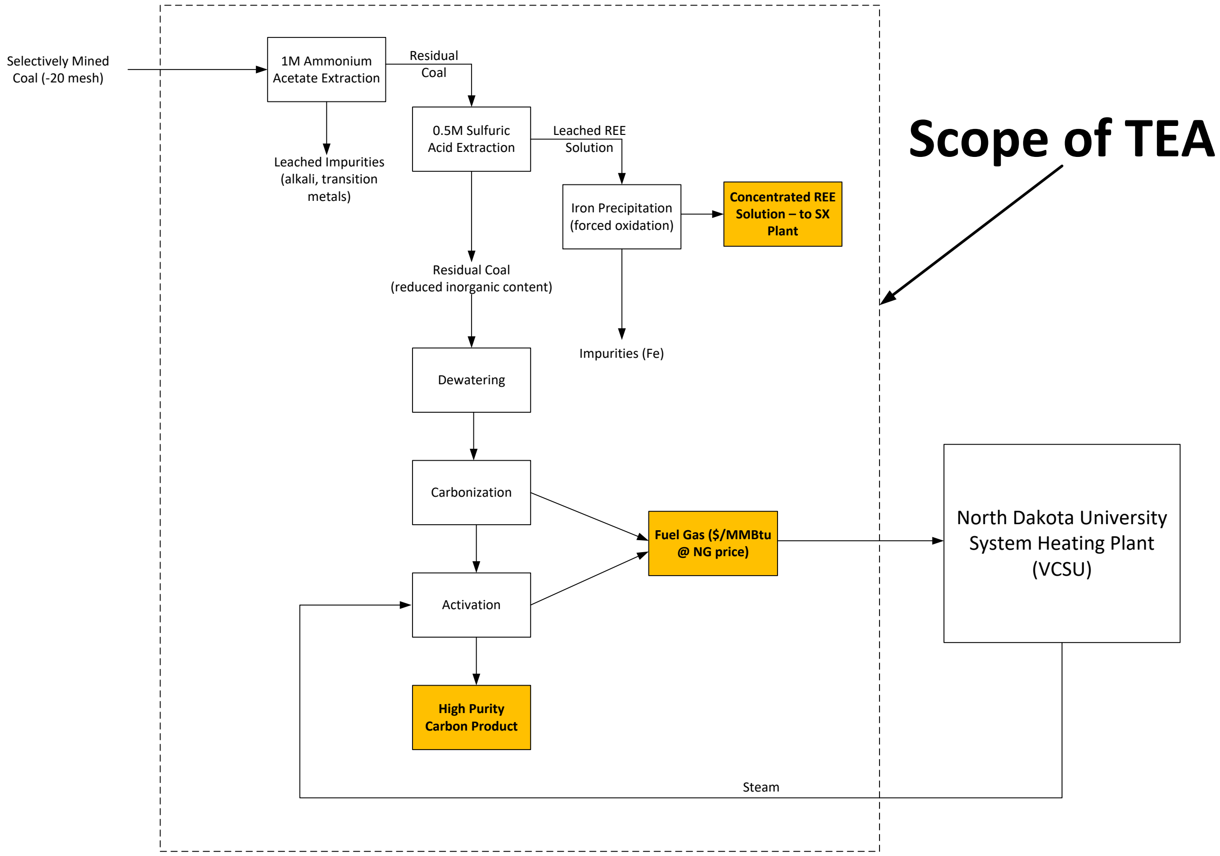

Figure 1-1 Schematic of the scope of economic modeling for the Technical and Economic Assessment

2.0 Design Basis/Approach

2.1 Feedstock Identification

Selectively mined coal is sourced from the Harmon-Hansen seam in North Dakota (560 ppm REE+Y, whole coal dry basis and 2,300 ppm REE+Y, 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 Harmon-Hansen coal for this study. This does not have a significant impact on the economics of the overall process. Detailed analysis of the Harmon-Hansen coal can be found in Section 2.3. According to the USGS,[1] The Harmon-Hansen 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.

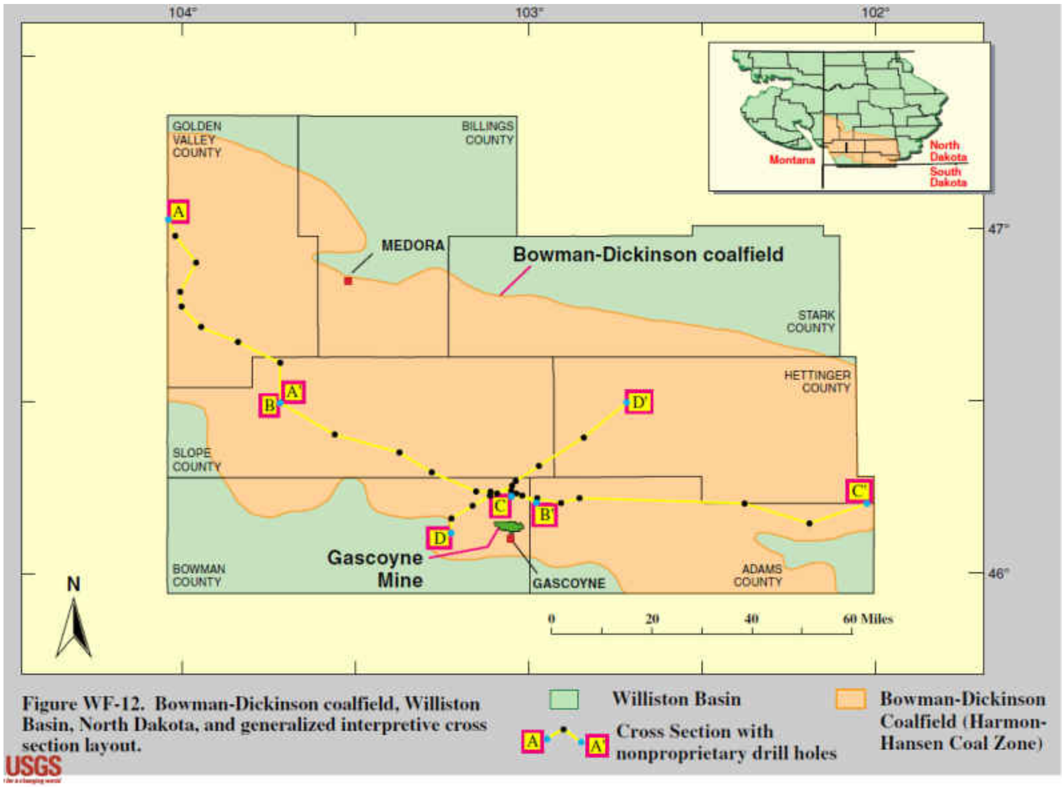

Figure 2-1 **Coverage of the Harmon-Hansen Coal Zone in southwestern ND**[2]

As part of this work, an alternate, but lower REE content feedstock—Hagel B coal from Falkirk Mine in Underwood, ND—has been identified and will be evaluated in a sensitivity analysis. 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 Harmon-Hansen coal. Although complete results are not publically available yet, 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 several samples throughout the state with REE content higher than the Hagel B coal, as well as multiple other samples with incomplete REE analysis, but high levels of individual REEs analyzed. The project team believes the Harmon-Hansen 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.

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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/

2.2 Concentrating Methods

A summary of the technical details leading to selection of the proposed concentrating process are attached as Exhibit E to this report. 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 the raw coal with excellent recovery efficiency of about 90% for the REE and Y and about 80% for Sc. The overall process is summarized as follows:

- Selectively mined coal is sourced from the Harmon-Hansen coal zone in North Dakota (560 ppm REE+Y, whole coal dry basis)
- In an optional pre-treatment step, the coal is slurried with 1M ammonium acetate solution to remove impurities, mainly alkali and alkaline earth metals, and some transition metal elements
- The intermediate residual coal is then slurried with 0.5M sulfuric acid to extract REEs
- 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 forced oxidation
- The final 2-wt% concentrated REE solution is sent for purification and separation at an offsite refinery

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

- 60 grams dried coal with known REE content
- 125 mL leaching solution (1M ammonium acetate, and 0.5M sulfuric acid)
- Coal/leaching solution stirred at 40°C for 48 hours
- pH measured as a function of time
- Residual solids filtered, dried, and analyzed for REE, other target elements and impurities content
- Extraction of elements to solution determined by difference in starting coal and leached coal

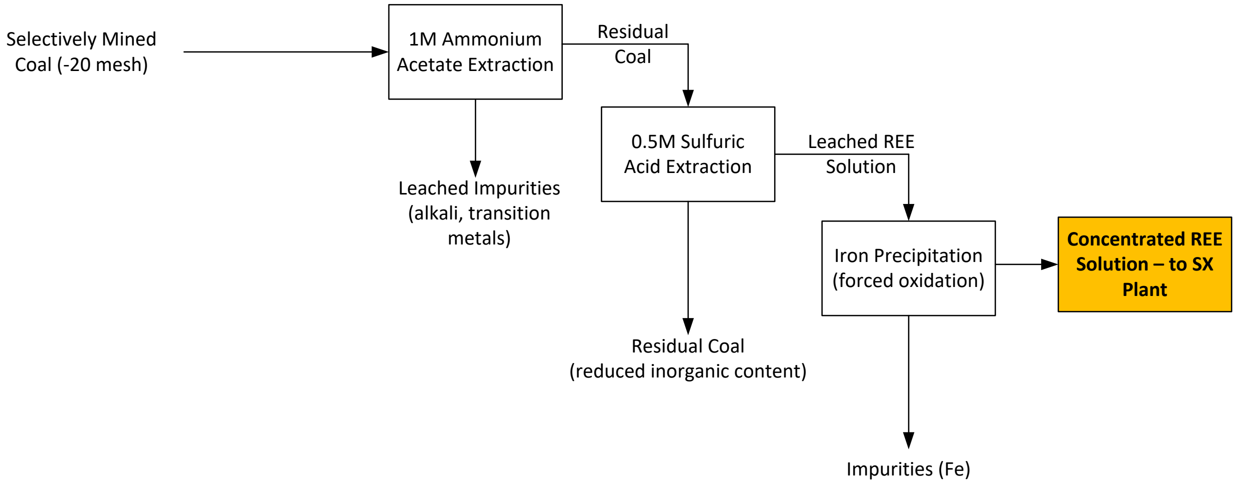

Figure 2-2 Simplified diagram of the REE concentrating process

Figure 2-2 includes the simplified diagram of the REE concentrating process evaluated in the TEA. **NOTE**: the ammonium acetate extraction step is included as an option in this study. The base case involves only the sulfuric acid extraction and iron precipitation steps. The concentrated REE solution is sent for final purification (i.e., by solvent extraction—SX) and could be located off-site or co-located. For this study, it was assumed a commercial buyer would purchase the concentrated REE solution.

2.3 Development / Testing

2.3.1 Coal Leaching Tests

A series of preliminary REE extraction tests were done with hydrochloric, sulfuric, and phosphoric acids in multiple concentrations (details in Exhibit E). The 0.5M sulfuric acid (H2SO4) was chosen for evaluation in the TEA based on the following:

- Lowest acid concentration that provided good total REE extraction
- H2SO4 is the least expensive of the strong mineral acids used for industrial mineral processing
- Higher scandium extraction was noted when compared with hydrochloric acid
- Higher total REE extraction than phosphoric acid
- The potential of producing supplemental sulfuric acid on-site via the SO2-containing flue gas from the steam plant; thus reducing acid costs and SO2 emissions.

Assumptions for the TEA

- Target ratio of 125 mL acid (0.5 M H2SO4) to 60 g dry coal (as conservative value based on laboratory results)
- 24-hour residence time (tests were done with 48 hours, but pH vs. time data indicates acid consumption only during initial 30 minutes); 24 hours represents a very conservative value
- Optimization of the particle size/acid type/acid concentration/residence time/temperature combination will improve selectivity of REE extraction via minimizing extraction of iron and other impurities and maximizing extraction of target elements
- Assume size reduction of coal feedstock for leaching at -200 mesh particle size (i.e., approximate size range for powdered activated carbon); laboratory tests performed using this size
- Laboratory tests showed 40% acid consumption due to reaction with alkali and alkaline earth components in the coal; assume 10% consumption if ammonium acetate pre-treatment is used (a conservative value based on laboratory results)
- Ambient temperature (~25°C or room temperature) operation. Laboratory tests done at 40°C, but pH vs. time for tests done at 25°C were identical. Heat coils for the leaching steps are included in the cost estimates (both capital and operating) in the event they are needed.

Baseline leaching data for the two feedstocks is listed in Table 2-1. Several other lignite coals were evaluated, and all had similar leaching behavior (data available in Exhibit E). This study will focus on the Harmon-Hansen feedstock with a dry coal feed rate of 3,772 lb/hr (5,084 lb/hr as-received). 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).

Table 2-1 Leaching Results of the Harmon-Hansen and Hagel B

Feedstock 1 (Harmon-Hansen)					Feedstock 2 (Hagel B)				
Element	Initial ppmw	Leached ppmw	Percent Extracted	lb/hr	Element	Initial ppmw	Leached ppmw	Percent Extracted	lb/hr
Sc	36.33	7.16	82.5	0.11	Sc	1.97	0.94	53.2	0.0040
Y	45.59	6.15	88.0	0.15	Y	11.77	1.93	84.0	0.04
La	63.30	9.56	86.6	0.21	La	7.27	2.63	64.5	0.02
Ce	176.44	21.63	89.1	0.59	Ce	9.66	3.64	63.1	0.02
Pr	26.59	3.20	89.3	0.09	Pr	1.04	0.39	63.3	0.00
Nd	121.88	14.85	89.2	0.41	Nd	4.06	1.46	64.7	0.01
Sm	29.32	3.59	89.1	0.10	Sm	0.96	0.31	68.4	0.0025
Eu	6.55	0.78	89.3	0.02	Eu	0.26	0.09	66.1	0.0006
Gd	22.28	2.59	89.7	0.08	Gd	1.23	0.31	75.6	0.0035
Tb	2.98	0.34	90.0	0.01	Tb	0.20	0.05	77.3	0.0006
Dy	14.94	1.69	89.9	0.05	Dy	1.34	0.29	79.1	0.0040
Ho	2.51	0.29	89.6	0.01	Ho	0.31	0.06	80.8	0.0009
Er	6.38	0.79	89.1	0.02	Er	0.91	0.17	81.7	0.0028
Tm	0.85	0.11	88.7	0.00	Tm	0.12	0.02	82.2	0.0004
Yb	5.38	0.72	88.2	0.02	Yb	0.76	0.14	82.0	0.0023
Lu	0.74	0.10	87.7	0.00	Lu	0.12	0.02	82.0	0.0004
Co	865.00	20.60	97.9	3.19	Co	39.30	2.60	93.5	0.14
Cu	172.00	126.00	34.9	0.23	Cu	11.10	5.20	54.1	0.02
Ga	23.80	6.30	76.5	0.07	Ga	2.10	1.10	48.6	0.004
Ge	28.00	9.10	71.1	0.08	Ge	0.90	0.50	45.5	0.002
In	0.00	0.00	0.0	0.00	In	nd	nd	n/a	n/a
Li	25.00	23.10	17.9	0.02	Li	3.70	2.70	28.4	0.004
Ni	75.40	6.00	92.9	0.26	Ni	6.90	4.10	41.7	0.01
Se	2.70	1.40	53.9	0.01	Se	0.55	0.14	75.0	0.00
Ag	0.58	0.59	9.6	0.00	Ag	nd	nd	n/a	n/a
Te	0.00	0.00	0.0	0.00	Te	nd	nd	n/a	n/a
V	616.00	122.00	82.4	1.91	V	3.80	1.70	56.1	0.01
Zn	26.80	4.60	84.7	0.09	Zn	3.30	0.50	85.1	0.01
Cd	0.55	0.04	93.5	0.00	Cd	0.05	0.00	100.0	0.00
Pb	14.70	10.90	34.1	0.02	Pb	1.60	1.00	38.7	0.00

Feedstock 1 (Harmon-Hansen)					Feedstock 2 (Hagel B)				
Element	Initial ppmw	Leached ppmw	Percent Extracted	lb/hr	Element	Initial ppmw	Leached ppmw	Percent Extracted	lb/hr
Hg	0.16	0.17	5.6	0.00	Hg	0.02	0.03	0.0	0.00
Th	29.90	6.90	79.5	0.09	Th	1.00	0.80	21.5	0.00
U	16.30	4.60	74.9	0.05	U	1.10	0.90	19.8	0.00
Si	82129	94138	0.0	0.00	Si	7325	10746	0.0	0.00
Al	48341	55253	0.0	0.00	Al	6749	4521	34.3	8.73
Fe	76425	35689	58.5	168.62	Fe	3966	1143	71.7	10.73
Ti	3369	3109	18.0	2.28	Ti	159	215	0.0	0.00
P	646	303	58.4	1.42	P	98	25	74.8	0.28
Ca	7847	1279	85.5	25.31	Ca	25773	22702	13.6	13.24
Mg	893	352	64.9	2.19	Mg	5289	28	99.5	19.85
Na	1131	217	83.0	3.54	Na	3686	17	99.5	13.84
K	2062	1850	20.3	1.58	K	385	135	65.7	0.95
Sr	241	320	0.0	0.00	Sr	484	452	8.4	0.15
Ba	1732	1980	0.0	0.00	Ba	626.71	599	6.3	0.15
Mn	51	23	60.3	0.12	Mn	115.12	25	78.9	0.34

NOTE: In some instances concentration of elements in leached coal is higher than initial coal – this is due to lower mass of leached coal compared to initial coal. This may or may not indicate that zero extraction of that particular element occurred, depending on the overall mass balance.

2.3.2 Coal Leaching Tests with Ammonium Acetate Pre-leach

Early test work utilizing an ammonium acetate pre-leach of the coals has shown selective leaching to remove some alkali, alkaline earth, and transition metal elements prior to REE extraction. For the Harmon-Hansen coal, less than 5wt% of the REE+Y (0% for Sc) are extracted via the ammonium acetate, and for the Hagel B coal, testing showed no removal of any of the REEs, Y or Sc. Based on previous experience and testing at UND regarding leaching of ND lignite coals with ammonium acetate,[5] it is expected that approximately 80 wt% of the Ca, Mg, and Na is leached along with about 10 wt% of the K. Laboratory data specifically for the Harmon-Hansen coal seam shows approximate removal of 68% of the Co, 42 wt% of the Ni, and 57 wt% of the Zn and 57% of the Mn also occurs. Non-REE lab data for UND ammonium acetate pre-leach is not available for Hagel B coal at this time. It is assumed at this time that the same removal efficiency with ammonium acetate will be used for both coals. The major benefit of adding this pre-leach step is a higher concentration of REE in the PLS after sulfuric acid leaching, which should reduce costs of downstream impurities removal and purification steps. It may also reduce acid consumption, as the ammonium acetate removes much of the acid-neutralizing alkali and alkaline earth components.

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[5] Benson, S.A.; Holm, P.L. Comparison of Inorganics in Three Low-Rank Coals. Ind. Eng. Chem. Prod. Res. Dev. 24:145–149, 1985.

Table 2-2 shows the mass flow rates of REEs extracted into the PLS during 0.5 M H2SO4 leaching when the ammonium acetate pre-leaching step is included. In this study, it is assumed that the elements extracted by the ammonium acetate will be considered a waste stream, but future analysis could determine if the valuable elements could be monetized as well. The ammonium acetate leaching process parameters includes a leach temperature of 25°C, 24-hour residence time (same conditions as sulfuric acid leach), and a water wash cycle between the pre-leach and the leach steps.

Table 2-2 Leaching Results for 0.5M H2SO4 after the 1M Ammonium Acetate Preleach for the Harmon-Hansen Coal

0.5M H2SO4 Leaching Results when using 1M Ammonium Acetate Preleach				
Element	Initial ppmw	Leached ppmw	Percent Extracted	lb/hr
Sc	36.33	7.16	82.5	0.133
Y	45.59	6.15	88.0	0.14
La	63.30	9.56	86.6	0.20
Ce	176.44	21.63	89.1	0.58
Pr	26.59	3.20	89.3	0.09
Nd	121.88	14.85	89.2	0.41
Sm	29.32	3.59	89.1	0.10
Eu	6.55	0.78	89.3	0.02
Gd	22.28	2.59	89.7	0.07
Tb	2.98	0.34	90.0	0.01
Dy	14.94	1.69	89.9	0.05
Ho	2.51	0.29	89.6	0.01
Er	6.38	0.79	89.1	0.02
Tm	0.85	0.11	88.7	0.00
Yb	5.38	0.72	88.2	0.02
Lu	0.74	0.10	87.7	0.00
Co	865.00	20.60	97.9	0.98
Cu	172.00	126.00	34.9	0.23
Ga	23.80	6.30	76.5	0.07
Ge	28.00	9.10	71.1	0.08
In	0.00	0.00	0.0	0.00
Li	25.00	23.10	17.9	0.02
Ni	75.40	6.00	92.9	0.15
Se	2.70	1.40	53.9	0.01

0.5M H2SO4 Leaching Results when using 1M Ammonium Acetate Preleach				
Element	**Initial ppmw**	**Leached ppmw**	**Percent Extracted**	**lb/hr**
Ag	0.58	0.59	9.6	0.00
Te	0.00	0.00	0.0	0.00
V	616.00	122.00	82.4	1.92
Zn	26.80	4.60	84.7	0.03
Cd	0.55	0.04	93.5	0.00
Pb	14.70	10.90	34.1	0.02
Hg	0.16	0.17	5.6	0.00
Th	29.90	6.90	79.5	0.09
U	16.30	4.60	74.9	0.05
Si	82129	94138	0.0	0.00
Al	48341	55253	0.0	0.00
Fe	76425	35689	58.5	168.60
Ti	3369	3109	18.0	2.28
P	646	303	58.4	1.42
Ca	7847	1279	85.5	1.63
Mg	893	352	64.9	0.00
Na	1131	217	83.0	0.13
K	2062	1850	20.3	0.80
Sr	241	320	0.0	0.00
Ba	1731.74	1980	0.0	0.00
Mn	50.62	23	60.3	0.01

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 ‘loose’ 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).[6] [7] [8] [9] [10] [11] 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:

- No physical beneficiation processes are required prior to the extraction process – Decreased complexity, energy/chemical usage and cost
  - ✓ Other REE deposits require extensive physical beneficiation, such as ultra-fine grinding to liberate fine REE-bearing mineral grains, magnetic separations to remove impurities, and flotation to recover REE-bearing minerals.
  - ✓ Physical beneficiation of coal-related materials is a huge technical/economic challenge due to fine mineral grains and relatively low REE concentration—beneficiation processes that are applicable in this size range are limited, questionably effective, and costly
- 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.
- REEs can be leached directly from the raw coal using simple, highly effective, industrially proven processes – a highly economical approach
  - ✓ Carbon does not need to be removed because the REEs are actually primarily associated with the organic matter

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[6] 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.

[7] 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

[8] 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.

[9] 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/.

[10] Eskenazy, G.M., Rare earth elements in a sampled coal from the Pirin deposit, Bulgaria. Int. J. Coal Geol. 7, 301–314, 1987.

[11] Seredin, V.V. and Dai, S., Coal Deposits as potential alternative sources for lathanides and yttrium, International Journal of Coal Geology, 94 (2012)87-93.

- ✓ The resulting residual coal has significantly 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 to form H2SO4 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 Use of Oxidation Air for Iron Impurity Removal

Forced oxidation was determined as a possible technology for impurity removal that did not involve using other chemical dosing systems and did not add extra byproduct streams (additional discussion and references available in Sections 3.2 and 3.3). If the iron solids that are extracted from the process cannot be sold, the iron solids will be considered a waste byproduct. This study does not consider revenue of the iron stream. There is a cost considered for hauling off the iron waste product as a non-hazardous waste.

2.4.3 Activated Carbon and Syngas Production from Solids Byproduct

The pregnant REE leachate is produced from the filtrate of thickened and pressed coal solids left over from the leaching process. The design developed the solid 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.

2.4.4 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 (i.e., for heating of the leaching processes of the REE extraction components, if necessary), but not considered as a savings in the operating expense parameters during this study.

3.0 Process Design

This section presents the process design for achieving the 2-wt% REE concentrate and the final activated carbon product. This design is preliminary and based on available information and will change as additional testing is completed and evaluated.

3.1 Coal Pulverizing

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 carbonation/activation. The crusher and pulverizer will reduce the coal to about 200 mesh (74 micron) prior to the leaching process, a size compatible for use as a feedstock in production of powdered activated carbon (i.e., for mercury capture applications). This is displayed in the process flow diagram (FS-1) provided in Exhibit A. 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

3.2 Leaching and Precipitation

The pulverized coal is conveyed to the acid leaching tank with sulfuric acid to begin leaching for approximately 24 hours. The proper ratio of acid and water is added to the coal to achieve 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 thickener to settle out the coal solids as underflow and recover the clarified overflow PLS. The PLS is sent to the iron precipitation unit where it is aerated with forced air to oxidize and precipitate the insoluble iron oxides. The oxidized solution reports to the iron settling tank to drop out the iron solids to produce a 2-wt% REE PLS prior to final processing. The iron solids are periodically removed with a sludge pump and sent to a filter dewatering step where the iron is discarded and the filtrate retained for further processing. The 2-wt% REE PLS will be processed at an offsite refinery. The refinery is not defined as part of this project. Barren liquor resulting from the refinery could be recirculated to the leaching process to reduce acid input rate if the refinery is co-located, but this cost savings is not included in this study (i.e., assumption of 100% acid make-up is evaluated). The coal is further dewatered using a filter press and dried prior to carbonation and activation, processing which is discussed further in Section 3.4. The following list summarizes the major pieces of equipment:

- Ammonium acetate pre-leach tank and water wash (optional)
- Acid leach tank
- Thickener
- Filter press feed tank
- Filter press
- Rotary kiln dryer

- Aeration tank
- Iron settling tank
- Precipitated iron filter
- Barren liquor solution tank
- Acid scrubber

Post acid leaching, the REE solution has a pH of around 0.5, as measured in laboratory tests. According to the technical paper discussed in Section 3.3, the iron precipitation with induced air is more effective at a pH of around 3.75. Due to the low pH of the solution, the oxidation step for the iron would require acid neutralization with a base such as sodium hydroxide. However, it was determined during the lab results that within the first 30 minutes of leaching the pH increased from initial 0.3 to 0.5 and for the remainder of 24 hours the pH held constant at 0.5. Change from 0.3 to 0.5 pH represents 40% acid consumption (acid makeup rate). This indicates that the acid concentration could be reduced and still achieve the element extraction but at a higher pH (and possibly a longer contact time) thus eliminating the need for acid neutralization. Another consideration is the presence of catalysts in solution (i.e., copper) that can be expected to significantly increase iron oxidation rates, even at low pH.[12] For these reasons, the process design does not include an acid neutralization step. Further testing will need to be completed to determine if this theory is accurate. It is important to note that this study does not include operating cost credit for an acid recycle, and thus incorporation of a neutralization step would only include additional costs associated with chemical (base) addition, which could be accomplished directly in the aeration tank. An added benefit of neutralization would be the likely precipitation of some additional impurities that would further increase REE concentration in the PLS.

3.3 Impurity Removal

Under the conditions evaluated in the laboratory, the target of 2-wt% REE in the PLS was not attainable without additional impurity removal after the leaching process. Evaluating the Harmon-Hansen feedstock, the removal of the iron component from the leachate would achieve the 2-wt% REE target. This process would require that a minimum of 72% of the iron is removed from this stream. “The Search Minerals Direct Extraction Technology for Rare Earth Recovery”[13] reports how iron precipitation using forced air oxidation can be utilized to achieve iron removal of 90%. The paper “Testing and Application of Iron Precipitate as Geothite Using a Strong Air Flow”[14] shows correlation with precipitation of Fe at 40°C would be approximately 72%. The following points below indicate the calculated results of the REE concentration with respect to different processing cases. Note that in the below cases, REE concentration is represented

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[12] Stumm, W., Lee, F. “Oxygenation of Ferrous Iron”. Industrial Engineering Chemistry. Division of Water and Waste Chemistry, 137th Meeting, ACS, Cleveland, Ohio, April 1960.

[13] Dreisinger, D., Verbaan, N., Johnson, M., Andres, G. “The Search Minerals Direct Extraction Technology for Rare Earth Recovery.” IMPC 2016: XXVIII International Mineral Processing Congress Proceedings – ISBN: 978-1-926872-29-2

[14] Dai, X., Zeng, P., Li, Y., Huang, M., Yang, M., Chen, G., Li, G., Wang, H. “Testing and Application of Iron Precipitation as Goethite (FEOOH) Using a Strong Air Flow. IMPC 2016: XXVIII International Mineral Processing Congress Proceedings – ISBN: 978-1-926872-29-2

as weight percent of REE+Y+Sc in solution, which is on a dry elemental basis and does not include mass of acid (i.e., represents mass of components extracted from the coal into solution).

- 0.88 wt% REE with no ammonium acetate pre-leach
- 1.01 wt% REE with ammonium acetate pre-leach
- Case 1: 1.94 wt% REE with 72% Fe precipitation, no ammonium acetate pre-leach
- Case 2: 2.91 wt% REE with 90% Fe precipitation, no ammonium acetate pre-leach
- Case 3: 2.94 wt% REE with 72% Fe precipitation with ammonium acetate pre-leach
- Case 4: 6.07 wt% REE with 90% Fe precipitation with ammonium acetate pre-leach

For Cases 1-4, forced precipitation of iron assumes that 5 wt% of REE is also lost. These are further discussed in Section 4.0

3.4 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 leached 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 and potentially used as a heat source for the leaching process, if needed. 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 4.3.

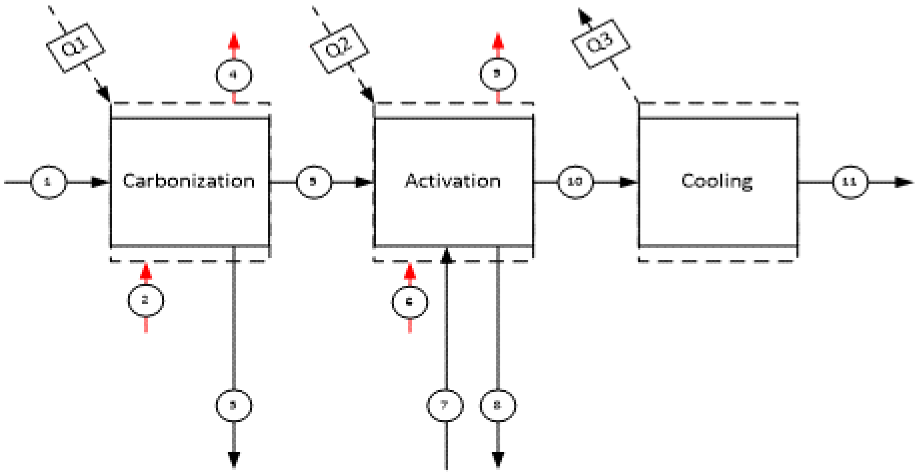

Figure 3-1 Simplified Flow Diagram of Carbonization and Activation

4.0 Mass and Energy Balances

4.1 Acid Requirements

As discussed in Section 2.0 Design Basis/Approach, 0.5M sulfuric acid was chosen for evaluation. The TEA focuses on the Harmon-Hansen feedstock with a dry coal feed rate of 3772 lb/hr (5084 lb/hr as-received), which is based on the sizing for the activated carbon plant in evaluation for installation with the existing steam generation plant at VCSU.

- Using 3772 lb/hr of dry coal calls for 125.6 ft^3/hr of 0.5 M sulfuric acid based on scaled lab results
- Lab-scale testing indicated that approximately 40% of the acid is consumed within the process. However for a conservative operating cost estimate, and the assumption of an off-site refiner, the operating cost estimate assumes 100% makeup rate

The Base Case evaluated in this study does not include the ammonium acetate pre-leach step which is only referenced/discussed as a potential option for increased impurity removal.

4.2 REE Concentrate & Iron Precipitation

REE concentration is a major factor in measuring the success and viability of the proposed system, as a higher concentration will decrease costs of downstream purification. 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. Harmon-Hansen coal used in this study has an REE+Y concentration of about 560 ppm on a whole coal basis. Table 4-1 shows the values of REE concentration in the PLS pre- and post-iron precipitation based on lab data and literature. As discussed in Section 2.0 Design Basis/Approach, iron is the major impurity causing the REE concentration of the leachate to be reduced. Based on literature, it has been found that 90% Fe removal can be achieved, with a loss of 5% REE in the solution through oxidation at a pH of around 3.75 based on "The Search Minerals Direct Extraction Technology for Rare Earth Recovery.[15] The paper "Testing and Application of Iron Precipitate as Geothite Using a Strong Air Flow"[16] shows correlation with precipitation of Fe at 40°C would be approximately 72%. Based on these assumptions, Table 4-1 was created to show the wt% in solution. We assumed 72% removal as a low end to show the spectrum of Fe removal as pH and temperature are large factors in determining Fe precipitation out of an acid leachate. In a similar application, large-scale

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[15] Dreisinger, D., Verbaan, N., Johnson, M., Andres, G. "The Search Minerals Direct Extraction Technology for Rare Earth Recovery." IMPC 2016: XXVIII International Mineral Processing Congress Proceedings – ISBN: 978-1-926872-29-2

[16] Dai, X., Zeng, P., Li, Y., Huang, M., Yang, M., Chen, G., Li, G., Wang, H. "Testing and Application of Iron Precipitation as Goethite (FEOOH) Using a Strong Air Flow. IMPC 2016: XXVIII International Mineral Processing Congress Proceedings – ISBN: 978-1-926872-29-2

forced oxidation methods are used in wet sulfur dioxide scrubbers to oxidize calcium sulfite to calcium sulfate.[17]

Barr has experience designing iron oxidation systems for a similar application. This involved conducting an alternative analysis for a client in the Minnesota Iron Range. Tests were conducted to use forced aeration and pH adjustment to oxidize iron from relief well water. The iron would then settle out before it was discharged. A conceptual design and cost estimate was completed and provided to the client as one of the alternatives to treat and discharge the water.

Table 4-1 Fe precipitation baselines and resulting REE concentration in solution

REE wt% for Multiple Cases (dry elemental basis not including mass of acid)	
Case Description	**wt% REE**
Post Leaching, no NH4OAc pre-leach	0.88
Post Leaching, w/ NH4OAc pre-leach	1.01
Case 1 – 72% Fe precipitation, no NH4OAc pre-leach	1.94
Case 2 – 90% Fe precipitation, no NH4OAc pre-leach	2.91
Case 3 – 72% Fe precipitation, w/ NH4OAc pre-leach	2.94
Case 4 – 90% Fe precipitation, w/ NH4OAc pre-leach	6.07

Notes: Cases 1-4 assume 5wt% REE loss to the Fe precipitation; NH4OAc is ammonium acetate; concentrations represent total REE, Y, Sc in solution

4.3 Production of Syngas and Activated Carbon

Table 4-2 shows the estimated compositions expected based on simulation modelling and lab testing. Further, the hydrogen developed in the syngas as well as some of the carbon-containing compounds have an estimated heating value of about 10,000 BTU/lb. The process yields 1769 lb/hr of activated carbon and over 2600 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.

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[17] Yuran, L, Jinting, Z., Tingyu, Z., Pengfei, J. "Calcium Sulfite Oxidation and Crystal Growth in the Process of Calcium Carbide Residuue to Produce Gypsum." Waste and Biomass Valorization. February 2014, Volume 5, Issue 1, pp 125-131.

Table 4-2 Production of Syngas and Activated Carbon

Description	Dry Coal	Syngas - Carbonation	Char	Reaction Steam	Syngas - Activation	Activated Carbon
Component Flow (lb/hr)						
O2	0	0	0	0	0	0
CO	0	1101	0	0	1086	0
H2	0	139	0	0	77	0
CO2	0	0	0	0	0	0
H2O	0	0	0	713	17	0
CH4	0	0	0	0	0	0
N2	0	0	0	0	0	0
H2S	0	27	0	0	0	0
C6H6	0	240	0	0	0	0
HCN	0	30	0	0	0	0
COAL	3772	0	0	0	0	0
CHAR	0	0	2236	0	0	0
ACT-CARB	0	0	0	0	0	1769
Total Flow lb/hr	**3772**	**1537**	**2236**	**713**	**1181**	**1769**
Temperature (°F)	77	1112	1112	345	1652	1652
Pressure (psia)	14.7	14.7	14.7	125	14.7	14.7

4.4 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 rotary kilns
- 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
- Heating of the leaching processes was not included, even though heat coils have been built into the capital expenses.

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.

Table 4-3 shows the fuel usage considered, heat input, and output temperatures of the Drying, Carbonation, and Activation in the system. 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.

Table 4-3 Heat Balance of the Coal Solids Processing which includes using waste heat

		Source of waste heat	Total Energy - Combustion	Total Fuel Gas Used	Total Combustion Air Used	Combustion Air Temp	Heater Air Temp	Exhaust Gas Temp	Syn Gas Temp
Units			mmbtu/hr	lb/hr	lb/hr	°F	°F	°F	°F
Drying	w/o waste heat	N/A	2.00	100	2000	70	3265	320	1100
	w/ waste heat	1250 °F Exhaust - Dryer	1.88	90	1800	300	3397	220	n/a
Carbonation	w/o waste heat	N/A	1.60	74	1500	70	3238	1143	1100
	w/ waste heat	1452 °F Exhaust - Carbonation	1.17	60	1200	1300	3918	339	1100
Activation	w/o waste heat	N/A	1.60	80	1600	70	3272	1623	1652
	w/ waste heat	1153 °F Exhaust-Activation	1.05	50	1000	1000	3800	371	1652
Cooling	w/o waste heat	Glycol / Cooling Water	0.76	N/A	9600	70	N/A	405	1100
	w/ waste heat	not evaluated							

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 and impurity removal steps to extract and concentrate REEs and other target elements from coal in conjunction with activated carbon production. In conducting the TEA we considered the principal process drivers such as 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 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 2 wt% 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. *We have identified a potential purchaser of our REE concentrate. A letter of interest from this company is provided in Exhibit F.* 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, as well as other metals that have a large impact on the economics of the proposed plant. Data is obtained from the 2016 USGS Mineral Commodities Report. It is important to note that these discussions are based on production rates from the proposed plant. 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 11,000 to 17,000 metric tons from 2011 to 2015. The U.S. is a net importer with about 4,100 metric tons produced from the Mountain Pass Mine in 2015, most of which consists of the light REE. A larger proportion of the heavy REE are imported. For instance, for Yttrium, the content within the Mountain Pass Mine ore is estimated at about 0.12% of the total REE content, and due to this low concentration was not processed/produced. Total domestic consumption of Yttrium was about 200 metric tons in 2015, all of which was imported. Approximately 11 tons per year of REE+Y oxides are produced from the plant evaluated in this study after final purification. 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 and Y.

Production of approximately 1 ton/year of Scandium oxide, 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 10 to 15 tons in 2015. 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 to expand the market utilization. To understand the impact of Scandium sale price on the overall economics of the proposed plant, a sensitivity analysis point has been included that excludes Scandium from the list of saleable products.

Another major contributor to sales from the proposed plant is Germanium oxide, with a production rate of about 0.5 ton/year from the proposed plant. According to the USGS Mineral Commodities Report, total domestic consumption of Germanium was about 30 metric tons in 2015, down from 38 metric tons in 2012. The U.S. is a net importer of Germanium, with total imports of about 37 metric tons in 2015. 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. To understand the impact of Germanium sale price, a sensitivity analysis point has been included that reduces the price by half for only Germanium.

5.2 TEA Assumptions & Conditions

Our (preliminary) TEA makes the following assumptions/conditions:

1. The processing facility that receives the 2-wt% concentrate is located nearby to eliminate shipping costs and/or the cost of shipping is built into the refiner's processing costs.
2. CAPEX for the finishing refinery facility is ignored, 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 PLS at 75 to 80% recovery, depending on the element
4. REE and other target element purification costs, including 20% refiner's profit for toll refiner, are estimated at present prices to be:
    a. $1000 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 7,450 tons/yr
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 = $8 per 100 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. Sulfuric acid cost = $0.15 per lb (assumed 100% makeup rate)
        i. Quote from Hawkins Chemical
    g. Yearly operator cost = $400,000
        i. Based on assuming 8 operators at $50,000 salary
    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).[18]

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-scale testing results and complete further design to provide a higher accuracy cost

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[18] 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

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 includes the following process steps:

1. Coal crushing and pulverizing
2. Sulfuric acid leaching
3. Leached coal solids thickening and dewatering
4. Impurity precipitation of leachate (iron oxidation)
    a. Remove impurities to achieve 2 wt% REE
5. Iron settling
6. Iron filtering and disposal

7. Leached coal dewatering
    b. Filter Press
    c. Drying
8. Carbonization
9. Activation

The Base Case CAPEX was generated using the preliminary process flow diagram provided in Exhibit A as the basis for the equipment selections (Base Case does not include ammonium acetate pre-leach). The OPEX was generated assuming operating and maintenance rates for each equipment item and using the Harmon-Hansen lab results and a dry coal mass flow rate of 3,772 lb/hr.

The Base Case TEA uses the results of the Harmon-Hansen coal leaching results 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.[19] 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 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).[20] The equipment was sized assuming a leaching processing rate of 3,772 dry lb/hr of coal.

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
- Acid Leach Tank, Mixer, Pump

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[19] Argus Media Ltd. (UK) and Stormcrow Capital Ltd. (Canada)

https://minerals.usgs.gov/minerals/pubs/mcs/2016/mcs2016.pdf,

http://investingnews.com/daily/resource-investing/critical-metals-investing/scandium-investing/scandium-price-need-to-know/

[20] 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

- Acid Scrubber
- Thickener and Underflow Pump
- Filter Press Feed Tank and Feed Pump
- Filter Press (Leached Coal Dewatering)
- Barren Liquor Solution Tank, Mixer, Pump
- Indirect Fired Rotary Dryer
- Indirect Fired Rotary Kiln (Carbonation)
- Indirect Fired Rotary Kiln (Activation)
- Tank Heaters
- Rotary Air Cooler
- High Temperature Fans (Syngas Capture and Transfer)
- Air Compressor
- Aeration Tank and Blower (Iron Precipitation)
- Waste Heat Recovery Unit
- Iron Sludge Pump
- Filter Press (Iron Sludge)
- Building
- Ductwork and Piping

The total estimated project cost for the base case plant is $28.3 million. The cost 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 detailed estimate that summarizes all these components is provided in Exhibit B.

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
- Sulfuric 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 $4.7 million per year. The detailed estimate is summarized in Exhibit B.

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
- Barren Liquid Solution Tank was assumed to be the smallest size calculated for the Acid Leach Tank
- Aeration Tank for Iron Oxidation was assumed to be the largest available stainless steel tank shown in the Mine and Mill Equipment Cost Binder (see detailed estimate in Exhibit B)
  - Extrapolated from cost of stainless steel tanks in the cost binder
  - Actual vendor declined to bid
- All conveyors where 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
- Process flow is assumed to be 5 tph from Raw coal storage to Fine Coal Feed Bin
- Process flow is assumed to be 2.5 tph from Fine Coal Feed Bin throughout the remaining process
- Fine Coal Feed Bin assumed to be 30 ton capacity
- Raw Coal Storage assumed to be 200 ton capacity

- Filter press for Iron Sludge assumed to be same size as leached coal filter presses (conservative assumption)

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

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 Harmon-Hansen coal projects a total of 27,100 lb/yr of REE/target element oxides and about 23,800 lb/yr of base metals assuming 75 to 80% recovery during the refiner processing (i.e., overall recovery on dry whole coal basis is: leaching extraction recovery X refining recovery). The detailed analysis provided in Exhibit B summarizes the total pounds of each and market price to estimate a total revenue.

The calculated value of the finished REE and other element oxides products produced at the refinery is reduced by assuming a refining cost per ton of REE/target element and base metal produced. These were set at $1000 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.

Activated Carbon

After the REE and base metal leaching, the carbonation and activation process produces activated carbon at a rate of 7,450 tons/yr. The Base Case assumes a sale price of $1,400 per ton (wholesale price based on UND discussions with potential distributors) of activated carbon, totaling $10,430,000 per year in sales.

Syngas

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 2,700 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 $800,000 per year.

The total sales (REE, base metals, activated carbon and syngas) per year assuming Base Case operation is $14.5 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.

Table 5-2 Payback Analysis Summary

Item[1]	Amount
CAPEX	($28,300,000)
OPEX	($4,700,000)
REE/target element and Base Metal Payable Amount per year	$3,300,000
Activated Carbon Payable Amount per year	$10,400,000
Syngas Payable Amount per year	$800,000
Net Annual Revenue per year	$9,800,000
Simple Payback (years)	2.9
IRR (10 years)	32%
ROI (10 years)	21%
NPV (10 years) @15% discount rate	$18,600,000
IRR (20 years)	35%
ROI (20 years)	28%
NPV (20 years) @15% discount rate	$32,600,000
CAPEX/annual dry ton feed	$1,800
OPEX/annual dry ton feed	$300
Net Revenue/annual dry ton feed	$620

1 see acronym list for definitions

5.4 Sensitivity Analysis

Sensitivity Analysis above and below the Base Case was completed for the following cases:

- Hagel B Leaching Results
    - Production of REE/target elements and base metals is lower than Harmon-Hansen coal, and REE concentration in the PLS is lower (i.e., higher downstream processing costs)
- Base Case Half Element Price
    - Each sale price is reduced by half

- Base Case Double Element Price
    - Each sale price is doubled
- Higher Activated Carbon Sale Price
    - Increase price from $1,400 per ton to $2,000 per ton
- Lower Activated Carbon Sale Price
    - Decrease price from $1,400 per ton to $1,000 per ton
- Scandium excluded from saleable products
- Sale price of Germanium decreased by 50%
- Base Case CAPEX decreased by 50%
    - Overall Base Case CAPEX is reduced 50%
- Base Case CAPEX increased by 50%
    - Overall Base Case CAPEX is increased by 50%
- 86% Capacity verses 96% Capacity
    - 45 weeks per year of operation verses 50 weeks per year

The results of the sensitivity analysis are presented in Table 5-3.

Table 5-3 Sensitivity Analysis Summary

Economic Parameter	Net Annual Revenue	Simple Payback (years)	IRR (10 years)	ROI (10 years)	NPV (10 years) @15% DR	IRR (20 years)	ROI (20 years)	NPV (20 years) @15% DR
Base Case	$9,820,000	2.9	32%	21%	$18,600,000	35%	28%	$32,600,000
Hagel B Results	$6,960,000	4.1	20%	12%	$4,900,000	24%	18%	$14,800,000
Base Case Half Element Price	$8,170,000	3.5	25%	16%	$10,700,000	29%	22%	$22,300,000
Base Case Double Element Price	$13,110,000	2.2	45%	32%	$34,300,000	46%	39%	$53,000,000
Higher Activated Carbon Price	$14,290,000	2.0	49%	35%	$39,900,000	50%	43%	$60,300,000
Lower Activated Carbon Price	$6,840,000	4.1	19%	12%	$4,300,000	24%	18%	$14,100,000

Economic Parameter	Net Annual Revenue	Simple Payback (years)	IRR (10 years)	ROI (10 years)	NPV (10 years) @15% DR	IRR (20 years)	ROI (20 years)	NPV (20 years) @15% DR
No Sale of Scandium	$7,890,000	3.6	24%	15%	$9,300,000	28%	21%	$20,600,000
Germanium Half Price	$9,540,000	3.0	31%	20%	$17,200,000	34%	27%	$30,800,000
Base Case CAPEX Decrease by 50%	$9,820,000	1.4	69%	52%	$32,700,000	69%	61%	$46,700,000
Base Case CAPEX Increase by 50%	$9,820,000	4.3	18%	11%	$4,400,000	23%	17%	$18,400,000
86% Capacity (45 wks/yr)	$9,810,000	2.9	32%	21%	$18,500,000	35%	28%	$32,500,000

The economic/sensitivity analysis indicates that, although revenue is obtained from the sale of REEs and base metals, payable revenue due to generation of the activated carbon product has the largest impact on overall profitability. The sensitivity shows that increasing/decreasing the sale price of the activated carbon has simple payback from 1.9 to 4.0 years compared to 2.1 to 3.3 years for increasing/decreasing sale price of REEs and base metals. The most drastic change comes from increasing/decreasing the CAPEX with a simple payback from 1.4 to 4.2 years, which is expected with larger cash amounts. The sensitivity analysis also shows that the choice of feedstock impacts the economics dramatically. The Harmon-Hansen coal is considerably more favorable. However, even the Hagel B coal, with relatively low total REE content results in an overall profitable plant. It is important to recognize, though, that in the case of the Hagel B coal, that the economics of the activated carbon production process subsidize the production of REEs (i.e., incremental economics of the REE components produce negative cash flow). However, this may not necessarily be a deal-breaker for Hagel B in the event that REE prices increase in the future due to decrease in supply from foreign sources.

5.4.1 Ammonium Acetate Pre-leach

Another sensitivity case is to include the ammonium acetate pre-leach, which removes about 68% of the cobalt, as well as some of the nickel, zinc and manganese, along with a small fraction of the REEs in the Harmon-Hansen coal. It is assumed these would be lost as waste and lost revenue unless the impurities Ca, Na, Mg, and K could be precipitated and removed, allowing the cleaned pre-leach solution to be sold along with the REE concentrate (not tested in Phase I). Ammonium Acetate leach prior to the acid leaching would alter the economics as follows:

- Adds CAPEX and OPEX to the leaching and concentrating process
- Reduces the content of some target elements in our concentrate product

- With reduced impurities this “should” decrease the cost of REE processing (something less than $1000/ton as evaluated in the base case)

Due to limited data on the Ammonium Acetate Leach option at this time, this sensitivity analysis was not quantified and will require further testing in the next phase.

6.0 Summary & Conclusions

According to this TEA the project is clearly profitable. The following summarize the main conclusions from the TEA:

- The lab results indicate that a 2-wt% REE concentrate is achievable using 0.5M H_2SO_4 acid leach, but requires additional impurity removal (i.e., iron removal via forced oxidation)
- Profitability is significantly greater with the selling of activated carbon; approximately $10.4 million in sales
- REE/target element oxides and base metals also contribute a good portion in sales; approximately $3.3 million
    - Assumes the final product is REE/target element oxides
- The 10-year and 20-year NPV is $18.6 million and $32.6 million respectively assuming 15% discount rate
- The Harmon-Hansen 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 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, iii) complexity/number of processing steps, and iv) effectiveness of impurity removal to reduce costs of purification. Each of these categories are discussed below.

REE Recovery Efficiency: Since the REE recovery efficiency presented in this study is based on actual laboratory 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 purification processes (i.e., increase recovery efficiency from selective extraction steps). REE recovery efficiency also depends on the feedstock chemistry. The Harmon-Hansen coal had better recovery than the Hagel B coal. Other elements such as Scandium and Germanium were extracted with good efficiency as well and because of their high market prices have a large impact on overall economics. We would classify the worst-case scenario at about 70-75% recovery in the leaching step(s), and the best-case scenario at about 90% recovery in the leaching step(s).

REE Content in the Feedstock: We have evaluated the Harmon-Hansen coal in this study, which to date, is the highest REE content coal sampled in this project. It also has an attractive ratio of critical and heavy REE to light REE. However, based on data collected by the North Dakota Geological Survey (unpublished, personal discussion with Ned Kruger 2017), as well as by data available in the USGS CoalQual Database, we believe that other coals in the state have the necessary quantity/distribution of REE, as well as being present/mineable in sufficient quantity, to be commercially feasible. We therefore, classify the Harmon-Hansen coal as the likely scenario. The Hagel B coal, which was shown to be significantly less profitable in this study, but still profitable, can be considered the worst-case scenario. The best-case scenario is to identify large quantity of high REE content coal with the desired REE modes of occurrence in an existing mine (the Harmon-Hansen coal zone has not been mined since 1997) that has good/uniform distribution to minimize costs of selective mining. One other note regarding the Harmon-Hansen feedstock is that due to the samples being collected from an exposed portion of the seam, the coal had evidence of oxidation, which may have converted the iron content from a sulfide to an oxide form. This very likely would make it more amenable to leaching processes. With utilization of a non-oxidized coal, we may be able to decrease the extraction of iron into solution, thus improving the concentration of REE and minimizing impurity removal requirements.

Complexity/Number of Processing Steps: This study has presented the two-step approach to generating a 2wt% REE concentrate solution – sulfuric acid leaching following by forced oxidation to remove iron impurity. We have also investigated the option of adding a third step in the form of a pre-leach using ammonium acetate. We believe that the presented configuration is the likely case, but also believe there to be potential to achieve a one-step process with optimization of the acid leaching step and feedstock selection. The worst-case scenario can be considered the 3-step process that also needs an acid neutralization step to increase the kinetics of iron oxidation. The best-case scenario is an optimized acid leaching process that eliminates the pre-leach and impurities removal steps. An alternate best-case scenario could be implementation of a processing approach that significantly increases the concentration of the REE in the PLS (i.e., 6 wt% as shown in Case 4 in Table 4-1), which could sufficiently reduce the cost of downstream purification to justify the added capital/operating costs.

Effectiveness of Impurity Removal: The primary impurity in the leach solution is iron for the Harmon-Hanson coal. As noted above, this may be due to the iron being present as an oxidized form instead of the natural sulfide form. However, this study presented the case with 72% iron removal efficiency via forced oxidation, which we believe to be the likely case. A worst-case scenario is slow iron oxidation kinetics that require an acid neutralization step. The best-case scenario would be not needing iron removal at all due to prevention of extracting iron into the solution, either by optimizing the leaching steps or by identifying a feedstock with more stable iron content. We also note that with process optimization, we expect to be able to operate at a higher pH and combined with the presence of catalysts in solution (i.e., Cu) we do not believe neutralization to be a needed step in the process.

Economic Scenarios

The primary economic drivers are: (i) CAPEX/OPEX, (ii) REE/target element and carbon sales price, (iii) purification costs, and (iv) plant scale. 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. As discussed above, we envision three complexity scenarios – one-step, two-step and three-step, the two-step being presented in this study.

Product Sales Prices: 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 ½ and double 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. 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.

Purification Costs: For the purposes of this study, the downstream element purification costs were not defined, and estimates were applied to appraise the "value" of the 2-wt% REE concentrate product. At this stage of development it is difficult to quantify the uncertainty in our estimates, but we believe them to be conservative based on our industry experience.

Plant Scale: As discussed previously, we envision the application of this technology at VCSU to be a first-of-a-kind pilot that, if successful, will encourage installation at additional and larger facilities. To investigate the impact of scale, we have projected the economics of the application of REE extraction co-located with activated carbon production and steam production to a range of coal feed rates from "small demo" to scaled-up installations such as at the UND and NDSU campuses. CAPEX was scaled using the $^{6}/_{10}$ ths rule and OPEX and revenues were scaled linearly with throughput. The results are shown in Figure 6-1. Using these projections, the 10-year 'break-even' plant scale is about 1,000 lb/hr in terms of NPV (at 15% discount rate), but net revenues (cash flow) are positive even at the smallest 100 lb/hr scale.

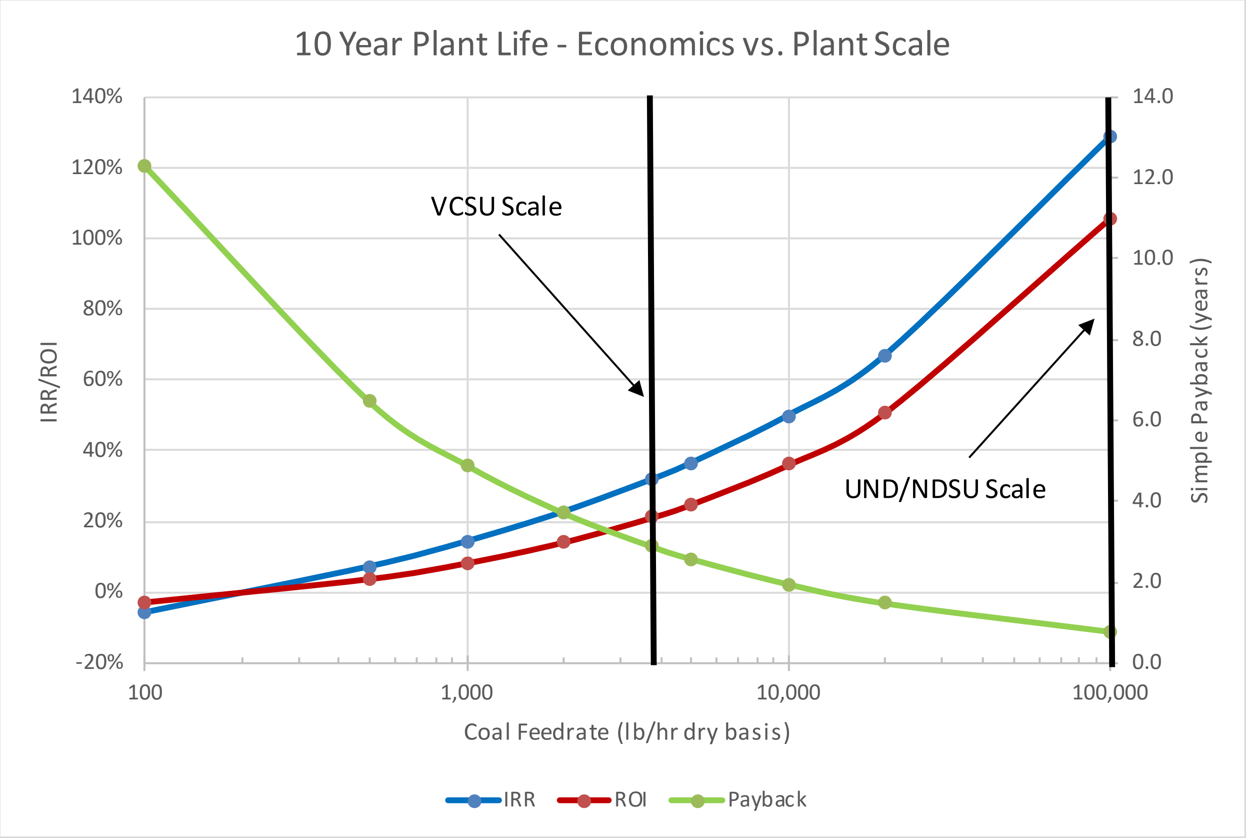


Figure 6-1 Economics projections as a function of plant scale (coal feed rate)

Results

The data presented in this document can reasonably be assumed as the likely or average scenario, accounting for conservative assumptions based on limited process definition to date. Best-case scenarios would involve: (i) simplifying the processing scheme to eliminate pre-leaching and impurities removal steps, or to significantly increase the concentration of REEs in the product, (ii) identification of an improved feedstock with either higher total REE content, higher critical or heavy REE content, more stable impurity forms or lower cost mining, (iii) increases in REE/target element sales prices, and (iv) scaling up the technology beyond the first implementation at VCSU. Worst-case scenarios would involve: (i) increased process complexity to achieve 2-wt% REE concentration, (ii) less desirable feedstock, and (iii) lower REE/target element and activated carbon sales prices.

The best-case scenario could be estimated as the following combined sensitivity case:

- Decrease in CAPEX/OPEX, including REE/target element purification costs by 10%
- Increase in REE/target element sales price by 10%
- Increase in activated carbon sales price by 10%

When combining the above, best-case economic metrics are as follows:

- 20 year IRR: 46%
- 20 year ROI: 38%

- Simple Payback: 2.2 years
- 20 year NPV (15% discount rate): $46,700,000

The worst-case scenario could be estimated as the following combined sensitivity case:
- Increase in CAPEX by 50%
- Increase in OPEX, including REE/target element purification costs by 10%
- Decrease in REE/target element sales price by 10%
- Decrease in activated carbon sales price by 10%

When combining the above, worst-case economic metrics are as follows:
- 20 year IRR: 18%
- 20 year ROI: 13%
- Simple Payback: 5.3 years
- 20 year NPV (15% discount rate): $6,900,000

6.2 Process Optimization Planned in Phase II

While some parametric evaluation has been completed to date, and the concentration process developed is very effective for the recovery of REEs and other elements of economic significance, *the project team believes there to be considerable room to improve the process via additional process studies and careful parametric optimization that can be accomplished during the Phase II project* if awarded by DOE. Some specific areas to explore that could improve the process efficiency and economics include:

- This evaluation assumes a 24-hour contact time for the leaching steps, which is currently believed to be a very conservative estimate. Reduced leaching time increases process efficiency and reduces the size of equipment needed providing improved economics and plant throughput.
    - Monitoring of pH as a function of time during the laboratory leaching tests showed that acid consumption only occurred during the initial 30 minutes, indicating that the REE leaching kinetics is likely very fast.

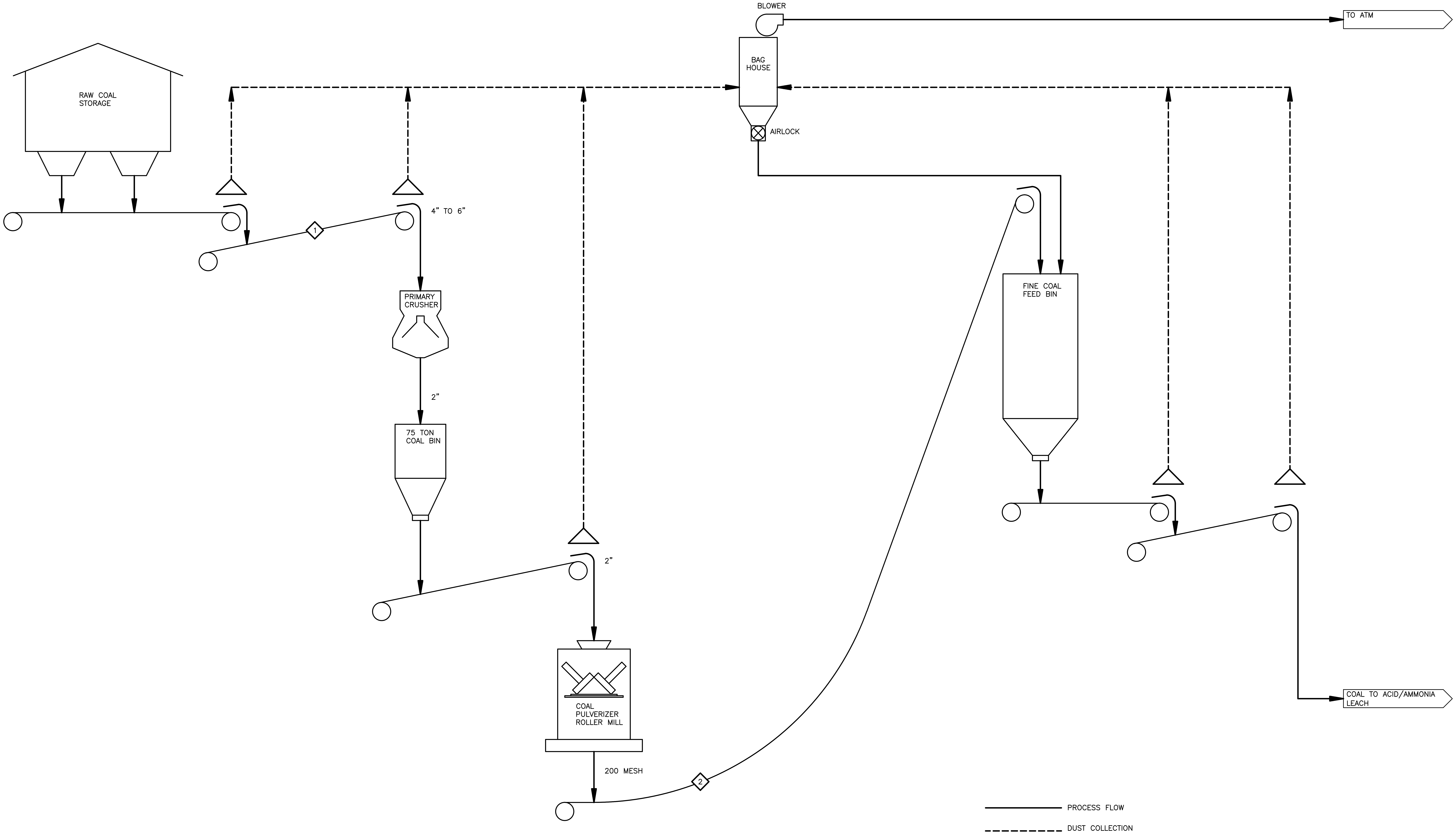
- Additionally, based on improved understanding of the modes of occurrence of the REEs in the proposed feedstocks, it is believed that there is the possibility to generate a more REE selective process. Better selectivity would minimize impurities extracted into solution and provide and a more concentrated product (possibly much higher than 2% REE), and/or eliminate additional steps required to achieve the 2wt% target (i.e., ammonium acetate pre-leach and/or iron precipitation).
    - Specific parameters of interest to optimize would include leaching solution concentration methods, acid concentration and composition, residence time, particle size and temperature. For instance, the kinetics of REE leaching may be significantly faster than kinetics of impurities leaching (iron) due to differing modes of occurrence/strength of the associations in the coal. It is possible that a one-step process is achievable (only acid leaching step).

- Optimizing acid concentration and composition – Ultimately, it is expected that operation at a higher pH (lower acid concentrations) can be accomplished without a significant decrease in REE recovery, which will improve process economics and simplify downstream impurity removal and purification steps. Further, appropriate additives to the acidic extraction solution could further improve performance and economics.

Exhibits

Exhibit A

Process Flow Diagrams with Mass Balance Tables



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UND-EXTRACTION OF REE FROM COAL

COAL CRUSH & PULVERIZE

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UND-EXTRACTION OF REE FROM COAL

LEACHING CIRCUIT

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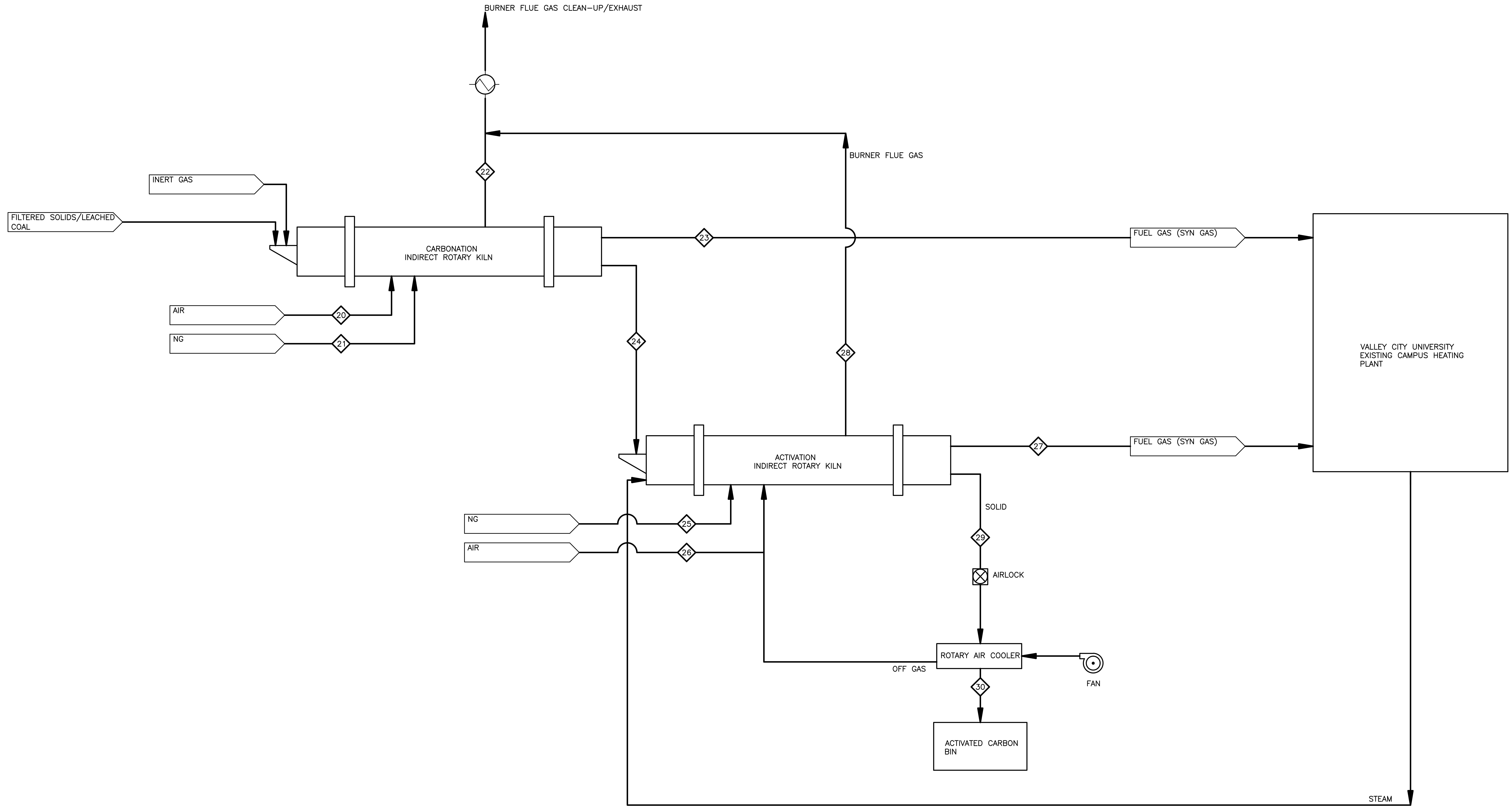
DWG. No. FS-2
REV. No. B



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UND–EXTRACTION OF REE FROM COAL

ACTIVATED CARBON CIRCUIT

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		FLOW-SHEET FS-1		FLOW-SHEET FS-2																	FLOW-SHEET FS-3										
STREAMS		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
Description		Coal Feed	Pulverized Coal	Leachate Feed	Acid	Dilution Water	Leachate Solution	Clarifier Overflow	Iron Settling Tank Overflow	Iron Extraction Filter Press Filtrate	REE Pregnant Solution	Iron Extract	Leached Coal Slurry / Filter Press Feed	Iron Extraction Filter Press Feed	Press Filtrate	Pressed Coal Slurry	Dryer Fuel Gas	Dryer Combustion Air	Dryer Exhaust	Dried Coal Byproduct	Carbonation Kiln Combution Air	Carbonation Kiln Fuel Gas	Carbonation Kiln Exhaust Gas	Syngas from Carbonation	Carbonated Solids	Activation Kiln Combustion Air	Activation Kiln Fuel Gas	Syngas from Activation	Activation Kiln Exhaust Gas	Hot Activated Carbon	Cooled Activated Carbon
State	Solid, Liquid, Gas	Solid	Solid	Solid	Liquid	Liquid	Solid, Liquid, Gas	Liquid, Solids	Liquid	Liquid	Liquid, Solids	Liquid, Solids	Solid, Liquid	Liquid	Liquid, Solids	Solid, Liquid	Gas	Gas	Gas	Solid, Liquid	Gas	Gas	Gas	Gas	Solid	Gas	Gas	Gas	Gas	Solid	Solid
Temp	F	70	70	70	70	70	104-194 F	104	104	104	104	104	104	104	70	70	70	300	220	77	1300	70	339	1100	1100	1000	70	1652	371	1652	200
Pressure	psig																														
Coal	lb/hr	3627	3627	3627			3627						3627			3627				3627											
Acid	lb/hr				324		392	196	98.1	68.7	167	29.4	98.1	98.1	68.7	29.4															
Acid	ft3/hr				2.8		3.4	1.7	0.9	0.6	1.5	0.3	0.9	0.9	0.6	0.3															
Water	lb/hr	1228	1228	1228		4145	7637	3819	1909	1337	3246	573	3819	1909	2264	1554			1554												
Water	ft3/hr	19.7	19.7	19.7		66.4	122	61.2	30.6	21.4	52.0	9.2	61.2	30.6	36.3	24.9			24.9												
Soluble Metals (Excluding REE)	lb/hr	356	356	356			356	211	34.7	55.2	90.0	121.1	145	176.3		144.7				144.7					145					145	145
REE	lb/hr	2.1	2.1	2.1			3.9	1.9	0.9	0.8	1.8	0.1	2.0	0.9	1.8	0.2				0.2					0.2					0.2	0.2
Char	lb/hr																								2091						
Activated Carbon	lb/hr																													1624	1624
Syngas	lb/hr																							1537				1181			
Natural Gas	lb/hr																90.0					60.0					50.0				
Air	lb/hr																	1800	1800		1200		1200			1000			1000		
Total Flow Rate	lb/hr	5213	5213	5213	324	4145	12017	4228	2043	1461	3504	723	7691	2185	2335	5356	90.0	1800	3354	3772	1200	60.0	1200	1537	2236	1000	50.0	1181	1000	1769	1769
REE wt% dry basis	%	0.6	0.6	0.6			1.1	0.9	2.6	1.5	1.9	0.1	1.4	0.5		0.1				0.1					0.1					0.1	0.1

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UND-EXTRACTION OF REE FROM COAL

MASS BALANCE TABLE

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Exhibit B

Capital Cost Estimates, Operating Cost Estimates, Rate of Investment Estimates

					Maintenance and Operation Costs					
								Natural Gas Rate (per MMBTU):	$ 3.50	
								Electrical Rate (per kWh):	$ 0.081	
Process Item	**Quantity**	**Cost Per Item**	**Total Cost**	**Notes/Assumptions**	Notes/Assumptions	O&M Cost/hr	Motor HP	NG lb/hr	Motor Cost/hr	NG Cost/hr
Raw Coal Storage Bin Option #1	1	$117,400	$117,400	200 ton 16ft x 16ft elevated steel plate bin with discharge belt feeder [1, pg. MISC 2 & 3]	$1.74/HR, includes overhaul parts and labor, maintenance parts and labor, electric and lube [1, pg. MISC 2 & 3]	$ 1.74			$ -	$ -
Belt Conveyors	6	$181,936	$1,091,616	24" belt width X 100' Length galleried conveyor with 10 hp motor (Extrapolated from Superior Industries Quote from project 34281037.02 for conveyor 24"X86' Truss Frame Conveyor Gallery Option)	$5.68/HR, based on 30" wide 100ft long conveyor, 55 pcf material, includes overhaul parts and labor, maintenance parts and labor, electric and lube [1, pg. MISC 14 & 15]	$ 34.08			$ -	$ -
Primary Crusher	1	$31,725	$31,725	Quote OP-0001633 from Terra Source Dated 1/27/2017	$15.19/HR, includes overhaul parts and labor, maintenance parts and labor, lube and wear parts [1, pg. Mill 14 & 15]	$ 15.19	50		$ 2.99	$ -
Coal Bin	1	$66,825	$66,825	75 ton 14ft x 14ft elevated steel plate bin with discharge belt feeder (interpolated from table) [1, MISC 2 & 3]	$1.00/HR (interpolated from table), includes overhaul parts and labor, maintenance parts and labor, electric and lube [1, pg. MISC 2 & 3]	$ 1.00			$ -	$ -
Coal Pulverizer	1	$987,573	$584,040	(Request out to Industrial Reps (Williams) for more accurate quote) 12 tph Williams DF-64 Roller Mill 350 hp, 1800 rpm and supporting equipment (as stated in the Williams Patent Crusher and Pulverizer Co Inc Proposal Q120306 System #1 dated 6/21/2012)	Scaled down from 12 tph to 5 tph using 6/10 rule		350		$ 20.92	$ -
Fine Coal Bin	1	$38,520	$38,520	30 ton 8.5ft x 8.5ft elevated steel plate bin with discharge belt feeder (Interpolated from table)[1, pg. MISC 2 & 3]	$0.70/HR (interpolated from table), includes overhaul parts and labor, maintenance parts and labor, electric and lube [1, pg. MISC 2 & 3]	$ 0.70			$ -	$ -
Dust collection Bag house	1	$55,261	$55,261	Donaldson Torit Model 156 RFW 10 AW customized design for coal industry, 10,900 cfm for coal dust fines (from Donaldson quote TOR-07-555 dated 9/13/2007, Item #2, from project 3428011)	$2.67/HR, based on 10,000 CFM collector, includes overhaul parts and labor, maintenance parts and labor, lube [1, pg. MISC 20 & 21) 60 HP estimated	$ 2.67	60		$ 3.59	$ -
Ammonia Leach Tank	0	$80,000	$0	20' Dia. X 25' H, 59,000 gal, Cost extrapolated from SS tank costs in table [1, pg. Misc 90 & 91]	$2.83/HR, includes overhaul parts and labor and maintenance parts and labor, costs extrapolated from SS tank costs in table [1, pg. Misc 90 & 91]	$ 2.83			$ -	$ -
Ammonia Leach Mixer	0	$56,000	$0	66GTH-60-30 Mixpro, 60 HP, for 18' diameter 21' tall tank [2, section 13]	Based on a large closed tank mixer with a 60 inch impeller diameter and 4 inch shaft, 13 hp motor, cost includes overhaul parts and labor, maintenance parts and labor, and electric and lube [1, pg. Mill 66 & 67]	$ 3.23			$ -	$ -
Acid Leach Tank	1	$110,000	$110,000	20' Dia. X 35' H, 82,000 gal, Cost extrapolated from SS tank costs in table [1, pg. Misc 90 & 91]	$3.77/HR, includes overhaul parts and labor and maintenance parts and labor, costs extrapolated from SS tank costs in table [1, pg. Misc 90 & 91]	$ 3.77			$ -	$ -
Acid Leach Mixer	1	$84,000	$84,000	74GTH-60-25 Mixpro, 60 HP, for 30' diameter 33' tall tank [2, section 13]	Based on a large closed tank mixer with a 60 inch impeller diameter and 4 inch shaft, 13 hp motor, cost includes overhaul parts and labor, maintenance parts and labor, and electric and lube [1, pg. Mill 66 & 67]	$ 3.23			$ -	$ -
Acid Leach Pump	1	$11,849	$11,849	Process pump, medium duty, Ni-Hard impeller and casing, 100 gpm, 100ft head, 5 HP [1, pg. Misc 60 & 61] Additional $1,349 has been included for totally enclosed fan cooled 5 HP motor [1, pg. Misc 32]	$1.23/HR, includes overhaul parts and labor, maintenance parts and labor, and lube [1, pg. Misc 60 & 61]	$ 1.23	5		$ 0.30	$ -
Acid Scrubber	1	$102,940	$102,940	Tri-Mer Corporation Quote 10/10/2008 from Gropher Project, Whirl/Wet Collector system process flow 26,000 cfm, polypropylene contstruction					$ -	$ -
Thickener	1	$181,100	$181,100	50 ft diameter bridge thickener, steel wall [1, pg. Mill 92 & 93]	$12.16/HR, includes overhaul parts and labor, maintenance parts and labor, electric, and lube [1, pg. Mill 92 & 93]	$ 12.16			$ -	$ -
Thickener Underflow Pump	1	$10,349	$10,349	Slurry pump, medium duty, high chromium iron casing and impeller, 100 gpm, 100 ft head, 5 HP [1, pg. Misc 64] Additional $1,349 has been included for totally enclosed fan cooled 5 HP motor [1, pg. Misc 32]	$1.06/HR, includes overhaul parts and labor, maintenance parts and labor, and lube [1, pg. Misc 64 & 65]	$ 1.06	5		$ 0.30	$ -
Filter press	1	$32,100	$32,100	Plate and Frame Pressure Filter 320 sq ft filtration area, sidebar design, 10 HP [1, pg. Mill 38 & 39)	$1.66/HR, includes overhaul parts and labor, maintenance parts and labor, electric and lube [1,pg. Mill 38 & 39]	$ 1.66			$ -	$ -
Barren Liquor Solution Tank	1	$50,000	$50,000	16' Dia. X 20' H, 30,000 gal, Cost extrapolated from SS tank costs in table [1, pg. Misc 90 & 91]	$1.81/HR, includes overhaul parts and labor and maintenance parts and labor, costs extrapolated from SS tank costs in table [1, pg. Misc 90 & 91]	$ 1.81			$ -	$ -
Barren Liquor Solution Mixer	1	$56,000	$56,000	66GTH-60-30 Mixpro, 60 HP, for 18' diameter 21' tall tank [2, section 13]	Based on a large closed tank mixer with a 60 inch impeller diameter and 4 inch shaft, 13 hp motor, cost includes overhaul parts and labor, maintenance parts and labor, and electric and lube [1, pg. Mill 66 & 67]	$ 3.23			$ -	$ -
Barren Liquor Solution Pump	1	$11,849	$11,849	Process pump, medium duty, Ni-Hard impeller and casing, 100 gpm, 100ft head, 5 HP [1, pg. Misc 60 & 61] Additional $1,349 has been included for totally enclosed fan cooled 5 HP motor [1, pg. Misc 32]	$1.23/HR, includes overhaul parts and labor, maintenance parts and labor, and lube [1, pg. Misc 60 & 61]	$ 1.23	5		$ 0.30	$ -
Indirect Rotary Dryer	1	$550,000	$550,000	7800 pounds per hour of lignin coal @ 30% free water – Dried in 60” Diameter Rotary to 10% free water. Natural gas burners, on the outside of the tube (indirect rotary system) ---$ 500,000 to $ 550,000		$ 4.34		100		$ 7.00
Indirect Rotary Kiln	2	$750,000	$1,500,000	6200 pounds per hour of lignite coal @ 10% free water – carbonization at 600 C in a sealed indirect rotary system 48” diameter rotary 30% weight loss will yield 4340 pounds of materials, $700,000 to $750.000. 4340 pounds per hour to be activated with 1300 pounds of steam per hour at temperature of 900C – off gas syngas 48” diameter indirect rotary furnace $700,000 to 750,000	Based on 400 lb/hr Indirect-fired Rotary Carbon Regeneration Kiln, $4.34/HR, includes overhaul parts and labor, maintenance parts and labor, electric, and lube (natural gas has been removed and added separately at a rate of 254 lb/hr per kiln)) [1, pg. Mill 60 & 61]	$ 8.68		508	$ -	$ 35.56
Tank heat exchanger	2	$19,950	$39,900	Wattco 440kW 18" flange heater [2, section 12]	OPEX assumes electric heat		1196.8		$ 71.54	$ -
Rotary Air Cooler	1	$600,000	$600,000	Cost estimate from Feeco, no formal quote, estimated that the cost would be 2.0 million for one kiln and one rotary air cooler with a 70/30 cost split (kiln/cooler)					$ -	$ -
High Temperature Fan	2	$245,000	$490,000	Robinson Fans, 40000 CFM, 8 FSPR, 1000F, 100 HP, Quote from 12/11/13 project 22521140.00	$3.54/HR, based on an auxiliary fan, 47,000 cfm, 30 hp motor, includes overhaul parts and labor, maintenance parts and labor, electric and lube [1, pg. UG 48 & 49]	$ 7.08			$ -	$ -
Air compressor	1	$55,600	$55,600	883 cfm @ 100 psi, 145 max psi variable speed rotary screw compressor [1, pg. Misc 6 & 7]	$14.78/HR, includes overhaul parts and labor, maintenance parts and labor, electric, and lube [1, pg. Misc 6 & 7]	$ 14.78			$ -	$ -
Aeration Tank for Iron Oxidation	1	$15,500	$15,500	9' diameter, 12' high, 5700 gal capacity, stainless steel, [1, pg. Misc 90 & 91]	$0.62/HR, includes overhaul parts and labor, maintenance parts and labor [1, pg. Misc. 90 & 91]	$ 0.62			$ -	$ -
Blower for Aeration	1	$4,100	$4,100	Heavy duty, dual gear, PD rotary blower, 30 HP, 580cfm at 10 psi	$1.61/HR, includes overhaul parts and labor, maintenance parts and labor, electric and lube [1, pg. Mill 6 & 7]	$ 1.61			$ -	$ -
Iron Settling Tank	1	$15,500	$15,500	9' diameter, 12' high, 5700 gal capacity, stainless steel, [1, pg. Misc 90 & 91]	$0.62/HR, includes overhaul parts and labor, maintenance parts and labor [1, pg. Misc. 90 & 91]	$ 0.62			$ -	$ -
Heat Recovery Unit	3	$60,000	$180,000	Heat recovery exhaust silencer heat exchanger for steam generation. Quote from Maxim Silencers, INC. Maximum heat recovery of 3.6 MMBTU/HR					$ -	$ -
Iron Sludge Pump	1	$10,349	$10,349	Slurry pump, medium duty, high chromium iron casing and impeller, 100 gpm, 100 ft head, 5 HP [1, pg. Misc 64] Additional $1,349 has been included for totally enclosed fan cooled 5 HP motor [1, pg. Misc 32]	$1.06/HR, includes overhaul parts and labor, maintenance parts and labor, and lube [1, pg. Misc 64 & 65]	$ 1.06	5		$ 0.30	$ -
Filter Press Iron Sludge	1	$32,100	$32,100	Plate and Frame Pressure Filter 320 sq ft filtration area, sidebar design, 10 HP [1, pg. Mill 38 & 39)	$1.66/HR, includes overhaul parts and labor, maintenance parts and labor, electric and lube [1,pg. Mill 38 & 39]	$ 1.66			$ -	$ -
Building cost	20,000	$150	$3,000,000	100 ft by 200 ft building assumed @ $150 per ft2						
Ductwork & piping	1	$2,738,587	$2,738,587	30% of equipment total, engineering judgement						
					Total:	$ 131.27			$ 100.24	$ 42.56
Subtotal Process Item Costs			**$11,900,000**	Total Cost of Process Items Above						
Installation 50%			$5,950,000		Total O&M Cost per Hour:	$ 274.07				
Site work Landscaping 5%			$600,000		Total O&M Cost per Week:	$ 46,000	(24 hr/day, 7 day/wk)			
Site Electrical & Controls 20%			$2,400,000		**Total O&M Cost per Year:**	**$ 2,300,000**	(50 wk/yr operating)			
Total Construction Cost			**$20,900,000**							
Engineering, Legal & Administrative 35%			$7,400,000							
Total Project Cost			**$28,300,000**	rounded to nearest 100,000						

References:

1) Mine and Mill Equipment Costs, An Estimator's Guide", InfoMine USA Inc., 2016
2) Mineral Processing Cost Estimate Database 1_7_16 Section 13 Mixing

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			Material Flow (lb/hr)	3,772			Material Flow (lb/hr)	3,772
Element	**Concentration**	**units**	**Percent Recovery (leaching through refining)**	**Recovered Amount per year (lb/yr)**	**Purchasing Unit**	**Price**	**Unit ($/lb)**	**Payable Amount ($)**
Cerium Ce 58	154.8	mg/kg	80%	4,820	lb	$0.96	$/lb	$4,627
Cobalt Co	844.4	mg/kg	80%	21,404	lb	$13.50	$/lb (USGS 2016 report)	$288,948
Copper Cu 29	46.0	mg/kg	80%	1,166	lb	$3	$3/lb	$3,498
Dysprosium Dy 66	13.2	mg/kg	80%	771	lb	$103	$/lb	$79,383
Erbium Er 68	5.6	mg/kg	80%	325	lb	$32	$/lb	$10,385
Europium Eu 63	5.8	mg/kg	80%	338	lb	$93	$/lb	$31,462
Gadolinium Gd 64	19.7	mg/kg	80%	1,150	lb	$9	$/lb	$10,354
Gallium Ga	17.5	mg/kg	80%	1,193	lb	$89	$88.6/lb ($195/kg USGS 2016 report)	$105,658
Germanium Ge	18.9	mg/kg	80%	690	lb	$798	$798/lb ($1,760/kg USGS 2016 report)	$550,705
Holmium Ho 67	2.2	mg/kg	80%	129	lb	$25	$/lb	$3,216
Lanthanum La 57	53.7	mg/kg	80%	3,195	lb	$0.96	$2.12/kg ($0.96/lb)	$3,067
Lutetium Lu 71	0.6	mg/kg	80%	37	lb	$498.95	$/lb	$18,289
Manganese Mn 25	28.0	mg/kg	80%	710	lb	$0.74	$1.63/kg ($0.74/lb)	$525
Neodymium Nd 60	107.0	mg/kg	80%	6,338	lb	$18.10	$/lb	$114,724
Praseodymium Pr 59	23.4	mg/kg	80%	1,388	lb	$25	$/lb	$34,697
Samarium Sm 62	25.7	mg/kg	80%	1,512	lb	$1.18	$/lb	$1,784.5
Terbium Tb 65	2.6	mg/kg	80%	315	lb	$204.12	$/lb	$64,330
Thulium Tm 69	0.7	mg/kg	80%	43	lb	$453.59	$/lb	$19,458
Scandium Sc 21	29.2	mg/kg	75%	2,127	lb	$907.19	$2000/kg ($907.19/lb)	$1,929,223
Ytterbium Yb 70	4.7	mg/kg	80%	270	lb	$22.68	$/lb	$6,113
Yttrium Y 39	39.4	mg/kg	80%	2,539	lb	$4.09	$4.09/lb ($9/kg USGS 2016 report)	$10,385
Zinc Zn 30	22.2	mg/kg	80%	563	lb	$0.70	$/lb	$394

Rare Earth Element (REE) + Ge & Ga	
Base Metal	

Total lb/yr (target metals)	51,021
REE + Ge & Ga lb/yr	27,179
Base metals lb/yr	23,842

Total Saleable Activated Carbon (tons/yr)	7,450
Total Syngas to VCSU (lb/yr)	22,831,200
REE and Element Total Payable Amount	$3,291,228
Activated Carbon Payable Amount	$10,430,000
Credit for fuel value (assume $/lb of NG), ($/yr)	$799,092
Coal cost (5,000 lb/hr coal feed)	($525,000)
Electricity, Natural Gas, and Maintenance Cost ($/yr)	($2,300,000)
Steam ($/yr)	($47,914)
Water ($/yr)	($51,626)
Operator Labor Cost ($/yr)	($400,000)
Acid Cost ($/yr)	($493,806)
REE + Ge & Ga Processing Cost	($244,608)
Base Processing Cost	($23,842)
Add 15% for misc. (sewer, waste disposal, precipitation, etc.)	($613,019)
Payable Revenue	**$9,820,505**

Assumptions:

80% recovery for all elements excluding Sc (75%) throughout the entire process to final saleable product

$1000 per dry ton REE per element processing cost, and assumes a shipping cost

$500 per dry ton base element processing cost, and assumes a shipping cost

Concentrate is a marketable product

Scandium price	Scandium Price Source
$2,000	per kg
$907.19	per lb

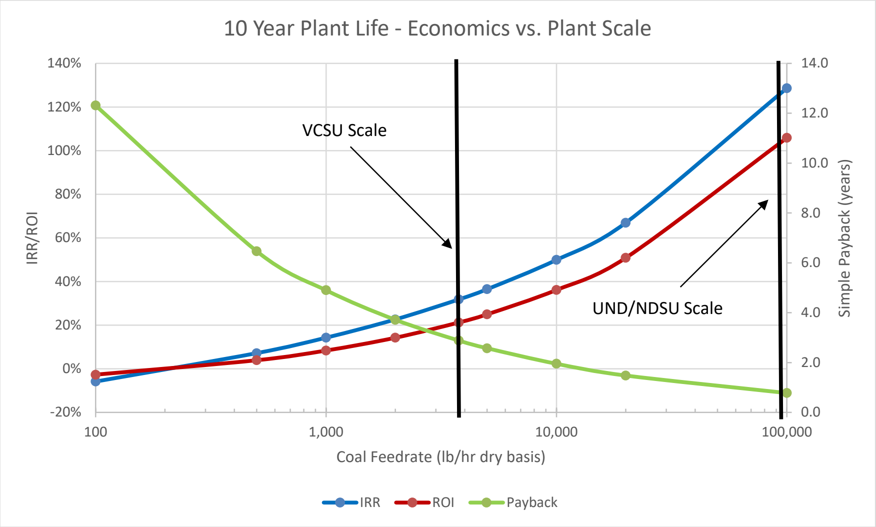
50 weeks per year operation (96% capacity)

AC sale price	$1,400	per ton	Provided by UND
coal cost	$25	per ton	Cost from Lyall Workman plus $5*
REE Processing	$1,000	per ton	For SX-EW only
Base Processing	$500	per ton	For SX-EW only
Electricity Cost	$0.0813	per kWh	
Natural gas	$3.50	per mmbtu	also assume credit price for syngas
Water Cost	$8	per 1000 gallons	Valley City, ND Public Works
Sulfuric Acid Cost	$0.15	per lb	Quote from Hawkins
Steam Cost	$8	per 1000 lbs	
Water Flow	768	gph	7.48 gal/ft3
Acid Flow	390	lb/h	114.6 lb/ft3
Steam Flow	713	lb/h	
Syngas Flow	2718	lb/h	from mass balance/Chemcad

*Lyall Workman is a Barr Engineering senior mining consultant with experience in coal mining.
$5 was added to be conservative for mining specific coal seams

Item		lb/hr
		3,772
CAPEX		($28,300,000)
OPEX		($4,700,000)
Element	% of Total	
Cerium Ce 58	*0.1%*	$4,627
Cobalt Co	*8.8%*	$288,948
Copper Cu 29	*0.1%*	$3,498
Dysprosium Dy 66	*2.4%*	$79,383
Erbium Er 68	*0.3%*	$10,385
Europium Eu 63	*1.0%*	$31,462
Gadolinium Gd 64	*0.3%*	$10,354
Gallium Ga	*3.2%*	$105,658
Germanium Ge	*16.7%*	$550,705
Holmium Ho 67	*0.1%*	$3,216
Lanthanum La 57	*0.1%*	$3,067
Lutetium Lu 71	*0.6%*	$18,289
Manganese Mn 25	*0.0%*	$525
Neodymium Nd 60	*3.5%*	$114,724
Praseodymium Pr 59	*1.1%*	$34,697
Samarium Sm 62	*0.1%*	$1,784
Terbium Tb 65	*2.0%*	$64,330
Thulium Tm 69	*0.6%*	$19,458
Scandium Sc 21	*58.6%*	$1,929,223
Ytterbium Yb 70	*0.2%*	$6,113
Yttrium Y 39	*0.3%*	$10,385
Zinc Zn 30	*0.0%*	$394
Total Payable Amount		$3,291,228
Activated Carbon Payable Amount		$10,430,000
Credit for Syngas		$799,092
Net Annual Revenue		$9,820,000
Simple Payback (years)		2.9
IRR (10 years)		32%
ROI (10 years)		21%
NPV (10 years) @15% Discount Rate		$18,600,000
IRR (20 years)		35%
ROI (20 years)		28%
NPV (20 years) @15% Discount Rate		$32,600,000
CAPEX/annual dry ton feed		$1,800
OPEX/annual dry ton feed		$300
Net Revenue/annual dry ton feed		$620

Coal Feed	CAPEX	OPEX	A.C. Revenue	Metals Revenue	Syngas Revenue	NET Revenue	IRR	ROI	Payback
100	$ 3,205,113.59	$ 124,602.33	$ 276,511.13	$ 87,254.18	$ 21,184.84	$ 260,347.81	-6%	-3%	12.3
500	$ 8,418,319.95	$ 623,011.66	$ 1,382,555.67	$ 436,270.89	$ 105,924.18	$ 1,301,739.07	7%	4%	6.5
1000	$ 12,759,787.01	$ 1,246,023.33	$ 2,765,111.35	$ 872,541.77	$ 211,848.36	$ 2,603,478.14	14%	8%	4.9
2000	$ 19,340,220.56	$ 2,492,046.66	$ 5,530,222.69	$ 1,745,083.54	$ 423,696.71	$ 5,206,956.29	23%	14%	3.7
3772	**$ 28,300,000.00**	**$ 4,700,000.00**	**$ 10,430,000.00**	**$ 3,291,227.56**	**$ 799,092.00**	**$ 9,820,319.56**	**32%**	**21%**	**2.9**
5000	$ 33,513,935.36	$ 6,230,116.65	$ 13,825,556.73	$ 4,362,708.85	$ 1,059,241.78	$ 13,017,390.72	36%	25%	2.6
10000	$ 50,797,627.03	$ 12,460,233.30	$ 27,651,113.47	$ 8,725,417.71	$ 2,118,483.56	$ 26,034,781.44	50%	36%	2.0
20000	$ 76,994,804.84	$ 24,920,466.60	$ 55,302,226.94	$ 17,450,835.41	$ 4,236,967.13	$ 52,069,562.88	67%	51%	1.5
100000	$ 202,228,995.70	$ 124,602,332.98	$ 276,511,134.68	$ 87,254,177.07	$ 21,184,835.63	$ 260,347,814.39	129%	106%	0.8



year	cash flow	net cash flow	
0	0	0	
1	$ (3,205,113.59)	($3,205,114)	
2	$ 260,348	($2,944,766)	
3	$ 260,348	($2,684,418)	
4	$ 260,348	($2,424,070)	
5	$ 260,348	($2,163,722)	
6	$ 260,348	($1,903,375)	
7	$ 260,348	($1,643,027)	
8	$ 260,348	($1,382,679)	
9	$ 260,348	($1,122,331)	
10	$ 260,348	($861,983)	
IRR	-6%	DRP2	
ROI	-3%	DRP2	
Payback	12.31		
NPV	($2,000,000)	DR	15%

year	cash flow	net cash flow	
0	0	0	
1	$ (8,418,319.95)	($8,418,320)	
2	$ 1,301,739	($7,116,581)	
3	$ 1,301,739	($5,814,842)	
4	$ 1,301,739	($4,513,103)	
5	$ 1,301,739	($3,211,364)	
6	$ 1,301,739	($1,909,625)	
7	$ 1,301,739	($607,886)	
8	$ 1,301,739	$693,854	
9	$ 1,301,739	$1,995,593	
10	$ 1,301,739	$3,297,332	
IRR	7%	DRP2	
ROI	4%	DRP2	
Payback	6.47		
NPV	($2,200,000)	DR	15%

year	cash flow	net cash flow	
0	0	0	
1	$ (12,759,787.01)	($12,759,787)	
2	$ 2,603,478	($10,156,309)	
3	$ 2,603,478	($7,552,831)	
4	$ 2,603,478	($4,949,353)	
5	$ 2,603,478	($2,345,874)	
6	$ 2,603,478	$257,604	
7	$ 2,603,478	$2,861,082	
8	$ 2,603,478	$5,464,560	
9	$ 2,603,478	$8,068,038	
10	$ 2,603,478	$10,671,516	
IRR	14%	DRP2	
ROI	8%	DRP2	
Payback	4.90		
NPV	($300,000)	DR	15%

year	cash flow	net cash flow	
0	0	0	
1	$ (3,205,113.59)	($3,205,114)	
2	$ 260,348	($2,944,766)	
3	$ 260,348	($2,684,418)	
4	$ 260,348	($2,424,070)	
5	$ 260,348	($2,163,722)	
6	$ 260,348	($1,903,375)	
7	$ 260,348	($1,643,027)	
8	$ 260,348	($1,382,679)	
9	$ 260,348	($1,122,331)	
10	$ 260,348	($861,983)	
11	$ 260,348	($601,635)	
12	$ 260,348	($341,288)	
13	$ 260,348	($80,940)	
14	$ 260,348	$179,408	
15	$ 260,348	$439,756	
16	$ 260,348	$700,104	
17	$ 260,348	$960,451	
18	$ 260,348	$1,220,799	
19	$ 260,348	$1,481,147	
20	$ 260,348	$1,741,495	
IRR	5%	DRP2	
ROI	3%	DRP2	
Payback	12.31		
NPV	($1,600,000.00)	DR	15%

year	cash flow	net cash flow	
0	0	0	
1	$ (8,418,319.95)	($8,418,320)	
2	$ 1,301,739	($7,116,581)	
3	$ 1,301,739	($5,814,842)	
4	$ 1,301,739	($4,513,103)	
5	$ 1,301,739	($3,211,364)	
6	$ 1,301,739	($1,909,625)	
7	$ 1,301,739	($607,886)	
8	$ 1,301,739	$693,854	
9	$ 1,301,739	$1,995,593	
10	$ 1,301,739	$3,297,332	
11	$ 1,301,739	$4,599,071	
12	$ 1,301,739	$5,900,810	
13	$ 1,301,739	$7,202,549	
14	$ 1,301,739	$8,504,288	
15	$ 1,301,739	$9,806,027	
16	$ 1,301,739	$11,107,766	
17	$ 1,301,739	$12,409,505	
18	$ 1,301,739	$13,711,244	
19	$ 1,301,739	$15,012,983	
20	$ 1,301,739	$16,314,722	
IRR	14%	DRP2	
ROI	10%	DRP2	
Payback	6.47		
NPV	($300,000.00)	DR	15%

year	cash flow	net cash flow	
0	0	0	
1	$ (12,759,787.01)	($12,759,787)	
2	$ 2,603,478	($10,156,309)	
3	$ 2,603,478	($7,552,831)	
4	$ 2,603,478	($4,949,353)	
5	$ 2,603,478	($2,345,874)	
6	$ 2,603,478	$257,604	
7	$ 2,603,478	$2,861,082	
8	$ 2,603,478	$5,464,560	
9	$ 2,603,478	$8,068,038	
10	$ 2,603,478	$10,671,516	
11	$ 2,603,478	$13,274,994	
12	$ 2,603,478	$15,878,473	
13	$ 2,603,478	$18,481,951	
14	$ 2,603,478	$21,085,429	
15	$ 2,603,478	$23,688,907	
16	$ 2,603,478	$26,292,385	
17	$ 2,603,478	$28,895,863	
18	$ 2,603,478	$31,499,341	
19	$ 2,603,478	$34,102,820	
20	$ 2,603,478	$36,706,298	
IRR	20%	DRP2	
ROI	14%	DRP2	
Payback	4.90		
NPV	$3,400,000.00	DR	15%

year	cash flow	net cash flow	
0	0	0	
1	$ (19,340,220.56)	($19,340,221)	
2	$ 5,206,956	($14,133,264)	
3	$ 5,206,956	($8,926,308)	
4	$ 5,206,956	($3,719,352)	
5	$ 5,206,956	$1,487,605	
6	$ 5,206,956	$6,694,561	
7	$ 5,206,956	$11,901,517	
8	$ 5,206,956	$17,108,473	
9	$ 5,206,956	$22,315,430	
10	$ 5,206,956	$27,522,386	
IRR	23%	DRP2	
ROI	14%	DRP2	
Payback	3.71		
NPV	$5,500,000	DR	15%

year	cash flow	net cash flow	
0	0	0	
1	$ (28,300,000.00)	($28,300,000)	
2	$ 9,820,320	($18,479,680)	
3	$ 9,820,320	($8,659,361)	
4	$ 9,820,320	$1,160,959	
5	$ 9,820,320	$10,981,278	
6	$ 9,820,320	$20,801,598	
7	$ 9,820,320	$30,621,917	
8	$ 9,820,320	$40,442,237	
9	$ 9,820,320	$50,262,556	
10	$ 9,820,320	$60,082,876	
IRR	32%	DRP2	
ROI	21%	DRP2	
Payback	2.88		
NPV	$18,600,000	DR	15%

year	cash flow	net cash flow	
0	0	0	
1	$ (33,513,935.36)	($33,513,935)	
2	$ 13,017,391	($20,496,545)	
3	$ 13,017,391	($7,479,154)	
4	$ 13,017,391	$5,538,237	
5	$ 13,017,391	$18,555,628	
6	$ 13,017,391	$31,573,018	
7	$ 13,017,391	$44,590,409	
8	$ 13,017,391	$57,607,800	
9	$ 13,017,391	$70,625,190	
10	$ 13,017,391	$83,642,581	
IRR	36%	DRP2	
ROI	25%	DRP2	
Payback	2.57		
NPV	$28,600,000	DR	15%

year	cash flow	net cash flow	
0	0	0	
1	$ (19,340,220.56)	($19,340,221)	
2	$ 5,206,956	($14,133,264)	
3	$ 5,206,956	($8,926,308)	
4	$ 5,206,956	($3,719,352)	
5	$ 5,206,956	$1,487,605	
6	$ 5,206,956	$6,694,561	
7	$ 5,206,956	$11,901,517	
8	$ 5,206,956	$17,108,473	
9	$ 5,206,956	$22,315,430	
10	$ 5,206,956	$27,522,386	
11	$ 5,206,956	$32,729,342	
12	$ 5,206,956	$37,936,299	
13	$ 5,206,956	$43,143,255	
14	$ 5,206,956	$48,350,211	
15	$ 5,206,956	$53,557,167	
16	$ 5,206,956	$58,764,124	
17	$ 5,206,956	$63,971,080	
18	$ 5,206,956	$69,178,036	
19	$ 5,206,956	$74,384,993	
20	$ 5,206,956	$79,591,949	
IRR	27%	DRP2	
ROI	21%	DRP2	
Payback	3.71		
NPV	$12,900,000.00	DR	15%

year	cash flow	net cash flow	
0	0	0	
1	$ (28,300,000.00)	($28,300,000)	
2	$ 9,820,320	($18,479,680)	
3	$ 9,820,320	($8,659,361)	
4	$ 9,820,320	$1,160,959	
5	$ 9,820,320	$10,981,278	
6	$ 9,820,320	$20,801,598	
7	$ 9,820,320	$30,621,917	
8	$ 9,820,320	$40,442,237	
9	$ 9,820,320	$50,262,556	
10	$ 9,820,320	$60,082,876	
11	$ 9,820,320	$69,903,196	
12	$ 9,820,320	$79,723,515	
13	$ 9,820,320	$89,543,835	
14	$ 9,820,320	$99,364,154	
15	$ 9,820,320	$109,184,474	
16	$ 9,820,320	$119,004,793	
17	$ 9,820,320	$128,825,113	
18	$ 9,820,320	$138,645,433	
19	$ 9,820,320	$148,465,752	
20	$ 9,820,320	$158,286,072	
IRR	35%	DRP2	
ROI	28%	DRP2	
Payback	2.88		
NPV	$32,600,000.00	DR	15%

year	cash flow	net cash flow	
0	0	0	
1	$ (33,513,935.36)	($33,513,935)	
2	$ 13,017,391	($20,496,545)	
3	$ 13,017,391	($7,479,154)	
4	$ 13,017,391	$5,538,237	
5	$ 13,017,391	$18,555,628	
6	$ 13,017,391	$31,573,018	
7	$ 13,017,391	$44,590,409	
8	$ 13,017,391	$57,607,800	
9	$ 13,017,391	$70,625,190	
10	$ 13,017,391	$83,642,581	
11	$ 13,017,391	$96,659,972	
12	$ 13,017,391	$109,677,363	
13	$ 13,017,391	$122,694,753	
14	$ 13,017,391	$135,712,144	
15	$ 13,017,391	$148,729,535	
16	$ 13,017,391	$161,746,925	
17	$ 13,017,391	$174,764,316	
18	$ 13,017,391	$187,781,707	
19	$ 13,017,391	$200,799,098	
20	$ 13,017,391	$213,816,488	
IRR	39%	DRP2	
ROI	32%	DRP2	
Payback	2.57		
NPV	$47,200,000.00	DR	15%

year	cash flow	net cash flow	
0	0	0	
1	$ (50,797,627.03)	($50,797,627)	
2	$ 26,034,781	($24,762,846)	
3	$ 26,034,781	$1,271,936	
4	$ 26,034,781	$27,306,717	
5	$ 26,034,781	$53,341,499	
6	$ 26,034,781	$79,376,280	
7	$ 26,034,781	$105,411,062	
8	$ 26,034,781	$131,445,843	
9	$ 26,034,781	$157,480,624	
10	$ 26,034,781	$183,515,406	
IRR	50%	DRP2	
ROI	36%	DRP2	
Payback	1.95		
NPV	$73,400,000	DR	15%

year	cash flow	net cash flow	
0	0	0	
1	$ (76,994,804.84)	($76,994,805)	
2	$ 52,069,563	($24,925,242)	
3	$ 52,069,563	$27,144,321	
4	$ 52,069,563	$79,213,884	
5	$ 52,069,563	$131,283,447	
6	$ 52,069,563	$183,353,010	
7	$ 52,069,563	$235,422,572	
8	$ 52,069,563	$287,492,135	
9	$ 52,069,563	$339,561,698	
10	$ 52,069,563	$391,631,261	
IRR	67%	DRP2	
ROI	51%	DRP2	
Payback	1.48		
NPV	$171,500,000	DR	15%

year	cash flow	net cash flow	
0	0	0	
1	$ (202,228,995.70)	($202,228,996)	
2	$ 260,347,814	$58,118,819	
3	$ 260,347,814	$318,466,633	
4	$ 260,347,814	$578,814,447	
5	$ 260,347,814	$839,162,262	
6	$ 260,347,814	$1,099,510,076	
7	$ 260,347,814	$1,359,857,891	
8	$ 260,347,814	$1,620,205,705	
9	$ 260,347,814	$1,880,553,519	
10	$ 260,347,814	$2,140,901,334	
IRR	129%	DRP2	
ROI	106%	DRP2	
Payback	0.78		
NPV	$1,040,000,000	DR	15%

year	cash flow	net cash flow	
0	0	0	
1	$ (50,797,627.03)	($50,797,627)	
2	$ 26,034,781	($24,762,846)	
3	$ 26,034,781	$1,271,936	
4	$ 26,034,781	$27,306,717	
5	$ 26,034,781	$53,341,499	
6	$ 26,034,781	$79,376,280	
7	$ 26,034,781	$105,411,062	
8	$ 26,034,781	$131,445,843	
9	$ 26,034,781	$157,480,624	
10	$ 26,034,781	$183,515,406	
11	$ 26,034,781	$209,550,187	
12	$ 26,034,781	$235,584,969	
13	$ 26,034,781	$261,619,750	
14	$ 26,034,781	$287,654,532	
15	$ 26,034,781	$313,689,313	
16	$ 26,034,781	$339,724,095	
17	$ 26,034,781	$365,758,876	
18	$ 26,034,781	$391,793,657	
19	$ 26,034,781	$417,828,439	
20	$ 26,034,781	$443,863,220	
IRR	51%	DRP2	
ROI	44%	DRP2	
Payback	1.95		
NPV	$110,600,000.00	DR	15%

year	cash flow	net cash flow	
0	0	0	
1	$ (76,994,804.84)	($76,994,805)	
2	$ 52,069,563	($24,925,242)	
3	$ 52,069,563	$27,144,321	
4	$ 52,069,563	$79,213,884	
5	$ 52,069,563	$131,283,447	
6	$ 52,069,563	$183,353,010	
7	$ 52,069,563	$235,422,572	
8	$ 52,069,563	$287,492,135	
9	$ 52,069,563	$339,561,698	
10	$ 52,069,563	$391,631,261	
11	$ 52,069,563	$443,700,824	
12	$ 52,069,563	$495,770,387	
13	$ 52,069,563	$547,839,950	
14	$ 52,069,563	$599,909,513	
15	$ 52,069,563	$651,979,075	
16	$ 52,069,563	$704,048,638	
17	$ 52,069,563	$756,118,201	
18	$ 52,069,563	$808,187,764	
19	$ 52,069,563	$860,257,327	
20	$ 52,069,563	$912,326,890	
IRR	68%	DRP2	
ROI	59%	DRP2	
Payback	1.48		
NPV	$245,700,000.00	DR	15%

year	cash flow	net cash flow	
0	0	0	
1	$ (202,228,995.70)	($202,228,996)	
2	$ 260,347,814	$58,118,819	
3	$ 260,347,814	$318,466,633	
4	$ 260,347,814	$578,814,447	
5	$ 260,347,814	$839,162,262	
6	$ 260,347,814	$1,099,510,076	
7	$ 260,347,814	$1,359,857,891	
8	$ 260,347,814	$1,620,205,705	
9	$ 260,347,814	$1,880,553,519	
10	$ 260,347,814	$2,140,901,334	
11	$ 260,347,814	$2,401,249,148	
12	$ 260,347,814	$2,661,596,963	
13	$ 260,347,814	$2,921,944,777	
14	$ 260,347,814	$3,182,292,591	
15	$ 260,347,814	$3,442,640,406	
16	$ 260,347,814	$3,702,988,220	
17	$ 260,347,814	$3,963,336,035	
18	$ 260,347,814	$4,223,683,849	
19	$ 260,347,814	$4,484,031,663	
20	$ 260,347,814	$4,744,379,478	
IRR	129%	DRP2	
ROI	117%	DRP2	
Payback	0.78		
NPV	$1,411,500,000.00	DR	15%

Exhibit C

Heat Balance Backup Data

2017 1-Feb
by NLN

Units

		Source of waste heat	Total Energy - Cumbustion	Total Fuel Gas Used	Total Combustion Air Used	Combustion Air Temp	Heater Air Temp	Exhaust Gas Temp	Syn Gas Temp
			mmbtu/hr	lb/hr	lb/hr	f	f	f	f
Drying	w/o waste heat		2	100	2000	70	3265	320	1100
	w/ waste heat	1250 F Exhaust from Dryer	1.88	90	1800	300	3397	220	n/a
Carbonation	w/o waste heat		1.6	74	1500	70	3238	1143	1100
	w/ waste heat	1452 F exhaust from carbonation	1.17	60	1200	1300	3918	339	1100
Activation	w/o waste heat		1.6	80	1600	70	3272	1623	1652
	w/ waste heat	1153 F Exhaust from Activation	1.05	50	1000	1000	3800	371	1652
Cooling	w/o waste heat		0.76		9600	70		405	1100
	w/ waste heat	not evaluated							

Assumptions -

Chemcad was used to evaluate energy balance reusing waste heat using countercurrent heat exchangers.

Waste heat exhaust temperature was high enough to maintain gaseous state while maintaining above heat exvhanger pinchpoint.

Dryer exhaust is combined with heater exhaust for waste heat recovery in the drying process.

Heating process uses .049 ratio of fuel / air in combustion process.

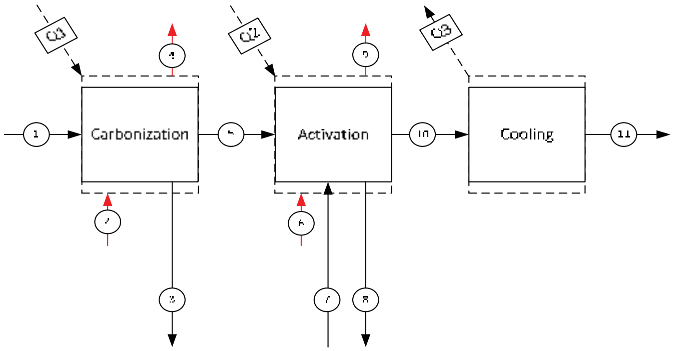
Combustion air, fuel, and coal feed is fed to system at 70 F atmospheric conditions.

Natural gas compostion is based on typical pipeline natural gas.

The process to make steam used in activation is not considered in the energy balance.

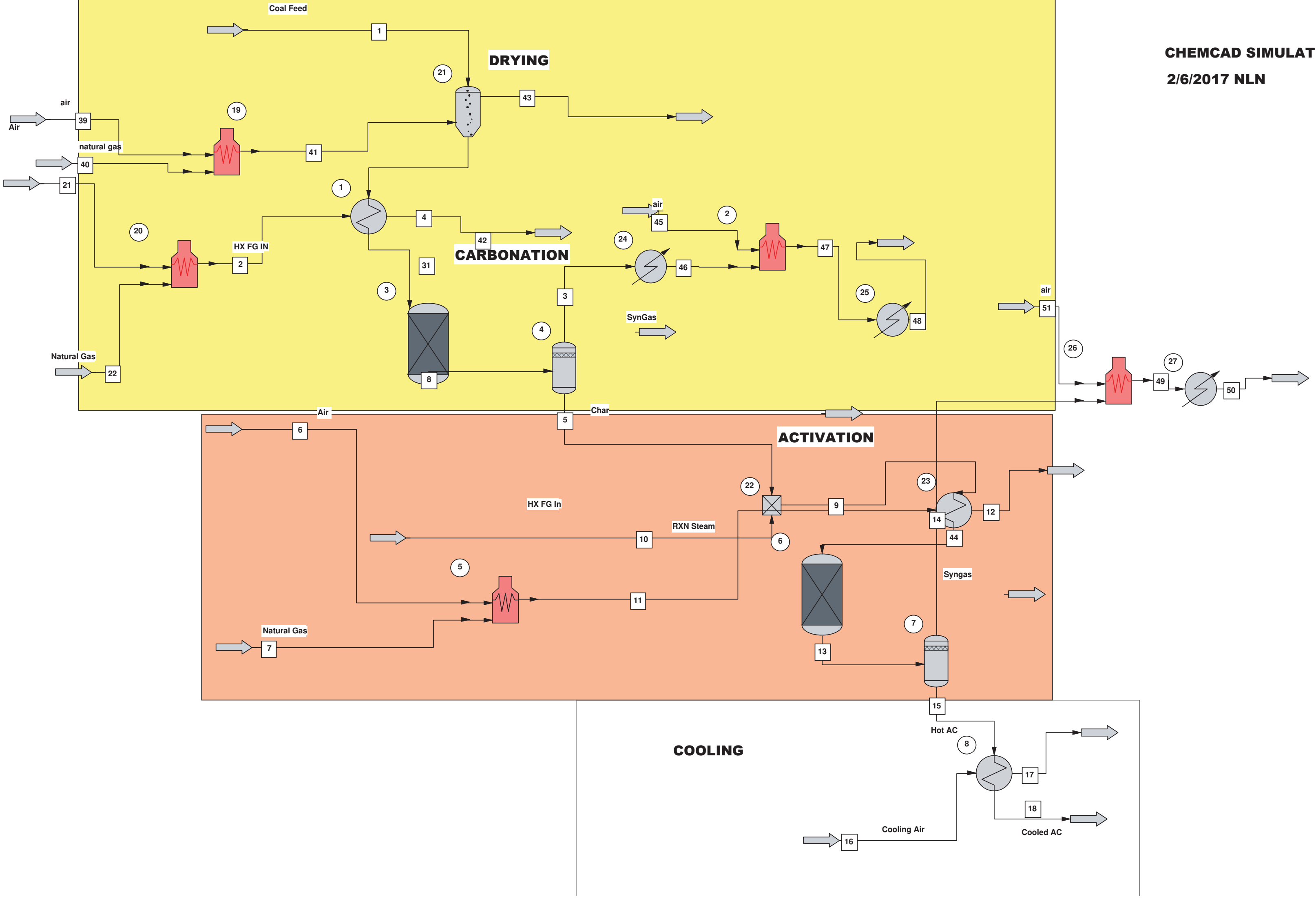
ASPEN AND LAB DATA MASS AND ENERGY BALANCE

Stream ID #	1	2	**3**	4	5	6	7	8	9	10	11
Description	Dry Coal	Indirect HX	Volatiles	Indirect HX FG	Char	Indirect HX	Rxn Steam	Syngas	Indirect HX FG	Hot AC	Cooled AC
Component Flow (lb/hr)											
O2	0	355	0	59	0	648	0	0	108	0	0
CO	0		1101	0	0		0	1086	0	0	0
H2	0		139	0	0		0	77	0	0	0
CO2	0		0	204	0		0	0	371	0	0
H2O	0		0	167	0		713	17	304	0	0
CH4	0	74	0	0	0	135	0	0	0	0	0
N2	0	1169	0	1169	0	2133	0	0	2133	0	0
H2S	0		27	0	0		0	0	0	0	0
C6H6	0		240	0	0		0	0	0	0	0
HCN	0		30	0	0		0	0	0	0	0
COAL	3772		0	0	0		0	0	0	0	0
CHAR	0		0	0	2236		0	0	0	0	0
ACT-CARB	0		0	0	0		0	0	0	1769	1769
Total Flow lb/hr	**3772**	**1598**	**1537**	**1598**	**2236**	**2916**	**713**	**1181**	**2916**	**1769**	**1769**
Temperature (°F)	77		1112	3620	1112		345	1652	3620	1652	200
Pressure (psia)	14.7		14.7	15	14.7		125	14.7	15	14.7	14.7
Vapor Frac	0		1	1	0		1	1	1	0	0
Proximate Analysis											
Moisture	0				0					0	0
FC	40.9				69.4					61.4	61.4
VM	41				0					0	0
Ash	18				30.6					38.6	38.6
Ultimate Analysis											
Ash	18.1				30.2					38.1	38.1
Carbon	59.4				68.5					60.5	60.5
Hydrogen	4.2				0					0	0
Nitrogen	0.8				0.7					0.7	0.7
Chlorine	0				0					0	0
Sulfur	1.1				0.7					0.7	0.7
Oxygen	16.4				0					0	0



CHEMCAD SIMULATION NO WASTE HEAT

2/6/2017 NLN



Report Output - No Waste Heat Recovery Considered

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CHEMCAD 6.5.1                                              Page 1

Simulation: Carbonation_Activation Simu  Date: 02/06/2017  Time: 12:49:46
STREAM PROPERTIES

Stream No.                     22             2            31             7
       Name           Natural Gas      HX FG IN                 Natural Gas
- - Overall - -
Molar flow lbmol/h         4.1390       56.5141       42.2556        4.3337
Mass flow  lb/h           74.0000     1573.9957     3772.0000       80.0000
Temp F                    70.0000     3238.3274     1100.0000       70.0000
Pres psia                 14.7000       15.0000       15.0000       14.7000
Vapor mole fraction         1.000         1.000        0.0000         1.000
Enth MMBtu/h             -0.13647      -0.16800       -35.874      -0.14577
Tc F                     -77.3768      -93.1481        0.0000      -62.7940
Pc psia                  837.5237      443.7213        0.0000      979.3206
Std. sp gr.  wtr = 1        0.316         0.830         1.209         0.327
Std. sp gr.  air = 1        0.617         0.962         3.082         0.637
Degree API               316.5435       38.9462      -14.4169      300.9711
Heating values (60 F)
  Gross Btu/lbmol      4.207E+005         247.4   -1.060E+005    4.321E+005
  Net   Btu/lbmol      3.800E+005        -2719.   -1.130E+005    3.906E+005
Average mol wt            17.8789       27.8514       89.2663       18.4601
Actual dens lb/ft3         0.0464        0.0105       75.4468        0.0479
Actual vol ft3/hr       1596.1232   149510.1094       49.9955     1671.0093
Std liq  ft3/hr            3.7533       30.3708       49.9955        3.9166
Std vap 60F scfh        1570.6443    21445.9063    16035.0879     1644.5361
- - Vapor only - -
Molar flow lbmol/h         4.1390       56.5141                      4.3337
Mass flow  lb/h           74.0000     1573.9957                     80.0000
Enth MMBtu/h             -0.13647      -0.16800                    -0.14577
Entropy    MMBtu/R/h  -8.931E-005     0.0008876                 -9.912E-005
Average mol wt            17.8789       27.8514                     18.4601
Actual dens lb/ft3         0.0464        0.0105                      0.0479
Actual vol ft3/hr       1596.1232   149510.1094                   1671.0093
Std liq  ft3/hr            3.7533       30.3708                      3.9166
Std vap 60F scfh        1570.6443    21445.9063                   1644.5361
Cp Btu/lbmol-F             9.0878        9.8087                      9.3323
Cp/Cv                      1.2839        1.2581                      1.2746
Cp/Cv  ideal               1.2798        1.2540                      1.2705
Z factor                   0.9974        1.0001                      0.9973
Visc cP                   0.01072       0.06681                     0.01065
Th cond Btu/hr-ft-F        0.0181        0.0787                      0.0180
- - Liquid only - -
Molar flow lbmol/h
Mass flow  lb/h
Average mol wt
Actual dens lb/ft3
Actual vol ft3/hr
Std liq  ft3/hr
Std vap 60F scfh
Cp Btu/lbmol-F
H latent Btu/lbmol
```

Report Output - No Waste Heat
Recovery Considered

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CHEMCAD 6.5.1                                                 Page 3

Simulation: Carbonation_Activation Simu  Date: 02/06/2017  Time: 12:49:46
STREAM PROPERTIES

Stream No.                         8             13             15             16
       Name                                                 Hot AC    Cooling Air
- - Overall - -
Molar flow lbmol/h          211.5960       176.4733        98.5273       566.4956
Mass flow  lb/h            3771.9565      2905.8748      1729.6633      9600.0000
Temp F                     1100.0000      1652.0000      1652.0000        70.0000
Pres psia                    15.0000        15.0000        15.0000        14.7000
Vapor mole fraction            1.000          1.000         0.0000          1.000
Enth MMBtu/h                 -5.6097        -4.7017        -3.6485      -0.014194
Tc F                       -233.5123      -285.3842         0.0000      -224.2532
Pc psia                     649.2445       563.0146         0.0000       519.3723
Std. sp gr.  wtr = 1           1.139          0.945          2.946          1.244
Std. sp gr.  air = 1           0.615          0.569          0.606          0.585
Degree API                   -7.2252        18.1755       -83.4688       -17.7131
Heating values (60 F)
  Gross Btu/lbmol          1.448E+005     1.370E+005     1.497E+005     1.193E+005
  Net   Btu/lbmol          1.426E+005     1.327E+005     1.497E+005     1.193E+005
Average mol wt               17.8262        16.4664        17.5552        16.9463
Actual dens lb/ft3            0.0454         0.0247       183.9125         0.1488
Actual vol ft3/hr         83156.7031    117775.6875         9.4048     64508.5117
Std liq  ft3/hr              53.0658        49.2371         9.4048       123.6598
Std vap 60F scfh          80296.1484     66967.8516     37389.0039    214972.9688
- - Vapor only - -
Molar flow lbmol/h           74.5024        77.9460                      166.8619
Mass flow  lb/h            1579.0745      1176.2115                     4800.0005
Enth MMBtu/h                 -1.7852        -1.0532                    -0.0086374
Entropy    MMBtu/R/h        0.001761       0.001692                     0.0001445
Average mol wt               21.1949        15.0901                       28.7663
Actual dens lb/ft3            0.0190         0.0100                        0.0744
Actual vol ft3/hr         83144.0000    117766.2813                    64474.3398
Std liq  ft3/hr              40.3632        39.8323                       89.4873
Std vap 60F scfh          28272.0859     29578.8457                    63320.5195
Cp Btu/lbmol-F                7.7469         7.8255                        6.9763
Cp/Cv                         1.3449         1.3401                        1.4006
Cp/Cv  ideal                  1.3450         1.3403                        1.3983
Z factor                      1.0003         1.0002                        0.9994
Visc cP                      0.03640        0.04304                       0.01807
Th cond Btu/hr-ft-F           0.0623         0.1179                        0.0146
- - Liquid only - -
Molar flow lbmol/h
Mass flow  lb/h
Average mol wt
Actual dens lb/ft3
Actual vol ft3/hr
Std liq  ft3/hr
Std vap 60F scfh
Cp Btu/lbmol-F
H latent Btu/lbmol
```

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CHEMCAD 6.5.1                                                  Page 5

Simulation: Carbonation_Activation Simu  Date: 02/06/2017  Time: 12:49:46
STREAM PROPERTIES

Stream No.                       17            18            40            41
       Name                              Cooled AC   natural gas
- - Overall - -
Molar flow lbmol/h         566.4956       98.5273        5.5936       75.4487
Mass flow  lb/h           9600.0000     1729.6633      100.0000     2099.9944
Temp F                     405.9112      200.0000       70.0000     3265.4199
Pres psia                   14.7000       15.0000       14.7000       15.0000
Vapor mole fraction           1.000        0.0000         1.000         1.000
Enth MMBtu/h                0.74544       -4.4081      -0.18443      -0.22645
Tc F                      -224.2532        0.0000      -77.4006      -91.7247
Pc psia                    519.3723        0.0000      837.4369      442.4066
Std. sp gr.  wtr = 1          1.244         2.946         0.316         0.830
Std. sp gr.  air = 1          0.585         0.606         0.617         0.961
Degree API                 -17.7131      -83.4688      316.5573       39.0280
Heating values (60 F)
  Gross Btu/lbmol         1.193E+005    1.497E+005    4.206E+005         301.7
  Net   Btu/lbmol         1.193E+005    1.497E+005    3.799E+005        -2701.
Average mol wt              16.9463       17.5552       17.8777       27.8334
Actual dens lb/ft3           0.0910      183.9125        0.0464        0.0104
Actual vol ft3/hr       105473.5469        9.4048     2157.0676   201064.2813
Std liq  ft3/hr            123.6598        9.4048        5.0722       40.5395
Std vap 60F scfh        214972.9688    37389.0039     2122.6338    28631.1621
- - Vapor only - -
Molar flow lbmol/h         166.8619                      5.5936       75.4487
Mass flow  lb/h           4800.0005                    100.0000     2099.9944
Enth MMBtu/h                0.38528                    -0.18443      -0.22645
Entropy    MMBtu/R/h      0.0007200                  -0.0001207      0.001190
Average mol wt              28.7663                     17.8777       27.8334
Actual dens lb/ft3           0.0455                      0.0464        0.0104
Actual vol ft3/hr       105439.3750                   2157.0676   201064.2813
Std liq  ft3/hr             89.4873                      5.0722       40.5395
Std vap 60F scfh         63320.5195                   2122.6338    28631.1621
Cp Btu/lbmol-F               7.1122                      9.0839        9.8321
Cp/Cv                        1.3882                      1.2839        1.2574
Cp/Cv  ideal                 1.3877                      1.2800        1.2533
Z factor                     1.0001                      0.9974        1.0001
Visc cP                     0.02607                     0.01073       0.06711
Th cond Btu/hr-ft-F          0.0220                      0.0181        0.0794
- - Liquid only - -
Molar flow lbmol/h
Mass flow  lb/h
Average mol wt
Actual dens lb/ft3
Actual vol ft3/hr
Std liq  ft3/hr
Std vap 60F scfh
Cp Btu/lbmol-F
H latent Btu/lbmol
```

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CHEMCAD 6.5.1                                 Page 7

Simulation: Carbonation_Activation Simu  Date: 02/06/2017  Time: 12:49:46
STREAM PROPERTIES

Stream No.                      1            42            43             4
       Name             Coal Feed
- - Overall - -
Molar flow lbmol/h       131.9586       42.2556      165.1517       56.5141
Mass flow  lb/h         5388.0000     3772.0000     3715.9944     1573.9957
Temp F                    77.0000       77.0000      391.2752     1143.5909
Pres psia                 14.7000       15.0000       15.0000       15.0000
Vapor mole fraction        0.0000        0.0000         1.000         1.000
Enth MMBtu/h              -47.993       -36.962       -11.257       -1.2561
Tc F                     705.5600        0.0000      283.7222      -93.1481
Pc psia                 3207.9768        0.0000      814.3447      443.7213
Std. sp gr.  wtr = 1        1.137         1.209         0.896         0.830
Std. sp gr.  air = 1        1.410         3.082         0.777         0.962
Degree API                -7.0936      -14.4169       26.4044       38.9462
Heating values (60 F)
  Gross Btu/lbmol     -3.394E+004   -1.060E+005         137.8         247.4
  Net   Btu/lbmol     -4.910E+004   -1.130E+005   -1.156E+004        -2719.
Average mol wt            40.8310       89.2663       22.5005       27.8514
Actual dens lb/ft3        70.9257       75.4468        0.0371        0.0243
Actual vol ft3/hr         75.9668       49.9955   100293.3359    64823.5703
Std liq  ft3/hr           75.8814       49.9955       66.4254       30.3708
Std vap 60F scfh       50075.4688    16035.0879    62671.5469    21445.9063
- - Vapor only - -
Molar flow lbmol/h                                   165.1517       56.5141
Mass flow  lb/h                                     3715.9944     1573.9957
Enth MMBtu/h                                          -11.257       -1.2561
Entropy    MMBtu/R/h                               -0.0003258     0.0004582
Average mol wt                                        22.5005       27.8514
Actual dens lb/ft3                                     0.0371        0.0243
Actual vol ft3/hr                                 100293.3359    64823.5703
Std liq  ft3/hr                                       66.4254       30.3708
Std vap 60F scfh                                   62671.5469    21445.9063
Cp Btu/lbmol-F                                         8.0176        8.3579
Cp/Cv                                                  1.3337        1.3116
Cp/Cv  ideal                                           1.3295        1.3119
Z factor                                               0.9977        1.0001
Visc cP                                               0.01972       0.03793
Th cond Btu/hr-ft-F                                    0.0205        0.0377
- - Liquid only - -
Molar flow lbmol/h        89.7030
Mass flow  lb/h         1616.0000
Average mol wt            18.0150
Actual dens lb/ft3        62.2225
Actual vol ft3/hr         25.9713
Std liq  ft3/hr           25.8859
Std vap 60F scfh       34040.3789
Cp Btu/lbmol-F            18.0156
H latent Btu/lbmol     1.886E+004
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CHEMCAD 6.5.1                                                 Page 9

Simulation: Carbonation_Activation Simu  Date: 02/06/2017  Time: 12:49:46
STREAM PROPERTIES

Stream No.                         6             21             39             10
       Name                      Air            Air            air      RXN Steam
- - Overall - -
Molar flow lbmol/h           55.4570        52.0470        69.3960        39.5781
Mass flow  lb/h            1600.0000      1500.0001      2000.0001       713.0000
Temp F                       70.0000        70.0000        70.0000       345.0000
Pres psia                    14.7000        14.7000        14.7000       125.0000
Vapor mole fraction            1.000          1.000          1.000          1.000
Enth MMBtu/h              -0.0028718      -0.031529      -0.042039        -4.0496
Tc F                       -223.2866      -223.1023      -223.1023       705.5600
Pc psia                     522.8154       522.5015       522.5013      3207.9768
Std. sp gr.  wtr = 1           0.865          0.859          0.859          1.000
Std. sp gr.  air = 1           0.996          0.995          0.995          0.622
Degree API                   32.0441        33.1654        33.1654        10.0000
Heating values (60 F)
  Gross Btu/lbmol
  Net   Btu/lbmol                                                    -1.901E+004
Average mol wt               28.8512        28.8201        28.8201        18.0150
Actual dens lb/ft3            0.0747         0.0746         0.0746         0.2753
Actual vol ft3/hr         21428.0254     20110.4512     26813.9375      2589.6172
Std liq  ft3/hr              29.6224        27.9614        37.2819        11.4212
Std vap 60F scfh          21044.7324     19750.7344     26334.3145     15019.0527
- - Vapor only - -
Molar flow lbmol/h           55.4570        52.0470        69.3960        39.5781
Mass flow  lb/h            1600.0000      1500.0001      2000.0001       713.0000
Enth MMBtu/h              -0.0028718      -0.031529      -0.042039        -4.0496
Entropy    MMBtu/R/h       5.127E-005     4.743E-005     6.324E-005     -0.0004725
Average mol wt               28.8512        28.8201        28.8201        18.0150
Actual dens lb/ft3            0.0747         0.0746         0.0746         0.2753
Actual vol ft3/hr         21428.0254     20110.4512     26813.9375      2589.6172
Std liq  ft3/hr              29.6224        27.9614        37.2819        11.4212
Std vap 60F scfh          21044.7324     19750.7344     26334.3145     15019.0527
Cp Btu/lbmol-F                6.9773         6.9826         6.9826        11.1016
Cp/Cv                         1.4005         1.4001         1.4001         1.3899
Cp/Cv  ideal                  1.3982         1.3978         1.3978         1.2180
Z factor                      0.9994         0.9994         0.9994         0.9473
Visc cP                      0.01813        0.01806        0.01806        0.01530
Th cond Btu/hr-ft-F           0.0146         0.0146         0.0146         0.0186
- - Liquid only - -
Molar flow lbmol/h
Mass flow  lb/h
Average mol wt
Actual dens lb/ft3
Actual vol ft3/hr
Std liq  ft3/hr
Std vap 60F scfh
Cp Btu/lbmol-F
H latent Btu/lbmol
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CHEMCAD 6.5.1                                            Page 11

Simulation: Carbonation_Activation Simu  Date: 02/06/2017  Time: 12:49:46
STREAM PROPERTIES

Stream No.                     11             5             9            44
       Name              HX FG In          Char      Hot Char
- - Overall - -
Molar flow lbmol/h        60.2110      137.0935      176.6716      176.6716
Mass flow  lb/h         1679.9955     2192.8821     2905.8818     2905.8818
Temp F                  3272.2520     1100.0000      843.4540     1652.0000
Pres psia                 15.0000       15.0000       15.0000       15.0000
Vapor mole fraction         1.000        0.0000         1.000         1.000
Enth MMBtu/h             -0.14864       -3.8245       -7.8741       -6.9431
Tc F                     -92.0083        0.0000      705.5600      705.5600
Pc psia                  450.4546        0.0000     3207.9768     3207.9768
Std. sp gr.  wtr = 1        0.835         2.765         1.930         1.930
Std. sp gr.  air = 1        0.963         0.552         0.568         0.568
Degree API                37.9467      -80.3304      -58.1665      -58.1665
Heating values (60 F)
  Gross Btu/lbmol           190.5    1.552E+005    1.204E+005    1.204E+005
  Net   Btu/lbmol          -2781.    1.552E+005    1.161E+005    1.161E+005
Average mol wt            27.9018       15.9955       16.4479       16.4479
Actual dens lb/ft3         0.0105      172.6326        0.0788        0.0486
Actual vol ft3/hr     160751.3438       12.7026    36862.4141    59783.7656
Std liq  ft3/hr           32.2260       12.7026       24.1238       24.1238
Std vap 60F scfh       22848.7988    52024.0625    67043.1094    67043.1094
- - Vapor only - -
Molar flow lbmol/h        60.2110                     39.5781       39.5781
Mass flow  lb/h         1679.9955                    713.0000      713.0000
Enth MMBtu/h             -0.14864                     -3.8625       -3.5537
Entropy    MMBtu/R/h    0.0009573                  -0.0001251    5.827E-005
Average mol wt            27.9018                     18.0150       18.0150
Actual dens lb/ft3         0.0105                      0.0193        0.0119
Actual vol ft3/hr     160751.3438                  36849.7109    59771.0625
Std liq  ft3/hr           32.2260                     11.4212       11.4212
Std vap 60F scfh       22848.7988                  15019.0527    15019.0527
Cp Btu/lbmol-F             9.8258                      8.9922       10.3281
Cp/Cv                      1.2577                      1.2836        1.2371
Cp/Cv  ideal               1.2535                      1.2836        1.2382
Z factor                   1.0001                      0.9988        0.9998
Visc cP                   0.06743                     0.02654       0.04429
Th cond Btu/hr-ft-F        0.0795                      0.0352        0.0707
- - Liquid only - -
Molar flow lbmol/h
Mass flow  lb/h
Average mol wt
Actual dens lb/ft3
Actual vol ft3/hr
Std liq  ft3/hr
Std vap 60F scfh
Cp Btu/lbmol-F
H latent Btu/lbmol
```

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CHEMCAD 6.5.1                                                Page 13

Simulation: Carbonation_Activation Simu  Date: 02/06/2017  Time: 12:49:46
STREAM PROPERTIES

Stream No.                    45             3            46            47
       Name                  air        SynGas
- - Overall - -
Molar flow lbmol/h     1040.8202       74.5024       74.5024     1082.8016
Mass flow  lb/h       30000.0000     1579.0745     1579.0745    31579.0898
Temp F                   70.0000     1100.0000      800.0001     1164.4694
Pres psia                14.7000       15.0000       15.0000       15.0000
Vapor mole fraction        1.000         1.000         1.000         1.000
Enth MMBtu/h            -0.63289       -1.7852       -1.9554       -2.5881
Tc F                   -223.0622     -233.5123     -233.5123     -182.0301
Pc psia                 522.6411      649.2445      649.2445      621.4660
Std. sp gr.  wtr = 1       0.860         0.627         0.627         0.853
Std. sp gr.  air = 1       0.995         0.732         0.732         1.007
Degree API               33.1235       94.2968       94.2968       34.4446
Heating values (60 F)
  Gross Btu/lbmol                    1.257E+005    1.257E+005         366.7
  Net   Btu/lbmol                    1.194E+005    1.194E+005        -63.72
Average mol wt           28.8234       21.1949       21.1949       29.1642
Actual dens lb/ft3        0.0746        0.0190        0.0235        0.0251
Actual vol ft3/hr    402162.3438    83144.0000    67153.4219  1258260.5000
Std liq  ft3/hr         559.0853       40.3632       40.3632      593.2365
Std vap 60F scfh     394969.0000    28272.0859    28272.0859   410900.0625
- - Vapor only - -
Molar flow lbmol/h     1040.8202       74.5024       74.5024     1082.8016
Mass flow  lb/h       30000.0000     1579.0745     1579.0745    31579.0898
Enth MMBtu/h            -0.63289       -1.7852       -1.9554       -2.5881
Entropy    MMBtu/R/h   0.0009511      0.001761      0.001640       0.01013
Average mol wt           28.8234       21.1949       21.1949       29.1642
Actual dens lb/ft3        0.0746        0.0190        0.0235        0.0251
Actual vol ft3/hr    402162.3438    83144.0000    67153.4219  1258260.5000
Std liq  ft3/hr         559.0853       40.3632       40.3632      593.2365
Std vap 60F scfh     394969.0000    28272.0859    28272.0859   410900.0625
Cp Btu/lbmol-F            6.9827        7.7469        7.4837        8.0070
Cp/Cv                     1.4001        1.3449        1.3615        1.3300
Cp/Cv  ideal              1.3977        1.3450        1.3615        1.3301
Z factor                  0.9994        1.0003        1.0003        1.0002
Visc cP                  0.01806       0.03640       0.03161       0.03954
Th cond Btu/hr-ft-F       0.0146        0.0623        0.0532        0.0366
- - Liquid only - -
Molar flow lbmol/h
Mass flow  lb/h
Average mol wt
Actual dens lb/ft3
Actual vol ft3/hr
Std liq  ft3/hr
Std vap 60F scfh
Cp Btu/lbmol-F
H latent Btu/lbmol
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CHEMCAD 6.5.1                                             Page 15

Simulation: Carbonation_Activation Simu  Date: 02/06/2017  Time: 12:49:46
STREAM PROPERTIES

Stream No.                     48            49            51            12
       Name                                               air
- - Overall - -
Molar flow lbmol/h      1082.8016     1184.6128     1145.0347       60.2110
Mass flow  lb/h        31579.0898    34176.2227    33000.0000     1679.9955
Temp F                   500.0000     1153.1973       70.0000     1623.5328
Pres psia                 15.0000       15.0000       14.7000       15.0000
Vapor mole fraction         1.000         1.000         1.000         1.000
Enth MMBtu/h              -8.1166       -1.7468      -0.69364       -1.0797
Tc F                    -182.0301     -190.2791     -223.1023      -92.0083
Pc psia                  621.4660      524.6246      522.5013      450.4546
Std. sp gr.  wtr = 1        0.853         0.853         0.859         0.835
Std. sp gr.  air = 1        1.007         0.996         0.995         0.963
Degree API                34.4446       34.4160       33.1654       37.9467
Heating values (60 F)
  Gross Btu/lbmol           366.7    2.701E-005                       190.5
  Net   Btu/lbmol          -63.72        -635.0                      -2781.
Average mol wt            29.1642       28.8501       28.8201       27.9018
Actual dens lb/ft3         0.0425        0.0250        0.0746        0.0187
Actual vol ft3/hr     743410.1875  1367014.8750   442429.9375    89738.7891
Std liq  ft3/hr          593.2365      641.9146      615.1505       32.2260
Std vap 60F scfh      410900.0625   449535.2188   434516.1875    22848.7988
- - Vapor only - -
Molar flow lbmol/h      1082.8016     1184.6128     1145.0347       60.2110
Mass flow  lb/h        31579.0898    34176.2227    33000.0000     1679.9955
Enth MMBtu/h              -8.1166       -1.7468      -0.69364       -1.0797
Entropy    MMBtu/R/h     0.005769       0.01079      0.001044     0.0006296
Average mol wt            29.1642       28.8501       28.8201       27.9018
Actual dens lb/ft3         0.0425        0.0250        0.0746        0.0187
Actual vol ft3/hr     743410.1875  1367014.8750   442429.9375    89738.7891
Std liq  ft3/hr          593.2365      641.9146      615.1505       32.2260
Std vap 60F scfh      410900.0625   449535.2188   434516.1875    22848.7988
Cp Btu/lbmol-F             7.3583        7.9781        6.9826        8.8244
Cp/Cv                      1.3703        1.3316        1.4001        1.2902
Cp/Cv  ideal               1.3699        1.3317        1.3978        1.2906
Z factor                   1.0001        1.0002        0.9994        1.0001
Visc cP                   0.02743       0.03952       0.01806       0.04572
Th cond Btu/hr-ft-F        0.0236        0.0367        0.0146        0.0478
- - Liquid only - -
Molar flow lbmol/h
Mass flow  lb/h
Average mol wt
Actual dens lb/ft3
Actual vol ft3/hr
Std liq  ft3/hr
Std vap 60F scfh
Cp Btu/lbmol-F
H latent Btu/lbmol
```

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CHEMCAD 6.5.1                                             Page 17

Simulation: Carbonation_Activation Simu  Date: 02/06/2017  Time: 12:49:46
STREAM PROPERTIES

Stream No.                     14
       Name                Syngas
- - Overall - -
Molar flow lbmol/h        77.9460
Mass flow  lb/h         1176.2115
Temp F                  1652.0000
Pres psia                 15.0000
Vapor mole fraction         1.000
Enth MMBtu/h              -1.0532
Tc F                    -285.3842
Pc psia                  563.0146
Std. sp gr.  wtr = 1        0.473
Std. sp gr.  air = 1        0.521
Degree API               167.6472
Heating values (60 F)
  Gross Btu/lbmol      1.210E+005
  Net   Btu/lbmol      1.113E+005
Average mol wt            15.0901
Actual dens lb/ft3         0.0100
Actual vol ft3/hr     117766.2813
Std liq  ft3/hr           39.8323
Std vap 60F scfh       29578.8457
- - Vapor only - -
Molar flow lbmol/h        77.9460
Mass flow  lb/h         1176.2115
Enth MMBtu/h              -1.0532
Entropy    MMBtu/R/h     0.001692
Average mol wt            15.0901
Actual dens lb/ft3         0.0100
Actual vol ft3/hr     117766.2813
Std liq  ft3/hr           39.8323
Std vap 60F scfh       29578.8457
Cp Btu/lbmol-F             7.8255
Cp/Cv                      1.3401
Cp/Cv  ideal               1.3403
Z factor                   1.0002
Visc cP                   0.04304
Th cond Btu/hr-ft-F        0.1179
- - Liquid only - -
Molar flow lbmol/h
Mass flow  lb/h
Average mol wt
Actual dens lb/ft3
Actual vol ft3/hr
Std liq  ft3/hr
Std vap 60F scfh
Cp Btu/lbmol-F
H latent Btu/lbmol
```
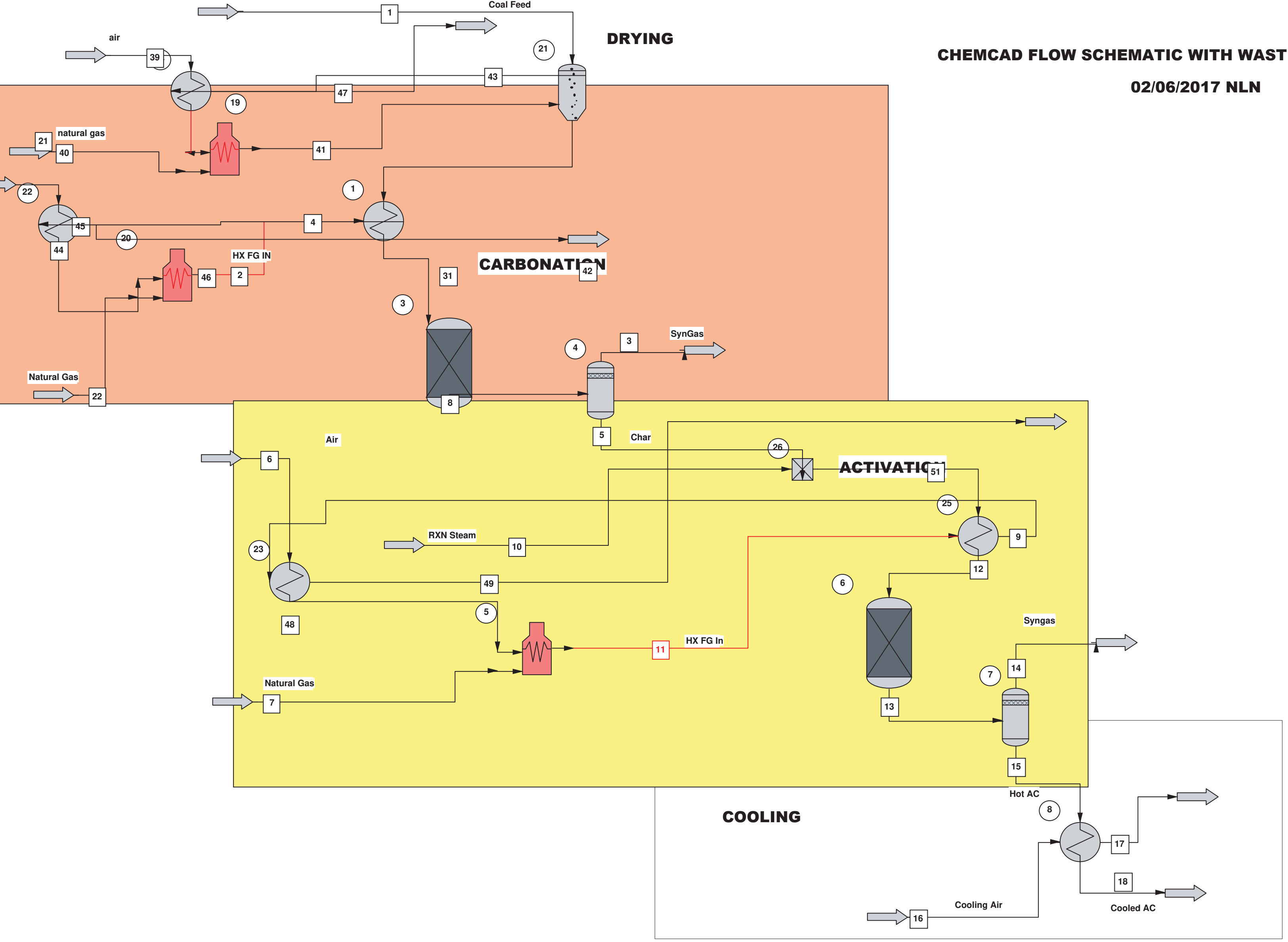

CHEMCAD FLOW SCHEMATIC WITH WASTE HEAT RECOVERY

02/06/2017 NLN



Report Output - Including Waste
Heat Recovery

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CHEMCAD 6.5.1                                              Page 1

Simulation: Carbonation_Activation Simu  Date: 02/06/2017  Time: 12:59:45
STREAM PROPERTIES

Stream No.                     22             2             3            31
       Name           Natural Gas      HX FG IN        SynGas
- - Overall - -
Molar flow lbmol/h         3.3559       45.6280       74.5024       42.2556
Mass flow  lb/h           60.0000     1259.9965     1579.0745     3772.0000
Temp F                    70.0000     3918.7314     1100.0000     1100.0000
Pres psia                 14.7000       15.0000       15.0000       15.0000
Vapor mole fraction         1.000         1.000         1.000        0.0000
Enth MMBtu/h             -0.11065       0.24209       -1.7852       -35.874
Tc F                     -77.3768      -99.5098     -233.5123        0.0000
Pc psia                  837.5237      439.2276      649.2445        0.0000
Std. sp gr.  wtr = 1        0.316         0.829         0.627         1.209
Std. sp gr.  air = 1        0.617         0.953         0.732         3.082
Degree API               316.5435       39.2577       94.2968      -14.4169
Average mol wt            17.8789       27.6146       21.1949       89.2663
Actual dens lb/ft3         0.0464        0.0088        0.0190       75.4468
Actual vol ft3/hr       1294.1545   142917.1875    83144.0000       49.9955
Std liq  ft3/hr            3.0432       24.3565       40.3632       49.9955
Std vap 60F scfh        1273.4958    17314.8359    28272.0859    16035.0879
- - Vapor only - -
Molar flow lbmol/h         3.3559       45.6280       74.5024
Mass flow  lb/h           60.0000     1259.9965     1579.0745
Average mol wt            17.8789       27.6146       21.1949
Actual dens lb/ft3         0.0464        0.0088        0.0190
Actual vol ft3/hr       1294.1545   142917.1875    83144.0000
Std liq  ft3/hr            3.0432       24.3565       40.3632
Std vap 60F scfh        1273.4958    17314.8359    28272.0859
Cp Btu/lbmol-F             9.0878       10.0060        7.7469
Cp/Cv                      1.2839        1.2552        1.3449
Cp/Cv  ideal               1.2798        1.2478        1.3450
Z factor                   0.9974        1.0001        1.0003
Visc cP                   0.01072       0.07448       0.03640
Th cond Btu/hr-ft-F        0.0181        0.0917        0.0623
- - Liquid only - -
Molar flow lbmol/h
Mass flow  lb/h
Average mol wt
Actual dens lb/ft3
Actual vol ft3/hr
Std liq  ft3/hr
Std vap 60F scfh
Cp Btu/lbmol-F
Z factor
Visc cP
Th cond Btu/hr-ft-F
Surf. tens. dyne/cm
```

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CHEMCAD 6.5.1                                                Page 2

Simulation: Carbonation_Activation Simu  Date: 02/06/2017  Time: 12:59:45
STREAM PROPERTIES

Stream No.                         7             8            13            14
       Name              Natural Gas                                    Syngas
- - Overall - -
Molar flow lbmol/h            2.7085      211.5960      176.4733       77.9460
Mass flow  lb/h              50.0000     3771.9565     2905.8748     1176.2115
Temp F                       70.0000     1100.0000     1652.0000     1652.0000
Pres psia                    14.7000       15.0000       15.0000       15.0000
Vapor mole fraction            1.000         1.000         1.000         1.000
Enth MMBtu/h               -0.091108       -5.6097       -4.7017       -1.0532
Tc F                        -62.7940     -233.5123     -285.3842     -285.3842
Pc psia                     979.3203      649.2445      563.0146      563.0146
Std. sp gr.  wtr = 1           0.327         1.139         0.945         0.473
Std. sp gr.  air = 1           0.637         0.615         0.569         0.521
Degree API                  300.9712       -7.2252       18.1755      167.6472
Average mol wt               18.4601       17.8262       16.4664       15.0901
Actual dens lb/ft3            0.0479        0.0454        0.0247        0.0100
Actual vol ft3/hr          1044.3806    83156.7031   117775.6875   117766.2813
Std liq  ft3/hr               2.4479       53.0658       49.2371       39.8323
Std vap 60F scfh           1027.8350    80296.1484    66967.8516    29578.8457
- - Vapor only - -
Molar flow lbmol/h            2.7085       74.5024       77.9460       77.9460
Mass flow  lb/h              50.0000     1579.0745     1176.2115     1176.2115
Average mol wt               18.4601       21.1949       15.0901       15.0901
Actual dens lb/ft3            0.0479        0.0190        0.0100        0.0100
Actual vol ft3/hr          1044.3806    83144.0000   117766.2813   117766.2813
Std liq  ft3/hr               2.4479       40.3632       39.8323       39.8323
Std vap 60F scfh           1027.8350    28272.0859    29578.8457    29578.8457
Cp Btu/lbmol-F                9.3323        7.7469        7.8255        7.8255
Cp/Cv                         1.2746        1.3449        1.3401        1.3401
Cp/Cv  ideal                  1.2705        1.3450        1.3403        1.3403
Z factor                      0.9973        1.0003        1.0002        1.0002
Visc cP                      0.01065       0.03640       0.04304       0.04304
Th cond Btu/hr-ft-F           0.0180        0.0623        0.1179        0.1179
- - Liquid only - -
Molar flow lbmol/h
Mass flow  lb/h
Average mol wt
Actual dens lb/ft3
Actual vol ft3/hr
Std liq  ft3/hr
Std vap 60F scfh
Cp Btu/lbmol-F
Z factor
Visc cP
Th cond Btu/hr-ft-F
Surf. tens. dyne/cm
```

Report Output - Including Waste
Heat Recovery

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CHEMCAD 6.5.1                                                 Page 3

Simulation: Carbonation_Activation Simu  Date: 02/06/2017  Time: 12:59:45
STREAM PROPERTIES

Stream No.                         15            16            17            18
       Name                    Hot AC   Cooling Air                    Cooled AC
- - Overall - -
Molar flow lbmol/h            98.5273      566.4956      566.4956       98.5273
Mass flow  lb/h             1729.6633     9600.0000     9600.0000     1729.6633
Temp F                      1652.0000       70.0000      405.9112      200.0000
Pres psia                     15.0000       14.7000       14.7000       15.0000
Vapor mole fraction            0.0000         1.000         1.000        0.0000
Enth MMBtu/h                  -3.6485     -0.014194       0.74544       -4.4081
Tc F                           0.0000     -224.2532     -224.2532        0.0000
Pc psia                        0.0000      519.3723      519.3723        0.0000
Std. sp gr.  wtr = 1            2.946         1.244         1.244         2.946
Std. sp gr.  air = 1            0.606         0.585         0.585         0.606
Degree API                   -83.4688      -17.7131      -17.7131      -83.4688
Average mol wt                17.5552       16.9463       16.9463       17.5552
Actual dens lb/ft3           183.9125        0.1488        0.0910      183.9125
Actual vol ft3/hr              9.4048    64508.5117   105473.5469        9.4048
Std liq  ft3/hr                9.4048      123.6598      123.6598        9.4048
Std vap 60F scfh           37389.0039   214972.9688   214972.9688    37389.0039
- - Vapor only - -
Molar flow lbmol/h                         166.8619      166.8619
Mass flow  lb/h                           4800.0005     4800.0005
Average mol wt                              28.7663       28.7663
Actual dens lb/ft3                           0.0744        0.0455
Actual vol ft3/hr                        64474.3398   105439.3750
Std liq  ft3/hr                             89.4873       89.4873
Std vap 60F scfh                         63320.5195    63320.5195
Cp Btu/lbmol-F                               6.9763        7.1122
Cp/Cv                                        1.4006        1.3882
Cp/Cv  ideal                                 1.3983        1.3877
Z factor                                     0.9994        1.0001
Visc cP                                     0.01807       0.02607
Th cond Btu/hr-ft-F                          0.0146        0.0220
- - Liquid only - -
Molar flow lbmol/h
Mass flow  lb/h
Average mol wt
Actual dens lb/ft3
Actual vol ft3/hr
Std liq  ft3/hr
Std vap 60F scfh
Cp Btu/lbmol-F
Z factor
Visc cP
Th cond Btu/hr-ft-F
Surf. tens. dyne/cm
```

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CHEMCAD 6.5.1                                              Page 4

Simulation: Carbonation_Activation Simu  Date: 02/06/2017  Time: 12:59:45
STREAM PROPERTIES

Stream No.                     33            40            41             1
       Name                         natural gas                   Coal Feed
- - Overall - -
Molar flow lbmol/h        48.6438        5.0342       67.9580      131.9586
Mass flow  lb/h         3886.4907       90.0000     1889.9946     5388.0000
Temp F                    70.0000       70.0000     3397.0405       77.0000
Pres psia                 14.7000       14.7000       15.0000       14.7000
Vapor mole fraction        0.0000         1.000         1.000        0.0000
Enth MMBtu/h              -37.750      -0.16598      -0.10307       -47.993
Tc F                     705.5600      -77.4006      -92.5179      705.5600
Pc psia                 3207.9768      837.4365      442.1274     3207.9768
Std. sp gr.  wtr = 1        1.201         0.316         0.830         1.137
Std. sp gr.  air = 1        2.759         0.617         0.960         1.410
Degree API               -13.6802      316.5573       39.0528       -7.0936
Average mol wt            79.8969       17.8777       27.8112       40.8310
Actual dens lb/ft3        74.9686        0.0464        0.0101       70.9257
Actual vol ft3/hr         51.8416     1941.3610   187500.3125       75.9668
Std liq  ft3/hr           51.8371        4.5650       36.4909       75.8814
Std vap 60F scfh       18459.2832     1910.3705    25788.5938    50075.4688
- - Vapor only - -
Molar flow lbmol/h                       5.0342       67.9580
Mass flow  lb/h                         90.0000     1889.9946
Average mol wt                          17.8777       27.8112
Actual dens lb/ft3                       0.0464        0.0101
Actual vol ft3/hr                     1941.3610   187500.3125
Std liq  ft3/hr                          4.5650       36.4909
Std vap 60F scfh                      1910.3705    25788.5938
Cp Btu/lbmol-F                           9.0878        9.8821
Cp/Cv                                    1.2839        1.2565
Cp/Cv  ideal                             1.2798        1.2517
Z factor                                 0.9974        1.0001
Visc cP                                 0.01073       0.06863
Th cond Btu/hr-ft-F                      0.0181        0.0818
- - Liquid only - -
Molar flow lbmol/h         6.4019                                   89.7030
Mass flow  lb/h          115.3309                                 1616.0000
Average mol wt            18.0150                                   18.0150
Actual dens lb/ft3        62.2789                                   62.2225
Actual vol ft3/hr          1.8518                                   25.9713
Std liq  ft3/hr            1.8474                                   25.8859
Std vap 60F scfh        2429.3982                                34040.3789
Cp Btu/lbmol-F            18.0156                                   18.0156
Z factor                   0.0009                                    0.0008
Visc cP                     1.007                                    0.9227
Th cond Btu/hr-ft-F        0.3470                                    0.3502
Surf. tens. dyne/cm       72.7749                                   72.1035
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CHEMCAD 6.5.1                                                 Page 5

Simulation: Carbonation_Activation Simu  Date: 02/06/2017  Time: 12:59:45
STREAM PROPERTIES

Stream No.                      42            21            44            45
       Name                                  Air
- - Overall - -
Molar flow lbmol/h         42.2556       41.6376       41.6376       45.6280
Mass flow  lb/h          3772.0000     1200.0000     1200.0000     1259.9965
Temp F                     77.0000       70.0000     1300.0000      339.1996
Pres psia                  15.0000       14.7000       14.7000       15.0000
Vapor mole fraction         0.0000         1.000         1.000         1.000
Enth MMBtu/h               -36.962     -0.025223       0.35273       -1.2240
Tc F                        0.0000     -223.1023     -223.1023      -99.5098
Pc psia                     0.0000      522.5015      522.5015      439.2276
Std. sp gr.  wtr = 1         1.209         0.859         0.859         0.829
Std. sp gr.  air = 1         3.082         0.995         0.995         0.953
Degree API                -14.4169       33.1654       33.1654       39.2577
Average mol wt             89.2663       28.8201       28.8201       27.6146
Actual dens lb/ft3         75.4468        0.0746        0.0224        0.0483
Actual vol ft3/hr          49.9955    16088.3623    53492.0820    26063.8203
Std liq  ft3/hr            49.9955       22.3691       22.3691       24.3565
Std vap 60F scfh        16035.0879    15800.5889    15800.5889    17314.8359
- - Vapor only - -
Molar flow lbmol/h                       41.6376       41.6376       45.6280
Mass flow  lb/h                        1200.0000     1200.0000     1259.9965
Average mol wt                           28.8201       28.8201       27.6146
Actual dens lb/ft3                        0.0746        0.0224        0.0483
Actual vol ft3/hr                     16088.3623    53492.0820    26063.8203
Std liq  ft3/hr                          22.3691       22.3691       24.3565
Std vap 60F scfh                      15800.5889    15800.5889    17314.8359
Cp Btu/lbmol-F                            6.9826        7.8943        7.4559
Cp/Cv                                     1.4001        1.3363        1.3645
Cp/Cv  ideal                              1.3978        1.3364        1.3633
Z factor                                  0.9994        1.0002        0.9996
Visc cP                                  0.01806       0.04233       0.02247
Th cond Btu/hr-ft-F                       0.0146        0.0390        0.0202
- - Liquid only - -
Molar flow lbmol/h
Mass flow  lb/h
Average mol wt
Actual dens lb/ft3
Actual vol ft3/hr
Std liq  ft3/hr
Std vap 60F scfh
Cp Btu/lbmol-F
Z factor
Visc cP
Th cond Btu/hr-ft-F
Surf. tens. dyne/cm
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CHEMCAD 6.5.1                                              Page 6

Simulation: Carbonation_Activation Simu  Date: 02/06/2017  Time: 12:59:45
STREAM PROPERTIES

Stream No.                       39            46             6            48
       Name                     air                         Air
- - Overall - -
Molar flow lbmol/h       62.4564       62.4564       34.6606       34.6606
Mass flow  lb/h        1800.0000     1800.0000     1000.0000     1000.0000
Temp F                   70.0000      300.0000       70.0000     1000.0001
Pres psia                14.7000       14.7000       14.7000       14.7000
Vapor mole fraction        1.000         1.000         1.000         1.000
Enth MMBtu/h           -0.037835      0.062905    -0.0017949       0.23186
Tc F                   -223.1023     -223.1023     -223.2866     -223.2866
Pc psia                 522.5013      522.5013      522.8152      522.8152
Std. sp gr.  wtr = 1       0.859         0.859         0.865         0.865
Std. sp gr.  air = 1       0.995         0.995         0.996         0.996
Degree API               33.1654       33.1654       32.0441       32.0441
Average mol wt           28.8201       28.8201       28.8512       28.8512
Actual dens lb/ft3        0.0746        0.0520        0.0747        0.0271
Actual vol ft3/hr     24132.5410    34633.5430    13392.5146    36937.6523
Std liq  ft3/hr          33.5537       33.5537       18.5140       18.5140
Std vap 60F scfh      23700.8828    23700.8828    13152.9561    13152.9561
- - Vapor only - -
Molar flow lbmol/h       62.4564       62.4564       34.6606       34.6606
Mass flow  lb/h        1800.0000     1800.0000     1000.0000     1000.0000
Average mol wt           28.8201       28.8201       28.8512       28.8512
Actual dens lb/ft3        0.0746        0.0520        0.0747        0.0271
Actual vol ft3/hr     24132.5410    34633.5430    13392.5146    36937.6523
Std liq  ft3/hr          33.5537       33.5537       18.5140       18.5140
Std vap 60F scfh      23700.8828    23700.8828    13152.9561    13152.9561
Cp Btu/lbmol-F            6.9826        7.0589        6.9773        7.6417
Cp/Cv                     1.4001        1.3926        1.4005        1.3514
Cp/Cv  ideal              1.3978        1.3918        1.3982        1.3514
Z factor                  0.9994        1.0000        0.9994        1.0002
Visc cP                  0.01806       0.02371       0.01813       0.03753
Th cond Btu/hr-ft-F       0.0146        0.0197        0.0146        0.0337
- - Liquid only - -
Molar flow lbmol/h
Mass flow  lb/h
Average mol wt
Actual dens lb/ft3
Actual vol ft3/hr
Std liq  ft3/hr
Std vap 60F scfh
Cp Btu/lbmol-F
Z factor
Visc cP
Th cond Btu/hr-ft-F
Surf. tens. dyne/cm
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CHEMCAD 6.5.1                                                Page 7

Simulation: Carbonation_Activation Simu  Date: 02/06/2017  Time: 12:59:45
STREAM PROPERTIES

Stream No.                     47            4            11             5
       Name                                           HX FG In          Char
- - Overall - -
Molar flow lbmol/h       157.6610      45.6280       37.7877      137.0935
Mass flow  lb/h         3505.9944    1259.9965     1049.9971     2192.8821
Temp F                   229.1450    1376.9180     3800.4780     1100.0000
Pres psia                 15.0000      15.0000       15.0000       15.0000
Vapor mole fraction         1.000        1.000         1.000        0.0000
Enth MMBtu/h              -11.234     -0.84600       0.14076       -3.8245
Tc F                     304.1582     -99.5098      -96.0877        0.0000
Pc psia                  883.6580     439.2276      448.5339        0.0000
Std. sp gr.  wtr = 1        0.900        0.829         0.834         2.765
Std. sp gr.  air = 1        0.768        0.953         0.959         0.552
Degree API                25.6616      39.2577       38.0634      -80.3304
Average mol wt            22.2376      27.6146       27.7868       15.9955
Actual dens lb/ft3         0.0454       0.0210        0.0091      172.6326
Actual vol ft3/hr      77280.0391   59954.0742   115163.1719       12.7026
Std liq  ft3/hr           62.3767      24.3565       20.1551       12.7026
Std vap 60F scfh       59828.9766   17314.8359    14339.6074    52024.0625
- - Vapor only - -
Molar flow lbmol/h       157.6610      45.6280       37.7877
Mass flow  lb/h         3505.9944    1259.9965     1049.9971
Average mol wt            22.2376      27.6146       27.7868
Actual dens lb/ft3         0.0454       0.0210        0.0091
Actual vol ft3/hr      77280.0391   59954.0742   115163.1719
Std liq  ft3/hr           62.3767      24.3565       20.1551
Std vap 60F scfh       59828.9766   17314.8359    14339.6074
Cp Btu/lbmol-F             8.0774       8.5285        9.9963
Cp/Cv                      1.3448       1.3033        1.2548
Cp/Cv  ideal               1.3263       1.3038        1.2481
Z factor                   0.9948       1.0002        1.0001
Visc cP                   0.01574      0.04180       0.07343
Th cond Btu/hr-ft-F        0.0162       0.0430        0.0894
- - Liquid only - -
Molar flow lbmol/h
Mass flow  lb/h
Average mol wt
Actual dens lb/ft3
Actual vol ft3/hr
Std liq  ft3/hr
Std vap 60F scfh
Cp Btu/lbmol-F
Z factor
Visc cP
Th cond Btu/hr-ft-F
Surf. tens. dyne/cm
```

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CHEMCAD 6.5.1                                              Page 8

Simulation: Carbonation_Activation Simu  Date: 02/06/2017  Time: 12:59:45
STREAM PROPERTIES

Stream No.                     10            51            12             9
       Name             RXN Steam
- - Overall - -
Molar flow lbmol/h        39.5781      176.6716      176.6716       37.7877
Mass flow  lb/h          713.0000     2905.8818     2905.8818     1049.9971
Temp F                   345.0000      843.4539     1652.0000     1153.3390
Pres psia                125.0000       15.0000       15.0000       15.0000
Vapor mole fraction         1.000         1.000         1.000         1.000
Enth MMBtu/h              -4.0496       -7.8741       -6.9431      -0.79031
Tc F                     705.5600      705.5600      705.5600      -96.0877
Pc psia                 3207.9768     3207.9768     3207.9768      448.5339
Std. sp gr.  wtr = 1        1.000         1.930         1.930         0.834
Std. sp gr.  air = 1        0.622         0.568         0.568         0.959
Degree API                10.0000      -58.1665      -58.1665       38.0634
Average mol wt            18.0150       16.4479       16.4479       27.7868
Actual dens lb/ft3         0.2753        0.0788        0.0486        0.0241
Actual vol ft3/hr       2589.6172    36862.4102    59783.7656    43607.2773
Std liq  ft3/hr           11.4212       24.1238       24.1238       20.1551
Std vap 60F scfh       15019.0527    67043.1094    67043.1094    14339.6074
- - Vapor only - -
Molar flow lbmol/h        39.5781       39.5781       39.5781       37.7877
Mass flow  lb/h          713.0000      713.0000      713.0000     1049.9971
Average mol wt            18.0150       18.0150       18.0150       27.7868
Actual dens lb/ft3         0.2753        0.0193        0.0119        0.0241
Actual vol ft3/hr       2589.6172    36849.7070    59771.0625    43607.2773
Std liq  ft3/hr           11.4212       11.4212       11.4212       20.1551
Std vap 60F scfh       15019.0527    15019.0527    15019.0527    14339.6074
Cp Btu/lbmol-F            11.1016        8.9922       10.3281        8.3368
Cp/Cv                      1.3899        1.2836        1.2371        1.3126
Cp/Cv  ideal               1.2180        1.2836        1.2382        1.3129
Z factor                   0.9473        0.9988        0.9998        1.0001
Visc cP                   0.01530       0.02654       0.04429       0.03825
Th cond Btu/hr-ft-F        0.0186        0.0352        0.0707        0.0382
- - Liquid only - -
Molar flow lbmol/h
Mass flow  lb/h
Average mol wt
Actual dens lb/ft3
Actual vol ft3/hr
Std liq  ft3/hr
Std vap 60F scfh
Cp Btu/lbmol-F
Z factor
Visc cP
Th cond Btu/hr-ft-F
Surf. tens. dyne/cm
```

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CHEMCAD 6.5.1                                                  Page 9

Simulation: Carbonation_Activation Simu  Date: 02/06/2017  Time: 12:59:45
STREAM PROPERTIES

Stream No.                        49            43
       Name
- - Overall - -
Molar flow lbmol/h           37.7877      157.6610
Mass flow  lb/h            1049.9971     3505.9944
Temp F                      371.2308      308.6891
Pres psia                    15.0000       15.0000
Vapor mole fraction            1.000         1.000
Enth MMBtu/h                 -1.0240       -11.134
Tc F                        -96.0877      304.1582
Pc psia                     448.5339      883.6580
Std. sp gr.  wtr = 1           0.834         0.900
Std. sp gr.  air = 1           0.959         0.768
Degree API                   38.0634       25.6616
Average mol wt               27.7868       22.2376
Actual dens lb/ft3            0.0468        0.0406
Actual vol ft3/hr         22452.2324    86348.2656
Std liq  ft3/hr              20.1551       62.3767
Std vap 60F scfh          14339.6084    59828.9766
- - Vapor only - -
Molar flow lbmol/h           37.7877      157.6610
Mass flow  lb/h            1049.9971     3505.9944
Average mol wt               27.7868       22.2376
Actual dens lb/ft3            0.0468        0.0406
Actual vol ft3/hr         22452.2324    86348.2656
Std liq  ft3/hr              20.1551       62.3767
Std vap 60F scfh          14339.6084    59828.9766
Cp Btu/lbmol-F                7.5010        8.0139
Cp/Cv                         1.3612        1.3389
Cp/Cv  ideal                  1.3604        1.3297
Z factor                      0.9997        0.9965
Visc cP                      0.02323       0.01761
Th cond Btu/hr-ft-F           0.0208        0.0182
- - Liquid only - -
Molar flow lbmol/h
Mass flow  lb/h
Average mol wt
Actual dens lb/ft3
Actual vol ft3/hr
Std liq  ft3/hr
Std vap 60F scfh
Cp Btu/lbmol-F
Z factor
Visc cP
Th cond Btu/hr-ft-F
Surf. tens. dyne/cm
```

Exhibit D

Mass Balance Backup Data

Assumptions - Mass Balance

1 Mass Balance Streams are shown on PFDs :FS-1, FS-2, and FS-3
2 Filter Press Product is 30% Moisture
3 Solids to liquid in leachate is based on 60 g/ 125 mL solids / .5 M H_2SO_4 acid ratio
4 Heat has not been added to leachate process
5 Coal Solids Removal Clarifier underflow sludge approx 50% liquid
6 Iron extraction removes 72 % metals and 5% REE
7 Fe Removal Clarifier underflow sludge approx 95% liquid
8 Mass Balance considers Recirculated Waste Heat to Heat Combustion Air
9 Soluble Metals and REE compostion based on Hansen Harmon Feed Stock Analysis
10 Soluble Metals and REE extract composition based on Hansen Harmon lab data testing from 60g/125 ML @ 40 C 0.5 M H_2SO_4
11 Stream 14 is a recirculation stream that is accounted for in Stream 6
12 Iron Extraction Process is approximately 17% solids
13 No Thickeners / Flocculants have been considered
14 Fuel and Air usage is based on Chemcad Simulation - See Exhibit E for Drying / Carbonation Process

need a dryer stage

STREAMS		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
Description		Coal Feed	Pulverized Coal	Leachate Feed	Acid	Dilution Water	Leachate Solution	Clarifier Overflow	Iron Extraction Tank Overflow	Iron Extraction Filter Press Filtrate	REE Pregnant Solution	Iron Extract	Leached Coal Slurry / Filter Press Feed	Iron Extraction Filter Press Feed	Press Filtrate	Pressed Coal Slurry	Dryer Fuel Gas
State	Solid, Liquid, Gas	Solid	Solid	Solid	Liquid	Liquid	Solid, Liquid, Gas	Liquid, Solids	Liquid	Liquid	Liquid, Solids	Liquid, Solids	Solid, Liquid	Liquid	Liquid, Solids	Solid, Liquid	Gas
Temp	F	70	70	70	70	70	104-194 F	104	104	104	104	104	104	104	70	70	70
Pressure	psig	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Coal	lb/hr	3627.1	3627.1	3627.1	0.0	0.0	3627.1	0.0	0.0	0.0	0.0	0.0	3627.1	0.0	0.0	3627.1	0.0
Acid	lb/hr	0.0	0.0	0.0	323.7	0.0	392.4	196.2	98.1	68.7	166.8	29.4	98.1	98.1	68.7	29.4	0.0
Acid	ft3/hr	0.0	0.0	0.0	2.8	0.0	3.4	1.7	0.9	0.6	1.5	0.3	0.9	0.9	0.6	0.3	0.0
Water	lb/hr	1228.0	1228.0	1228.0	0.0	4145.1	7637.3	3818.6	1909.3	1336.5	3245.9	572.8	3818.6	1909.3	2264.2	1554.5	0.0
Water	ft3/hr	19.7	19.7	19.7	0.0	66.4	122.3	61.2	30.6	21.4	52.0	9.2	61.2	30.6	36.3	24.9	0.0
Soluble Metals (Excluding REE)	lb/hr	355.8	355.8	355.8	0.0	0.0	355.8	211.1	34.7	55.2	90.0	121.1	144.7	176.3	0.0	144.7	0.0
REE	lb/hr	2.1	2.1	2.1	0.0	0.0	3.9	1.9	0.9	0.8	1.8	0.1	2.0	0.9	1.8	0.2	0.0
Char	lb/hr	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Activated Carbon	lb/hr	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Syngas	lb/hr	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Natural Gas	lb/hr	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	90.0
Air	lb/hr	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Total Flow Rate	lb/hr	5213.0	5213.0	5213.0	323.7	4145.1	12016.5	4227.8	2043.1	1461.2	3504.4	723.4	7690.6	2184.7	2334.6	5355.9	90.0
REE wt% dry basis		0.59	0.59	0.59			1.09	0.89	2.64	1.49	1.94	0.09	1.36	0.53		0.14	

BURNER FLUE GAS CLEAN–UP/EXHAUST

17	18	19	20	21	22	23	24	25	26	27	28	29	30
Dryer Combustion Air	Dryer Exhaust	Dried Coal Byproduct	Carbonation Kiln Combution Air	Carbonation Kiln Fuel Gas	Carbonation Kiln Exhaust Gas	Syngas from Carbonation	Carbonated Solids	Activation Kiln Combustion Air	Activation Kiln Fuel Gas	Syngas from Activation	Activation Kiln Exhaust Gas	Hot Activated Carbon	Cooled Activated Carbon
Gas	Gas	Solid, Liquid	Gas	Gas	Gas	Gas	Solid	Gas	Gas	Gas	Gas	Solid	Solid
300	220	77	1300	70	339	1100	1100	1000	70	1652	371	1652	200
0	0	0	0	0	0	0	0	0	0	0	0	0	0
0.0	0.0	3627.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
0.0	1554.5	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
0.0	24.9	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
0.0	0.0	144.7	0.0	0.0	0.0	0.0	144.7	0.0	0.0	0.0	0.0	144.7	144.7
0.0	0.0	0.2	0.0	0.0	0.0	0.0	0.2	0.0	0.0	0.0	0.0	0.2	0.2
0.0	0.0	0.0	0.0	0.0	0.0	0.0	2091.1	0.0	0.0	0.0	0.0	0.0	0.0
0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	1624.1	1624.1
0.0	0.0	0.0	0.0	0.0	0.0	1537.0	0.0	0.0	0.0	1181.0	0.0	0.0	0.0
0.0	0.0	0.0	0.0	60.0	0.0	0.0	0.0	0.0	50.0	0.0	0.0	0.0	0.0
1800.0	1800.0	0.0	1200.0	0.0	1200.0	0.0	0.0	1000.0	0.0	0.0	1000.0	0.0	0.0
1800.0	3354.5	3772.0	1200.0	60.0	1200.0	1537.0	2236.0	1000.0	50.0	1181.0	1000.0	1769.0	1769.0
		0.14					0.14					0.14	0.14

					Dry Basis (5000) lb/hr as received)
	Initial, ppmw	Leached, ppmw	**% Extracted**	mg Extracted	**Normalized - 3772 lb/hr**
Sc	36.32730673	7.155197538	**82.49**	1.602064296	**0.113037533**
Y	45.5856214	6.153617378	**88.00**	2.144605883	**0.151317871**
La	63.30477561	9.562987538	**86.57**	2.929868825	**0.206724003**
Ce	176.4394557	21.62911708	**89.10**	8.404702543	**0.593014179**
Pr	26.59431611	3.2013274	**89.30**	1.269614665	**0.089580743**
Nd	121.8802831	14.8450616	**89.17**	5.810327144	**0.409961728**
Sm	29.31808964	3.593803937	**89.10**	1.39657829	**0.09853897**
Eu	6.548181056	0.784998575	**89.34**	0.312764982	**0.022067892**
Gd	22.27800659	2.59008852	**89.67**	1.067908996	**0.07534891**
Tb	2.978466182	0.335701847	**89.98**	0.143277257	**0.010109275**
Dy	14.93942146	1.69291875	**89.93**	0.718219051	**0.050675688**
Ho	2.509926461	0.294702126	**89.56**	0.120177308	**0.008479402**
Er	6.383071327	0.785303178	**89.06**	0.303923742	**0.021444077**
Tm	0.849368008	0.108439625	**88.65**	0.040254488	**0.002840253**
Yb	5.384463405	0.715013372	**88.20**	0.253878123	**0.017912987**
Lu	0.738211928	0.10238217	**87.67**	0.034599916	**0.002441281**
Co	865	20.6	**97.88**	45.2640498	**3.193714849**
Cu	172	126	**34.89**	3.207978	**0.226346671**
Ga	23.8	6.3	**76.47**	0.9729909	**0.068651734**
Ge	28	9.1	**71.11**	1.0644753	**0.075106637**
In	0	0	**#DIV/0!**	0	**0**
Li	25	23.1	**17.87**	0.2388573	**0.016853156**
Ni	75.4	6	**92.93**	3.745782	**0.264292737**
Se	2.7	1.4	**53.91**	0.0778182	**0.005490652**
Ag	0.58	0.59	**9.58**	0.00297177	**0.00020968**
Te	0	0	**#DIV/0!**	0	**0**
V	616	122	**82.40**	27.134286	**1.91452538**
Zn	26.8	4.6	**84.74**	1.2141498	**0.085667285**
Cd	0.55	0.04	**93.54**	0.02750232	**0.001940493**
Pb	14.7	10.9	**34.09**	0.2679267	**0.018904218**
Hg	0.16	0.17	**5.56**	0.00047571	**3.35649E-05**
Th	29.9	6.9	**79.49**	1.2705867	**0.089649327**
U	16.3	4.6	**74.92**	0.6528198	**0.046061285**
Si	82129.37285	94137.78616	**-1.88**	-82.50891224	**0**
Al	48340.98967	55253.46018	**-1.59**	-41.16935991	**0**
Fe	76424.87491	35688.68492	**58.49**	2389.854572	**168.6219874**
Ti	3368.899267	3108.948972	**17.98**	32.37342649	**2.284185648**
P	646.4653253	302.8634421	**58.36**	20.16887411	**1.423063845**
Ca	7847.040595	1279.170317	**85.51**	358.7204542	**25.31039195**
Mg	893.407969	352.4664806	**64.93**	31.01344027	**2.18822852**
Na	1131.344818	216.792308	**82.97**	50.18037386	**3.540598021**
K	2061.516646	1849.561428	**20.26**	22.32306953	**1.575058329**
Sr	240.5801171	319.6787991	**-18.11**	-2.328764432	**0**
Ba	1731.74108	1980.455154	**-1.65**	-1.526409408	**0**
Mn	50.61675012	22.63184291	**60.26**	1.630574182	**0.115049117**
				TOTAL	**212.9395053**
					61.17971662
					91.53167435

Mass REEs Extracted	1.873494791	lb/hr	**Baseline Case**
Total Mass Extracted	**212.9395053**	lb/hr	
wt% REEs in Solution	0.879824901	wt%	
Rejection for 2wt% REEs	119.2647657	lb/hr	

	ash basis		**ash basis, SO3-free (norm to 100%)**		**coal basis**	
	Initial, ppmw	Leached, ppmw	Initial, ppmw	Leached, ppmw	Initial, ppmw	Leached, ppmw
Si	203469.4276	253125.326	365235.5732	483967.7972	82129.37285	94137.78616
Al	119761.2152	148569.9918	214976.061	284061.2309	48340.98967	55253.46018
Fe	189336.9572	95962.63489	339867.2366	183477.591	76424.87491	35688.68492
Ti	8346.197977	8359.594527	14981.7515	15983.28628	3368.899267	3108.948972
P	1601.569879	814.3638237	2874.880514	1557.038453	646.4653253	302.8634421
Ca	19440.46086	3439.537051	34896.38688	6576.2885	7847.040595	1279.170317
Mg	2213.351957	947.7405028	3973.053249	1812.05054	893.407969	352.4664806
Na	2802.822846	582.9287672	5031.176529	1114.54178	1131.344818	216.792308
K	5107.254536	4973.251003	9167.72146	9508.702156	2061.516646	1849.561428
Sr	596.0193903	859.5783215	1069.878095	1643.487175	240.5801171	319.6787991
Ba	4290.260038	5325.208683	7701.184411	10181.63436	1731.74108	1980.455154
Mn	125.3992429	60.85433754	225.096541	116.3516119	50.61675012	22.63184291
	557090.9368	523021.0097				
Ash wt%	22.85	19.5				
wt% SO3	1.59	0.25				
Ash wt% (SO3 corrected)	22.486685	19.45125				
Dry Coal	53.46 g					
Dry Residue	47.517 g					

	H2SO4 Leach				Dry Basis (5000) lb/hr as received)	Amonnium Acetate Pre-Leach			
	Initial, ppmw	Leached, ppmw	**% Extracted**	mg Extracted	**Normalized - 3772 lb/hr**	NH4OAc extraction (wt% initial content)	w/ NH4OAc leach (mg extracted)	Normalized NH4OAc leach (lb/hr)	H2SO4 lb/hr after Pre-leach
Sc	36.32730673	7.155197538	**82.49**	1.602064296	**0.113037533**	0	0	0	0.113037533
Y	45.5856214	6.153617378	**88.00**	2.144605883	**0.151317871**	9.220650506	0.224707928	0.015854813	0.135463058
La	63.30477561	9.562987538	**86.57**	2.929868825	**0.206724003**	2.728914891	0.092353938	0.006516256	0.200207747
Ce	176.4394557	21.62911708	**89.10**	8.404702543	**0.593014179**	1.697389135	0.160105437	0.011296628	0.581717551
Pr	26.59431611	3.2013274	**89.30**	1.269614665	**0.089580743**	0.616017676	0.008758121	0.00061795	0.088962792
Nd	121.8802831	14.8450616	**89.17**	5.810327144	**0.409961728**	0.688763027	0.04487787	0.003166467	0.406795261
Sm	29.31808964	3.593803937	**89.10**	1.39657829	**0.09853897**	1.325233247	0.020770978	0.001465547	0.097073423
Eu	6.548181056	0.784998575	**89.34**	0.312764982	**0.022067892**	2.098660178	0.007346691	0.000518364	0.021549529
Gd	22.27800659	2.59008852	**89.67**	1.067908996	**0.07534891**	3.730571719	0.044430446	0.003134898	0.072214012
Tb	2.978466182	0.335701847	**89.98**	0.143277257	**0.010109275**	4.084042584	0.006502972	0.000458833	0.009650442
Dy	14.93942146	1.69291875	**89.93**	0.718219051	**0.050675688**	4.64284651	0.037080626	0.002616314	0.048059374
Ho	2.509926461	0.294702126	**89.56**	0.120177308	**0.008479402**	5.501288856	0.007381666	0.000520831	0.00795857
Er	6.383071327	0.785303178	**89.06**	0.303923742	**0.021444077**	6.877117423	0.023467406	0.0016558	0.019788277
Tm	0.849368008	0.108439625	**88.65**	0.040254488	**0.002840253**	6.753768632	0.003066698	0.000216378	0.002623875
Yb	5.384463405	0.715013372	**88.20**	0.253878123	**0.017912987**	6.333728465	0.018231854	0.001286393	0.016626594
Lu	0.738211928	0.10238217	**87.67**	0.034599916	**0.002441281**	7.84952839	0.003097801	0.000218573	0.002222708
Co	865	20.6	**97.88**	45.2640498	**3.193714849**	68	31.445172	2.2186904	0.975024449
Cu	172	126	**34.89**	3.207978	**0.226346671**				0.226346671
Ga	23.8	6.3	**76.47**	0.9729909	**0.068651734**				0.068651734
Ge	28	9.1	**71.11**	1.0644753	**0.075106637**				0.075106637
In	0	0	**#DIV/0!**	0	**0**				0
Li	25	23.1	**17.87**	0.2388573	**0.016853156**				0.016853156
Ni	75.4	6	**92.93**	3.745782	**0.264292737**	42	1.69297128	0.119451696	0.144841041
Se	2.7	1.4	**53.91**	0.0778182	**0.005490652**				0.005490652
Ag	0.58	0.59	**9.58**	0.00297177	**0.00020968**				0.00020968
Te	0	0	**#DIV/0!**	0	**0**				0
V	616	122	**82.40**	27.134286	**1.91452538**				1.91452538
Zn	26.8	4.6	**84.74**	1.2141498	**0.085667285**	57	0.81665496	0.057621072	0.028046213
Cd	0.55	0.04	**93.54**	0.02750232	**0.001940493**				0.001940493
Pb	14.7	10.9	**34.09**	0.2679267	**0.018904218**				0.018904218
Hg	0.16	0.17	**5.56**	0.00047571	**3.35649E-05**				3.35649E-05
Th	29.9	6.9	**79.49**	1.2705867	**0.089649327**				0.089649327
U	16.3	4.6	**74.92**	0.6528198	**0.046061285**				0.046061285
Si	82129.37285	94137.78616	**-1.88**	-82.5089122	**0**				0
Al	48340.98967	55253.46018	**-1.59**	-41.1693599	**0**				0
Fe	76424.87491	35688.68492	**58.49**	2389.854572	**168.6219874**				168.6219874
Ti	3368.899267	3108.948972	**17.98**	32.37342649	**2.284185648**				2.284185648
P	646.4653253	302.8634421	**58.36**	20.16887411	**1.423063845**				1.423063845
Ca	7847.040595	1279.170317	**85.51**	358.7204542	**25.31039195**	80	335.6022322	23.6792297	1.631162247
Mg	893.407969	352.4664806	**64.93**	31.01344027	**2.18822852**	80	38.20927202	2.695947887	0
Na	1131.344818	216.792308	**82.97**	50.18037386	**3.540598021**	80	48.38535517	3.413946122	0.126651899
K	2061.516646	1849.561428	**20.26**	22.32306953	**1.575058329**	10	11.02086799	0.777604079	0.79745425
Sr	240.5801171	319.6787991	**-18.11**	-2.32876443	**0**				0
Ba	1731.74108	1980.455154	**-1.65**	-1.52640941	**0**				0
Mn	50.61675012	22.63184291	**60.26**	1.630574182	**0.115049117**	57	1.542403733	0.108828037	0.00622108
				TOTAL	**212.9395053**				**180.3263616**
					61.17971662				28.56657295
					91.53167435				58.91853068

Mass REEs Extracted	1.873494791	lb/hr	**Baseline Case**	1.779820051
Total Mass Extracted	**212.9395053**	lb/hr		61.17971662
wt% REEs in Solution	0.879824901	wt%		91.53167435
Rejection for 2wt% REEs	119.2647657	lb/hr		
				2.909166877
				1.944485408

Mass REEs Extracted	1.823950747	lb/hr	**w/NH4OAc Pre-leach**	1.73275
Total Mass Extracted	**180.3263616**	lb/hr		28.5666
wt% REEs in Solution	1.01147205	wt%		58.9185
Rejection for 2wt% REEs	89.12882425	lb/hr		
				6.06567
				2.94093

	ash basis		**ash basis, SO3-free (norm to 100%)**		**coal basis**	
	Initial, ppmw	Leached, ppmw	Initial, ppmw	Leached, ppmw	Initial, ppmw	Leached, ppmw
Si	203469.4276	253125.326	365235.5732	483967.7972	82129.37285	94137.78616
Al	119761.2152	148569.9918	214976.061	284061.2309	48340.98967	55253.46018
Fe	189336.9572	95962.63489	339867.2366	183477.591	76424.87491	35688.68492
Ti	8346.197977	8359.594527	14981.7515	15983.28628	3368.899267	3108.948972
P	1601.569879	814.3638237	2874.880514	1557.038453	646.4653253	302.8634421
Ca	19440.46086	3439.537051	34896.38688	6576.2885	7847.040595	1279.170317
Mg	2213.351957	947.7405028	3973.053249	1812.05054	893.407969	352.4664806
Na	2802.822846	582.9287672	5031.176529	1114.54178	1131.344818	216.792308
K	5107.254536	4973.251003	9167.72146	9508.702156	2061.516646	1849.561428
Sr	596.0193903	859.5783215	1069.878095	1643.487175	240.5801171	319.6787991
Ba	4290.260038	5325.208683	7701.184411	10181.63436	1731.74108	1980.455154
Mn	125.3992429	60.85433754	225.096541	116.3516119	50.61675012	22.63184291
	557090.9368	523021.0097				
Ash wt%	22.85	19.5				
wt% SO3	1.59	0.25				
Ash wt% (SO3 corrected)	22.486685	19.45125				

Dry Coal	53.46	g
Dry Residue	47.517	g

0.5M H2SO4 Extraction Results - NO Ammonium Acetate Pre-leach

Element	lb/hr (3772 dry coal feed rate)
Sc	0.113
Y	0.151
La	0.207
Ce	0.593
Pr	0.090
Nd	0.410
Sm	0.099
Eu	0.022
Gd	0.075
Tb	0.010
Dy	0.051
Ho	0.008
Er	0.021
Tm	0.003
Yb	0.018
Lu	0.002
Co	3.194
Cu	0.226
Ga	0.069
Ge	0.075
In	0
Li	0.017
Ni	0.264
Se	0.005
Ag	0.000
Te	0
V	1.915
Zn	0.086
Cd	0.002
Pb	0.019
Hg	0.000
Th	0.090
U	0.046
Si	0
Al	0
Fe	168.6
Ti	2.284
P	1.423
Ca	25.310
Mg	2.188
Na	3.541
K	1.575
Sr	0
Ba	0
Mn	0.115
Total	212.9
w/ 72% Fe removal	91.5
w/ 90% Fe removal	61.2

1M Ammonium Acetate Pre-Leach Extraction Results

element	wt% extracted by NH4OAc	Normalized to 3772 lb/hr dry coal feed
Sc	0	0
Y	9.2	0.01585
La	2.7	0.00652
Ce	1.7	0.01130
Pr	0.6	0.00062
Nd	0.7	0.00317
Sm	1.3	0.00147
Eu	2.1	0.00052
Gd	3.7	0.00313
Tb	4.1	0.00046
Dy	4.6	0.00262
Ho	5.5	0.00052
Er	6.9	0.00166
Tm	6.8	0.00022
Yb	6.3	0.00129
Lu	7.8	0.00022
Co	68	2.22
Ni	42	0.12
Zn	57	0.06
Ca	80	23.68
Mg	80	2.70
Na	80	3.41
K	10	0.78
Mn	57	0.11

NOTE: % extracted for REEs, CO, Ni, Zn, Mn based on laboratory data; % extracted for alkali based on prior testing of ND lignites

0.5M H2SO4 Extraction Results when Using Ammonium Acetate Pre-leach

Element	lb/hr (3772 dry coal feed rate)
Sc	0.113
Y	0.135
La	0.200
Ce	0.582
Pr	0.089
Nd	0.407
Sm	0.097
Eu	0.022
Gd	0.072
Tb	0.010
Dy	0.048
Ho	0.008
Er	0.020
Tm	0.003
Yb	0.017
Lu	0.002
Co	0.975
Cu	0.226
Ga	0.069
Ge	0.075
In	0
Li	0.017
Ni	0.145
Se	0.005
Ag	0.000
Te	0
V	1.915
Zn	0.028
Cd	0.002
Pb	0.019
Hg	0.000
Th	0.090
U	0.046
Si	0
Al	0
Fe	168.6
Ti	2.28
P	1.42
Ca	1.63
Mg	0
Na	0.13
K	0.80
Sr	0
Ba	0
Mn	0.0062
Total	180.3
w/ 72% Fe removal	58.9
w/ 90% Fe removal	28.6

REE Wt% In Solution for Multiple Cases (dry basis not including mass of acid)

Case Description	Wt% REE in solution
Post Leaching, no NH4OAc pre-leach	0.88
Post Leaching, w/ NH4OAc pre-leach	1.01
Case 1 - 72% Fe precipitation, no NH4OAc pre-leach	1.94
Case 2 - 90% Fe precipitation, no NH4OAc pre-leach	2.91
Case 3 - 72% Fe precipitation, w/ NH4OAc pre-leach	2.94
Case 4 - 90% Fe precipitation, w/ NH4OAc pre-leach	6.07

NOTE: Cases 1-4 assume 5wt% REE loss to the Fe precipitate

	Initial, ppmw	Leached, ppmw	% Extracted	mg Extracted	**Dry Basis (5000) lb/hr as received** **Normalized - 3772 lb/hr**
Sc	1.973367086	0.942728554	53.15	0.061021146	**0.003956269**
Y	11.77226259	1.925069748	83.96	0.575063611	**0.037283899**
La	7.272922085	2.632098671	64.51	0.272956944	**0.017696997**
Ce	9.659337492	3.637385393	63.07	0.354439572	**0.022979874**
Pr	1.035204225	0.386971554	63.34	0.038148485	**0.002473334**
Nd	4.061247593	1.462552642	64.68	0.152833383	**0.009908859**
Sm	0.960708201	0.309500979	68.41	0.038234464	**0.002478908**
Eu	0.25989101	0.089861843	66.09	0.009993132	**0.000647899**
Gd	1.225836269	0.305609104	75.55	0.053881401	**0.003493368**
Tb	0.202702594	0.046958366	77.28	0.009113825	**0.000590889**
Dy	1.33908779	0.286009764	79.05	0.061588501	**0.003993053**
Ho	0.305572872	0.059941158	80.76	0.014357981	**0.000930891**
Er	0.908253091	0.169369238	81.71	0.043177895	**0.002799412**
Tm	0.123893458	0.022479949	82.21	0.005925404	**0.00038417**
Yb	0.757401764	0.13920273	81.98	0.036122665	**0.002341991**
Lu	0.118870804	0.021851755	81.97	0.005669033	**0.000367548**
Co	39.3	2.6	93.51	2.1380917	**0.138621872**
Cu	11.1	5.2	54.06	0.3491009	**0.022633744**
Ga	2.1	1.1	48.63	0.0594154	**0.003852161**
Ge	0.9	0.5	45.52	0.0238336	**0.001545237**
In	0	0	#DIV/0!	0	**0**
Li	3.7	2.7	28.44	0.0612138	**0.003968759**
Ni	6.9	4.1	41.73	0.1675096	**0.010860383**
Se	0.55	0.14	75.04	0.02401075	**0.001556722**
Ag	0	0	#DIV/0!	0	**0**
Te	0	0	#DIV/0!	0	**0**
V	3.8	1.7	56.13	0.1240867	**0.008045086**
Zn	3.3	0.5	85.14	0.1634632	**0.010598037**
Cd	0.05	0	100.00	0.00290895	**0.0001886**
Pb	1.6	1	38.71	0.0360314	**0.002336074**
Hg	0.02	0.03	-47.10	-0.00054807	**0**
Th	1	0.8	21.55	0.012535	**0.000812699**
U	1.1	0.9	19.76	0.0126474	**0.000819986**
Si	7325.312166	10746.22348	-43.87	-186.9464444	**0**
Al	6749.100517	4521.282748	34.30	134.6941318	**8.732811926**
Fe	3965.720306	1142.800003	71.74	165.5191875	**10.73133562**
Ti	158.8178887	215.3296947	-32.96	-3.045769785	**0**
P	98.28479753	25.28600611	74.77	4.275418157	**0.27719413**
Ca	25772.97705	22701.69632	13.62	204.200748	**13.23923102**
Mg	5289.321944	27.95598586	99.48	306.1324326	**19.84790966**
Na	3685.779268	17.19494769	99.54	213.4538943	**13.83915312**
K	384.9028637	134.6740565	65.69	14.70943541	**0.953677278**
Sr	483.9510151	452.1349266	8.38	2.359227875	**0.152959101**
Ba	626.7078951	598.9501134	6.28	2.288139907	**0.148350156**
Mn	115.1242895	24.77171053	78.90	5.284466097	**0.342615138**
				TOTAL	**68.58340387 lb/hr**

Mass REEs Extracted	0.112327361	lb/hr
Total Mass Extracted	**68.58340387**	lb/hr
wt% REEs in Solution	0.163782131	wt%
Rejection for 2wt% REEs	62.96703584	lb/hr

Dry Coal	58.179	g
Dry Residue	57.055	g

	ash basis, SO3-free		**ash basis, SO3-free (norm to 100%)**		**coal basis, SO3-free**	
	Initial, ppmw	Leached, ppmw	Initial, ppmw	Leached, ppmw	Initial, ppmw	Leached, ppmw
Si	84711.79243	160502.63	134025.7642	264631.208	7325.312166	10746.22348
Al	78048.33283	67528.63208	123483.2501	111338.8826	6749.100517	4521.282748
Fe	45860.60877	17068.54564	72557.82175	28142.03015	3965.720306	1142.800003
Ti	1836.61088	3216.104929	2905.772261	5302.603033	158.8178887	215.3296947
P	1136.590657	377.664813	1798.243515	622.6807354	98.28479753	25.28600611
Ca	298045.33	339066.2748	471548.9068	559040.7952	25772.97705	22701.69632
Mg	61167.07828	417.542894	96774.77211	688.430342	5289.321944	27.95598586
Na	42623.29867	256.8189961	67435.94972	423.434315	3685.779268	17.19494769
K	4451.115632	2011.454563	7042.280146	3316.417002	384.9028637	134.6740565
Sr	5596.53391	6752.962557	8854.490177	11134.05207	483.9510151	452.1349266
Ba	7247.411157	8945.753694	11466.40616	14749.45057	626.7078951	598.9501134
Mn	1331.32687	369.9834361	2106.343119	610.0159458	115.1242895	24.77171053
	632056.0301	606514.3684				
Ash wt%	7	6.07				
wt% SO3	21.92	33.1				
Ash wt% (SO3 corrected)	5.4656	4.06083				

					Dry Basis (5000) lb/hr as received)		Amonnium Acetate Pre-Leach			
	Initial, ppmw	Leached, ppmw	% Extracted	mg Extracted	**Normalized - 3772 lb/hr**	NH4OAc extraction (wt% initial content)	w/ NH4OAc leach (mg extracted)	Normalized NH4OAc leach (lb/hr)	H2SO4 lb/hr after Pre-leach	
Sc	1.973367086	0.942728554	53.15	0.061021146	**0.003956269**	0	0	0	0.003956269	
Y	11.77226259	1.925069748	83.96	0.575063611	**0.037283899**	0	0	0	0.037283899	
La	7.272922085	2.632098671	64.51	0.272956944	**0.017696997**	0	0	0	0.017696997	
Ce	9.659337492	3.637385393	63.07	0.354439572	**0.022979874**	0	0	0	0.022979874	
Pr	1.035204225	0.386971554	63.34	0.038148485	**0.002473334**	0	0	0	0.002473334	
Nd	4.061247593	1.462552642	64.68	0.152833383	**0.009908859**	0	0	0	0.009908859	
Sm	0.960708201	0.309500979	68.41	0.038234464	**0.002478908**	0	0	0	0.002478908	
Eu	0.25989101	0.089861843	66.09	0.009993132	**0.000647899**	0	0	0	0.000647899	
Gd	1.225836269	0.305609104	75.55	0.053881401	**0.003493368**	0	0	0	0.003493368	
Tb	0.202702594	0.046958366	77.28	0.009113825	**0.000590889**	0	0	0	0.000590889	
Dy	1.33908779	0.286009764	79.05	0.061588501	**0.003993053**	0	0	0	0.003993053	
Ho	0.305572872	0.059941158	80.76	0.014357981	**0.000930891**	0	0	0	0.000930891	
Er	0.908253091	0.169369238	81.71	0.043177895	**0.002799412**	0	0	0	0.002799412	
Tm	0.123893458	0.022479949	82.21	0.005925404	**0.00038417**	0	0	0	0.00038417	
Yb	0.757401764	0.13920273	81.98	0.036122665	**0.002341991**	0	0	0	0.002341991	
Lu	0.118870804	0.021851755	81.97	0.005669033	**0.000367548**	0	0	0	0.000367548	
Co	39.3	2.6	93.51	2.1380917	**0.138621872**	68	1.554775596	0.100802928	0.037818944	
Cu	11.1	5.2	54.06	0.3491009	**0.022633744**				0.022633744	
Ga	2.1	1.1	48.63	0.0594154	**0.003852161**				0.003852161	
Ge	0.9	0.5	45.52	0.0238336	**0.001545237**				0.001545237	
In	0	0	#DIV/0!	0	**0**				0	
Li	3.7	2.7	28.44	0.0612138	**0.003968759**				0.003968759	
Ni	6.9	4.1	41.73	0.1675096	**0.010860383**	42	0.168602742	0.010931256	0	
Se	0.55	0.14	75.04	0.02401075	**0.001556722**				0.001556722	
Ag	0	0	#DIV/0!	0	**0**				0	
Te	0	0	#DIV/0!	0	**0**				0	
V	3.8	1.7	56.13	0.1240867	**0.008045086**				0.008045086	
Zn	3.3	0.5	85.14	0.1634632	**0.010598037**	57	0.109434699	0.007095132	0.003502905	
Cd	0.05	0	100.00	0.00290895	**0.0001886**				0.0001886	
Pb	1.6	1	38.71	0.0360314	**0.002336074**				0.002336074	
Hg	0.02	0.03	-47.10	-0.00054807	**0**				0	
Th	1	0.8	21.55	0.012535	**0.000812699**				0.000812699	
U	1.1	0.9	19.76	0.0126474	**0.000819986**				0.000819986	
Si	7325.312166	10746.22348	-43.87	-186.9464444	**0**				0	
Al	6749.100517	4521.282748	34.30	134.6941318	**8.732811926**				8.732811926	
Fe	3965.720306	1142.800003	71.74	165.5191875	**10.73133562**				10.73133562	
Ti	158.8178887	215.3296947	-32.96	-3.045769785	**0**				0	
P	98.28479753	25.28600611	74.77	4.275418157	**0.27719413**				0.27719413	
Ca	25772.97705	22701.69632	13.62	204.200748	**13.23923102**	80	1199.556825	77.77253555	0	
Mg	5289.321944	27.95598586	99.48	306.1324326	**19.84790966**	80	246.1819691	15.9610579	3.886851757	
Na	3685.779268	17.19494769	99.54	213.4538943	**13.83915312**	80	171.5479616	11.12220752	2.716945599	
K	384.9028637	134.6740565	65.69	14.70943541	**0.953677278**	10	2.239326371	0.14518536	0.808491918	
Sr	483.9510151	452.1349266	8.38	2.359227875	**0.152959101**				0.152959101	
Ba	626.7078951	598.9501134	6.28	2.288139907	**0.148350156**				0.148350156	
Mn	115.1242895	24.77171053	78.90	5.284466097	**0.342615138**	57	3.817755143	0.247521827	0.095093311	
				TOTAL	**68.58340387**				**27.7494418**	**lb/hr**
									18.09123974	
									20.02288015	

Mass REEs Extracted	0.112327361	lb/hr
Total Mass Extracted	**68.58340387**	lb/hr
wt% REEs in Solution	0.163782131	wt%
Rejection for 2wt% REEs	62.96703584	lb/hr

	ash basis, SO3-free		**ash basis, SO3-free (norm to 100%)**		**coal basis, SO3-free**	
	Initial, ppmw	Leached, ppmw	Initial, ppmw	Leached, ppmw	Initial, ppmw	Leached, ppmw
Si	84711.79243	160502.63	134025.7642	264631.208	7325.312166	10746.22348
Al	78048.33283	67528.63208	123483.2501	111338.8826	6749.100517	4521.282748
Fe	45860.60877	17068.54564	72557.82175	28142.03015	3965.720306	1142.800003
Ti	1836.61088	3216.104929	2905.772261	5302.603033	158.8178887	215.3296947
P	1136.590657	377.664813	1798.243515	622.6807354	98.28479753	25.28600611
Ca	298045.33	339066.2748	471548.9068	559040.7952	25772.97705	22701.69632
Mg	61167.07828	417.542894	96774.77211	688.430342	5289.321944	27.95598586
Na	42623.29867	256.8189961	67435.94972	423.434315	3685.779268	17.19494769
K	4451.115632	2011.454563	7042.280146	3316.417002	384.9028637	134.6740565
Sr	5596.53391	6752.962557	8854.490177	11134.05207	483.9510151	452.1349266
Ba	7247.411157	8945.753694	11466.40616	14749.45057	626.7078951	598.9501134
Mn	1331.32687	369.9834361	2106.343119	610.0159458	115.1242895	24.77171053
	632056.0301	606514.3684				
Ash wt%	7	6.07				
wt% SO3	21.92	33.1				
Ash wt% (SO3 corrected)	5.4656	4.06083				

Dry Coal	58.179	g
Dry Residue	57.055	g

0.5M H2SO4 Extraction Results - NO Ammonium Acetate Pre-leach

Element	lb/hr (3772 dry coal feed rate)
Sc	0.004
Y	0.037
La	0.018
Ce	0.023
Pr	0.002
Nd	0.010
Sm	0.002
Eu	0.001
Gd	0.003
Tb	0.001
Dy	0.004
Ho	0.001
Er	0.003
Tm	0.000
Yb	0.002
Lu	0.000
Co	0.139
Cu	0.023
Ga	0.004
Ge	0.002
In	0
Li	0.004
Ni	0.011
Se	0.002
Ag	0.000
Te	0
V	0.008
Zn	0.011
Cd	0.00019
Pb	0.002
Hg	0
Th	0.001
U	0.001
Si	0
Al	8.73
Fe	10.7
Ti	0
P	0.277
Ca	13.239
Mg	19.848
Na	13.839
K	0.954
Sr	0.15
Ba	0.15
Mn	0.343
Total	68.6
w/ 72% Fe removal	60.9
w/ 90% Fe removal	58.9

1M Ammonium Acetate Pre-Leach Extraction Results

element	wt% extracted by NH4OAc	Normalized to 3772 lb/hr dry coal feed
Sc	0.0	0.0
Y	0.0	0.0
La	0.0	0.0
Ce	0.0	0.0
Pr	0.0	0.0
Nd	0.0	0.0
Sm	0.0	0.0
Eu	0.0	0.0
Gd	0.0	0.0
Tb	0.0	0.0
Dy	0.0	0.0
Ho	0.0	0.0
Er	0.0	0.0
Tm	0.0	0.0
Yb	0.0	0.0
Lu	0.0	0.0
Co	68	0.10
Ni	42	0.01
Zn	57	0.01
Ca	80	77.77
Mg	80	15.96
Na	80	11.12
K	10	0.15
Mn	57	0.25

NOTE: % extracted for REEs based on laboratory data; % extracted for alkali based on prior testing of ND lignites; % extracted for Co, Ni, Zn, Mn same as laboratory data for Hansen Harmon Coal

0.5M H2SO4 Extraction Results when Using Ammonium Acetate Pre-leach

Element	lb/hr (3772 dry coal feed rate)
Sc	0.0040
Y	0.0373
La	0.0177
Ce	0.0230
Pr	0.0025
Nd	0.0099
Sm	0.0025
Eu	0.0006
Gd	0.0035
Tb	0.0006
Dy	0.0040
Ho	0.0009
Er	0.0028
Tm	0.0004
Yb	0.0023
Lu	0.0004
Co	0.0378
Cu	0.0226
Ga	0.0039
Ge	0.0015
In	0
Li	0.0040
Ni	0
Se	0.0016
Ag	0.0000
Te	0
V	0.0080
Zn	0.0035
Cd	0.00019
Pb	0.0023
Hg	0
Th	0.0008
U	0.0008
Si	0
Al	8.733
Fe	10.7
Ti	0
P	0.28
Ca	0
Mg	3.8869
Na	2.72
K	0.81
Sr	0.153
Ba	0.148
Mn	0.095
Total	27.7
w/ 72% Fe removal	20.0
w/ 90% Fe removal	18.1

REE Wt% In Solution for Multiple Cases (dry basis not including mass of acid)

Case Description	Wt% REE in solution
Post Leaching, no NH4OAc pre-leach	0.16
Post Leaching, w/ NH4OAc pre-leach	0.40
Case 1 - 72% Fe precipitation, no NH4OAc pre-leach	0.18
Case 2 - 90% Fe precipitation, no NH4OAc pre-leach	0.18
Case 3 - 72% Fe precipitation, w/ NH4OAc pre-leach	0.53
Case 4 - 90% Fe precipitation, w/ NH4OAc pre-leach	0.59

NOTE: cases 1-4 assume 5wt% REE loss to the Fe precipitate

NOTE: For Hagel B, Al is large impurity source, unlike Hansen Harmon

Exhibit E

Technical Basis of the Technical and Economic Feasibility Assessment

EXHIBIT E –

TECHNICAL BASIS OF THE TECHNICAL AND ECONOMIC FEASIBILITY ASSESSMENT

Project Title:

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

The following sections provide a description of this Phase I bench-scale project, results of sampling and analysis and concentration tests and the technical justifications for the processes and mass balances evaluated in the Technical and Economic Assessment (TEA). Additional details of the sampling and analysis results can be located within the Topical Report submitted to DOE on October 31, 2016.

Project Team

The University of North Dakota Institute for Energy Studies (UND IES) has teamed with Barr Engineering (BARR) and Pacific Northwest National Laboratory (PNNL) 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 Company, Great River Energy, and the North Dakota Industrial Commission/Lignite Energy Council. The North Dakota Geological Survey is also providing technical support regarding lignite geology and selection of areas for sampling.

Summary of Sampling and Analysis Results

The project has involved an extensive sampling and analysis campaign that has evaluated a range of ND lignite-related materials including from the Falkirk Mine (Underwood, ND) – coal samples from three seams, roof/floor sediments from each coal seam – and from the Coal Creek Station power plant (Underwood, ND) – DryFining™ process streams, fly ash, bottom ash, and feed coal. Additional samples have also been collected from other mines in North Dakota as well as from an additional coal seam in Slope County, ND.

The initial focus of the project was on identifying opportunities to recover REEs from the Coal Creek Station DryFining™ lignite drying system. Preliminary results gathered in preparation of the original Phase I proposal showed high levels of REEs in the mineral-rich reject stream from the drying system. However, during the course of the project, it was discovered that the preliminary analysis was not as quantitative as anticipated, and actual REE content was significantly lower. The reject stream was subsequently determined not to be a feasible feedstock for continued evaluation.

Analysis of associated sediments (roof/floor) from the Falkirk Mine mostly showed total REE content of less than 150 ppm (whole sample basis), with a few exceptions approaching 200 ppm. Attempts were made to concentrate the REEs from the higher REE content roof/floor clays via two approaches: 1) novel dry elutriation method, and 2) size classification. Neither method showed any enrichment of the REEs. Due to the very small particle size of the REE-bearing minerals in the sediment samples, it was determined that physical beneficiation methods based on size and density were not feasible.

Several samples of feed coal and combustion ash products were collected from the Coal Creek Station, which showed an average REE content of about 240 ppm (dry ash basis), the highest REE content samples evaluated up to that date. Subsequently, it was realized that when evaluating REE content on an ash basis, that coal from certain seams and from certain locations within seams is actually more concentrated than the surrounding roof/floor clay sediments, which was an unexpected finding. Figure 1 displays the analysis results of samples collected along the stratigraphic sequence within the Falkirk

Mine. As shown, with each seam, the coal had a higher ash-based REE content, with the Hagel B seam generally have the highest content and most uniform distribution.

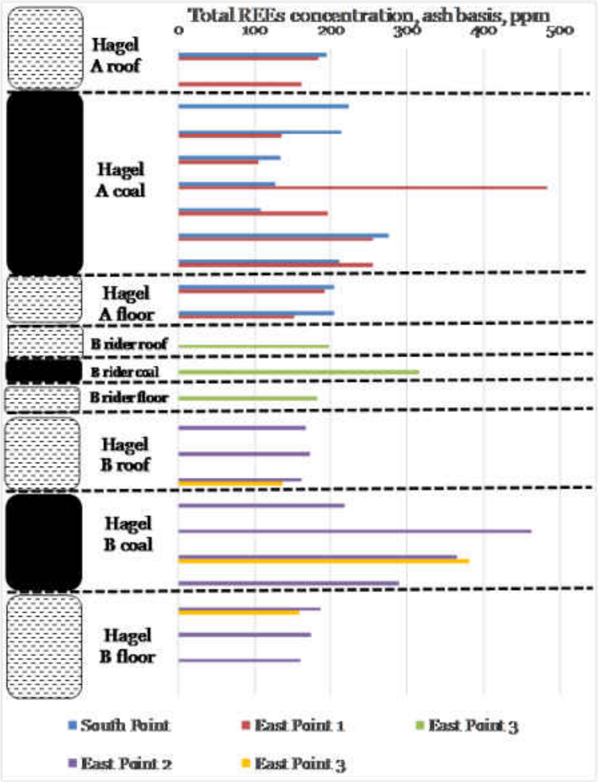

Figure 1. Analysis of REE+Y content in the Falkirk Mine stratigraphic sequence (dry ash basis)

Additional coal samples were collected from outside the Falkirk Mine, including samples from the Hansen Harmon seam in Slope County, ND. A roof sediment sample was also collected from the Hansen Harmon seam. Analysis of samples from this seam showed very high levels of REE+Y+Sc, with the coal sample at 560 ppm (whole coal basis) and 2300 ppm (ash basis), and the roof sediment also very high at about 450 ppm (whole sample basis) and 600 ppm (ash basis).

To understand the modes of occurrence of the REE+Y+Sc in ND lignite coal, a series of Chemical Fractionation tests were performed, which is a sequential extraction procedure using water, 1M ammonium acetate and 1M HCl. The water extracts water soluble minerals such as NaCl. The ammonium acetate extracts ion-exchangeable elements attached to carboxylic acid groups or hydroxide groups, and the HCl extracts elements associated as organic coordination complexes or acid soluble minerals such as carbonates, oxides and sulfates. The unleached residual elements are associated with silicates, aluminosilicates, sulfides and insoluble oxides. Testing was done on five coal samples with REE content greater than 400 ppm (ash basis). The results, shown in Table 1, indicate that the majority of REE are extractable, mostly in the HCl step. The Hagel A sample (16040) was the exception which showed highly ion-exchangeable REE content and the highest overall extraction of the REEs. Based on this data, as well as a thorough literature review, the UND project team believes that the majority of the REEs in ND lignite coals are associated organically as ion-exchangeable cations or coordination complexes, or as loosely adsorbed elements on the organic matter or the clay minerals.

Table 1. Chemical fractionation test results for five ND lignite coals

Sample ID	IES 16040			IES 16050			IES 16051			IES 16060			ND 15RE-6A		
Element	Oragnically Associated (Leached by H2O/NH4OAc)	Carbonates or Coordination Complexes (Leached by HCl)	Inorganically Associated (Not leached)	Oragnically Associated (Leached by H2O/NH4OAc)	Carbonates or Coordination Complexes (Leached by HCl)	Inorganically Associated (Not leached)	Oragnically Associated (Leached by H2O/NH4OAc)	Carbonates or Coordination Complexes (Leached by HCl)	Inorganically Associated (Not leached)	Oragnically Associated (Leached by H2O/NH4OAc)	Carbonates or Coordination Complexes (Leached by HCl)	Inorganically Associated (Not leached)	Oragnically Associated (Leached by H2O/NH4OAc)	Carbonates or Coordination Complexes (Leached by HCl)	Inorganically Associated (Not leached)
Y	76.3	21.0	2.6	0.0	87.2	12.8	7.2	76.6	16.1	0.0	92.5	7.5	9.2	79.2	11.6
La	84.8	13.9	1.3	0.0	94.8	5.2	12.7	75.7	11.6	1.0	83.7	15.4	2.7	88.9	8.4
Ce	77.1	21.0	1.9	0.0	93.4	6.6	14.8	73.8	11.4	5.3	83.5	11.2	1.7	91.5	6.8
Pr	72.6	25.2	2.2	0.0	91.6	8.4	14.5	73.3	12.2	4.2	85.8	10.0	0.6	92.7	6.7
Nd	68.2	29.3	2.5	0.0	90.7	9.3	15.5	71.9	12.6	5.3	86.0	8.7	0.7	92.7	6.6
Sm	68.4	29.3	2.3	0.0	90.7	9.3	13.9	72.6	13.5	2.3	90.7	7.0	1.3	92.0	6.7
Eu	71.5	26.7	1.9	0.0	91.6	8.4	12.7	70.6	16.6	0.0	93.8	6.2	2.1	91.7	6.2
Gd	71.5	26.4	2.1	0.0	90.8	9.2	16.7	70.3	13.0	0.0	93.6	6.4	3.7	90.9	5.3
Tb	73.8	23.8	2.4	0.0	89.1	10.9	15.4	70.5	14.1	0.0	93.3	6.7	4.1	89.9	6.0
Dy	75.3	21.9	2.8	0.0	87.7	12.3	15.3	69.3	15.4	0.0	92.9	7.1	4.6	88.1	7.2
Ho	76.1	20.8	3.1	0.0	86.2	13.8	14.7	68.7	16.6	0.0	92.4	7.6	5.5	85.3	9.2
Er	76.9	19.6	3.5	0.0	84.1	15.9	16.0	66.1	17.9	0.0	91.7	8.3	6.9	81.7	11.4
Tm	76.9	19.1	4.0	0.0	81.6	18.4	15.4	64.2	20.4	0.0	90.9	9.1	6.8	80.0	13.3
Yb	76.7	18.7	4.6	0.0	79.1	20.9	15.7	61.3	23.1	0.0	89.9	10.1	6.3	79.1	14.5
Lu	76.7	18.2	5.0	0.0	76.8	23.2	14.0	60.8	25.1	0.0	89.0	11.0	7.8	75.4	16.7

Laboratory-scale REE Concentration Testing Summary

Once understanding that the REEs in ND lignite coal are easily extractable via mild acid leaching, a series of screening tests was performed with the Hagel B coal (several hundred pound sample collected from Falkirk Mine that showed relatively uniform REE content distribution). Three acid types, each with two concentrations were evaluated in the laboratory using the following conditions:

- 60 grams dried coal – known REE content
- 125 mL acid
- Coal/acid slurried at 40°C for 48 hours
- pH measured as a function of time
- Unleached residual solids filtered, dried and analyzed for REE content
- Extraction of elements to solution determined by difference in starting coal and leached coal

The results of the testing are provided in Table 2. Results indicate that the higher concentrations were significantly more effective, with the HCl providing the best overall REE extraction from the coal. However, based on the below factors, 0.5M H_2SO_4 was chosen for additional testing:

- Lowest concentration acid that provided good extraction of REEs
- Higher Sc extraction than HCl, even though lower REE extraction
- Lowest extraction of other inorganics into solution (i.e. more REE selective)
- High recovery of critical and heavy REEs
- Lowest cost mineral acid
- Preferred acid for many industrial mineral extraction processes
- Potential for cost effective on-site generation

Table 2. Results of laboratory acid leaching screening tests

	wt% Extracted					
	0.1 M HCl	1.0 M HCl	0.1 M H2SO4	0.5 M H2SO4	0.1 M H3PO4	1.0 M H3PO4
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	11.04	86.81	4.50	70.94	7.90	64.56
LREE wt% extracted	11.17	83.86	4.31	63.79	7.59	60.35
HREE wt% extracted	10.83	91.84	4.82	83.13	8.41	71.73
CREE wt% extracted	10.94	90.80	4.66	78.95	8.09	69.16
n-CREE wt% extracted	11.12	83.66	4.37	64.60	7.75	60.92

Note: CREE is critical REE, and n-CREE is non-critical REE

With the selection of the sulfuric acid leaching, additional testing was done with both the Hagel B feedstock (580 ppm ash basis), and the Hansen Harmon feedstock (2300 ppm ash basis), with analysis conducted on both the REEs, as well as other high value elements and impurities that may be extracted into the solution. Interestingly, the sulfuric acid leaching was significantly more effective on the higher REE content Hansen Harmon coal, with REE recovery of about 90% for REE+Y, and about 82% for Sc. There was also significant recovery of other valuable elements, such as Co, Ge, Ga and others. However, even with the excellent extraction performance, the concentration of REE+Y in solution was only about 0.9wt%, lower than the programmatic target of 2wt%. To improve, addition of a 1M ammonium acetate leaching step was investigated ahead of the sulfuric acid leaching. From Chemical Fractionation tests, it was observed that for the two feedstocks (Hagel B, Hansen Harmon), minimal or no extraction of REEs occurred. However, there is significant rejection of impurities (alkali, some transition metals). When using the ammonium acetate step, the REE concentration in solution after the sulfuric acid leach improved to about 1wt%. The exploratory ammonium acetate work demonstrates that selective extraction methods could improve process performance. However, with added complexity and costs, it is not clear the overall benefit. The TEA is evaluating the economics of this optional step in a sensitivity analysis.

Finally, to achieve the 2wt% target, selective precipitation of iron from the sulfuric acid leach solution can be accomplished by a forced oxidation method, in which air is passed through the solution to oxidize iron ions into insoluble oxides. There are multiple literature examples that provide justification for this approach. For instance, in their evaluation of a Canadian REE mineral ore, Search Minerals [1] employed a forced oxidation method to precipitate iron after their acid digestion step. They reported a 90% removal efficiency, with REE losses to the precipitate of about 5%. A lower range of iron precipitation efficiency (72%) was derived from the work of Dai et al [2], in which the authors investigated a forced oxidation method to precipitate iron from zinc hydrometallurgy processing solution. Additionally, large-scale forced oxidation in acidic solutions is commonly practiced in wet flue gas desulfurization systems, to oxidize calcium sulfite to calcium sulfate [3]. For the purposes of evaluation in this TEA, we have chosen 70% efficiency as a conservative estimate. Although the kinetics of iron oxidation are quite slow in acidic medium [4], several catalytic ions are in solution, such as copper, that will significantly increase oxidation rates [5]. Additionally, with process optimization, it is expected that operation at a higher pH will be possible, mitigating risks of low iron oxidation rates.

Based on laboratory testing and analysis, as well as the literature regarding iron precipitation, Tables 3 and 4 display the overall concentration of REE+Y for the proposed REE extraction process for both the Hansen Harmon and Hagel B feedstocks. Close to the 2wt% target is achieved in the worst-case scenario (Case 1), but over 6wt% is achieved in Case 4 for the Hansen Harmon. The target is not achieved under any condition with Hagel B coal, which is due to the presence of significant quantity of aluminum in solution. A literature search has identified partial neutralization of the leach solution as a standard method for selective precipitation of aluminum.

Table 3. REE concentration in solution for Hansen Harmon coal feedstock

REE Wt% In Solution for Multiple Cases (dry basis not including mass of acid)	
Case Description	Wt% REE in solution
Post Leaching, no NH4OAc pre-leach	0.88
Post Leaching, w/ NH4OAc pre-leach	1.01
Case 1 - 72% Fe precipitation, no NH4OAc pre-leach	1.94
Case 2 - 90% Fe precipitation, no NH4OAc pre-leach	2.91
Case 3 - 72% Fe precipitation, w/ NH4OAc pre-leach	2.94
Case 4 - 90% Fe precipitation, w/ NH4OAc pre-leach	6.07
NOTE: Cases 1-4 assume 5wt% REE loss to the Fe precipitate	

Table 4. REE concentration in solution for the Hagel B feedstock

REE Wt% In Solution for Multiple Cases (dry basis not including mass of acid)	
Case Description	Wt% REE in solution
Post Leaching, no NH4OAc pre-leach	0.16
Post Leaching, w/ NH4OAc pre-leach	0.40
Case 1 - 72% Fe precipitation, no NH4OAc pre-leach	0.18
Case 2 - 90% Fe precipitation, no NH4OAc pre-leach	0.18
Case 3 - 72% Fe precipitation, w/ NH4OAc pre-leach	0.53
Case 4 - 90% Fe precipitation, w/ NH4OAc pre-leach	0.59
NOTE: cases 1-4 assume 5wt% REE loss to the Fe precipitate	

Base Case Boundary Conditions for the TEA

- Hansen Harmon coal feedstock (560 ppm coal basis and 2300 ppm ash basis REE content)
- 2-step process: i) 0.5M sulfuric acid leach, ii) forced oxidation iron precipitation
- Ambient temperature leaching with 24 hours residence time
- 40% acid consumption (initial pH: 0.3; final pH: 0.5)
- 70% iron precipitation efficiency

Sensitivity Analysis Cases for the TEA (economic sensitivity cases discussed within the TEA)

- Hagel B coal feedstock
    - Lower REE throughput
    - Lower high value metals throughput
    - Lower REE concentration in product (increased processing costs)

- Ammonium acetate ‘pre-leaching’ step
    - Adds capital and operating expense
    - Slightly decreases REE throughput
    - Decreases content of some high value metals throughput
    - Higher REE concentration in product (decreased processing costs)

REFERENCES

1. Dreisinger, D., Verbaan, N., Johnson, M., Andres, G. “The Search Minerals Direct Extraction Technology for Rare Earth Recovery.” IMPC 2016: XXVIII International Mineral Processing Congress Proceedings – ISBN: 978-1-926872-29-2
2. Dai, X., Zeng, P., Li, Y., Huang, M., Yang, M., Chen, G., Li, G., Wang, H. “Testing and Application of Iron Precipitation as Goethite (FEOOH) Using a Strong Air Flow. IMPC 2016: XXVIII International Mineral Processing Congress Proceedings – ISBN: 978-1-926872-29-2
3. Yuran, L, Jinting, Z., Tingyu, Z., Pengfei, J. “Calcium Sulfite Oxidation and Crystal Growith in the Process of Calcium Carbide Residuue to Produce Gypsum.” Waste and Biomass Valorization. February 2014, Volume 5, Issue 1, pp 125-131.
4. Morgan, B., Lahav, O. “The effect of pH on the kinetics of spontaneous Fe(II) oxidation by O2 in aqueous solution – basic principles and a simple heuristic description.” Chemosphere 68 (2007) 2080-2084.
5. Stumm, W., Lee, F. “Oxygenation of Ferrous Iron”. Industrial Engineering Chemistry. Division of Water and Waste Chemistry, 137th Meeting, ACS, Cleveland, Ohio, April 1960.

Exhibit F

Letters of Support from NDUS and VCSU & WT&C Innovates

NORTH DAKOTA
UNIVERSITY SYSTEM
ACCESS. INNOVATION. EXCELLENCE.

NORTH DAKOTA UNIVERSITY SYSTEM
Facility Planning Department
4349 James Ray Drive
P.O. Box 13597
Grand Forks, ND 58202-3597
701-777-4270

Dr. Steven A. Benson
Proffessor, UND Institute for Energy Studies
Associate Vice President for Research, UND Energy & Environmental Research Center
University of North Dakota
15 N. 23 Street
Grand Forks, ND 58202

Re: Support of the University of North Dakota's US Department of Energy project DE-FE0027006 entitled "Investigation of Rare Earth Element Extraction from North Dakota Coal-Related Feedstocks."

Dear Dr. Benson:

The North Dakota University System (NDUS) is pleased to support the University of North Dakota as they develop and evaluate the technical and economic feasibility of integrating a rare earth element (REE) recovery process with the next generation of NDUS campus heating plants. The NDUS is currently planning and seeking appropriations for an upgrade to the steam generators across the state and are excited to work with the UND Team to evaluate their novel co-generation plant concept that produces not only steam for campus heating, but also recovery of value-added rare earth elements and the production of high purity activated carbon products derived from ND lignite coal.

We understand that REEs provide significant value to our national security, energy independence, environmental future, and economic growth. We are encouraged by the recent work conducted by the UND team and are excited about the opportunity to add an REE recovery process to our next generation heating plant concept that integrates activated carbon production with steam generation.

Upgrades to the NDUS campus heating plants will be required in the near future. Valley City State University if the first university to update their steam plant. This plant is one of the smaller ones in the NDUS system and we anticipate scaling up the technology for application at the larger universities in the state. Based on the designs for the first implementation at VCSU, we can expect a roughly 50-fold increase in REE and carbon production rates if this technology is installed at our two largest campuses, UND and North Dakota State University. We expect to be able to garner support from the State to fund these installations with successful first-of-a-kind demonstration at VCSU.

We believe that the combination of new revenue streams and research and educational opportunities will tremendously benefit our state Universities and our students. NDUS will continue to work with the project team to advance their unique technology to the next stage and eventually for commercialization at VCSU and other campuses within NDUS.

We fully support the UND Team's efforts in their current Phase I project, and are excited at the prospects for a subsequent Phase II project and wish the UND team success as they move forward in their technology development. Please do not hesitate to contact me at the letterhead address or email below for any additional information or with questions.

Sincerely,

Rick Tonder, Director of Facility Planning, NDUS

The North Dakota University System is governed by the State Board of Higher Education and includes:
Bismarck State College • Dakota College at Bottineau • Dickinson State University • Lake Region State College • Mayville State University • Minot State University • North Dakota State College of Science • North Dakota State University • University of North Dakota • Valley City State University • Williston State College.

Office of the President

VALLEY CITY
STATE UNIVERSITY

February 8, 2017

Dr. Steven A. Benson
Professor, UND Institute for Energy Studies
Associate Vice President for Research, UND Energy & Environmental Research Center
University of North Dakota
15 N. 23 Street
Grand Forks, ND 58202

Re: Support of the University of North Dakota's US Department of Energy project DE-FE0027006 entitled "Investigation of Rare Earth Element Extraction from North Dakota Coal-Related Feedstocks."

Dear Dr. Benson:

Valley City State University (VCSU) is pleased to support the University of North Dakota as they develop and evaluate the technical and economic feasibility of integrating a rare earth element (REE) recovery process with an activated carbon and steam production facility. VCSU is currently upgrading its steam heating facility and is working on obtaining funding for integrating an activated carbon plant with the new steam plant. The steam/carbon plant project has been submitted to the State of North Dakota legislature for funding. The project was unanimously approved by the Senate appropriations committee in February, 2017 and is now up for approval in the house. If we receive approval for funding by July 2017, we would plan on initiating construction of the carbon plant in the middle of 2018.

We understand that REEs provide significant value to our national security, energy independence, environmental future, and economic growth. We are encouraged by the recent work conducted by the UND team and are excited about the opportunity to add a REE recovery process to our integrated activated carbon and steam plant. We are excited to work with the UND Team to evaluate the integration of their novel REE recovery process within our steam co-generation plant concept that would produce not only steam for campus heating, but also value-added activated carbon products and REEs produced from North Dakota's vast lignite resources. It is particularly attractive, as we understand that UND's REE recovery process will provide the opportunity to increase the purity and value of the carbon products produced at our facility.

The carbon and REE products will provide revenue streams for the University, which will not only offset costs of steam production, but based on UND's economic analysis, will generate a significant profit that can be used to supplement education and research offerings at VCSU. We are working with UND to develop collaborative science and engineering programs that will educate the next generation of energy experts. We believe that addition of the REE recovery process to our facility will provide additional infrastructure and funding opportunities to expand our research platform and provide additional value to our students, the state and the nation.

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We are excited about this first implementation of the next generation of university heating plants at the VCSU campus, and hope that it will serve as a pilot, that with success, will encourage subsequent implementation at other facilities. We believe the concept proposed by the UND team would be beneficial to both VCSU and the state of North Dakota and are excited to help in advancing it to the next stage of development. We look forward to collaborating with UND as they further develop their unique technology.

We wish the UND team success in its current Phase I project with DOE as well as success in securing funding for a subsequent Phase II project, of which we will be fully supportive. Please do not hesitate to contact me at the letterhead address or email below for any additional information or with questions.

Sincerely,

Tisa a Mason

Tisa A. Mason, Ed.D., CAE
VCSU President

February 13, 2017

Dr. Steven A. Benson
Professor, UND Institute for Energy Studies
Associate Vice President for Research, UND Energy & Environmental Research Center
University of North Dakota
15 N. 23 Street
Grand Forks, ND 58202

Re: Support of the University of North Dakota's US Department of Energy project DE-FE0027006 entitled "Investigation of Rare Earth Element Extraction from North Dakota Coal-Related Feedstocks."

Dear Dr. Benson:

WT&C Innovates is pleased to offer this letter of interest to the University of North Dakota as they develop and evaluate the technical and economic feasibility of a novel technology for extraction and concentration of rare earth elements (REE) from North Dakota lignite-related feedstocks. We understand that REEs provide significant value to our national security, energy independence, environmental future, and economic growth. We are encouraged by the work by the UND team and are excited by the potential to offer our services in the final processing and purification of the REE concentrate generated by the UND technology.

WT&C Innovates provides advanced industrial waste and waste water recovery/recycle systems and technologies to the natural resources industries, primarily: i) precious metals mining, ii) rare metals processing, iii) oil & gas source and produced water. We are very interested in evaluating the 2wt% REE concentrate product generated by UND and upon commercial implementation, may be interested in purchasing the product for processing at our facilities. Based on our initial discussions, we feel that the composition of the REE concentrate, as measured/estimated from your Phase I project, is amenable to our capabilities.

As the UND team moves forward in its development, we will be interested in obtaining a larger sample of the 2wt% REE concentrate so that we may evaluate it in our test facilities. We understand that this will be a possibility in a subsequent Phase II project, if awarded by DOE, in which the UND team will be constructing and testing a larger bench-scale test system. In the meantime, we will continue to discuss with the UND team and provide our insights so that the UND technology can be effectively developed to accommodate downstream purification steps.

We wish the UND team success in completion of its Phase I project, as well as in securing funding for a subsequent Phase II project, of which we plan to support through testing and evaluation of the UND REE concentrate products. If you have any questions, please do not hesitate to call or email.

Sincerely,

Bill W. Hayward

Bill Hayward
President

WT&C Innovates Inc.

APPENDIX E – PRO FORMA – VALLEY CITY STATE UNIVERSITY ACTIVATED CARBON PLANT

This section contains the business plan (Pro Forma) prepared by UND as part of a separate effort to investigate the feasibility of integrating activated carbon production with the Valley City State University steam heating plant. It contains the design details and background information of the activated carbon production components used within the technical and economic feasibility study contained in Appendix D. The formatting used in the Pro Forma is not consistent with the rest of this dissertation, and is to be taken as a stand-alone document.

ACTIVATED CARBON PLANT / HEAT PLANT INTEGRATION: VCSU & UND
Pro Forma

Prepared by:

University of North Dakota
Institute for Energy Studies
Energy & Environmental Research Center

Valley City State University

January 3, 2017

ACTIVATED CARBON PLANT / HEAT PLANT INTEGRATION: VCSU & UND
PRO FORMA SUMMARY

Introduction

Valley City State University and the University of North Dakota (VCSU/UND) intend to partner with a private sector business to produce and sell Activated Carbon (AC). VCSU will manufacture AC at lower costs than traditional methods by leveraging their approved new steam heating system to offset necessary capex required for manufacturing AC. Distribution and sales will be conducted by the private sector partner. The efficiencies provide a significant source of revenue (*annual cash flow of $2.5 million in years 1 – 10, $4.3 million after initial debt retired)* which can fully liquidate the capital procurement debt within a few years, after which revenues will build reserves for other needs. The model can be replicated at other NDUS campuses.

AC Market Values

- Current market value of $2400 per ton to end user with future projections of $4000/ton.
- VCSU plans to sell at $1400 per ton F.O.B under contract to private sector distribution.
- $1000 per ton mark-up covers transportation and marketing costs for re-seller. VSCU profit of $325/ton.

AC Market Demand

- VCSU production planned at 6,000 tons per year. We are exploring partnerships with Midwest Energy Emissions Corporation (ME2C) and Calgon Corporation.
- ND market alone exceeds 100,000 tons per year, with a global market projected to grow to more than 2 million tons by 2022.
- VCSU production 0.25% of current demand - will have no identifiable impact on market demand.

Self-liquidating Capital Construction Debt

- Total capital investment of $15.2M ±40% including working capital during construction.
- Gross revenue from annual production of 6,000 tons @ $1400 per ton = $9.4M.
- Annual cash flow of $2.5 million in years 1 – 10, $4.3 million after initial debt retired.
- Debt liquidation in 3.5 years.
- Model remains viable at $1000 per ton, with debt liquidation in 10 years or less.

Market Risks

- China may flood market with AC
  - Unlikely, but North Dakota – Regional market will have some insulation based on local demand and shipping costs to this area.
- Technology will displace AC usage
  - Currently not on the horizon, with debt liquidation occurring well before any anticipated reduction in demand.
- Other Market Variables
  - Increase in transportation costs would have minimal impact.
  - Feed stock (lignite) costs increases would have a minimal impact.
  - EPA regulations promulgated in next ten years may reduce overall functional life of plant, but impact on debt liquidation unlikely.

Primary benefit: New sources of revenue promote self-sufficiency in higher education.

ACTIVATED CARBON PLANT / HEAT PLANT INTEGRATION: VCSU & UND
PRIMER

Key Point – What is activated carbon?

- Activated carbon is produced from carbon-containing natural resources such as biomass and coal using well developed technology.
- Activated carbon is valuable as it absorbs contaminates from air, water, and other media.
- Activated carbon is mainly used for air and water purification in coal fired power plants and in municipal water treatment plants. It has many other uses as well.

Key Point – Activated carbon markets:

- Activated carbon sale is a growth market. Marketing surveys from eight different sources estimate a CAGR ranging from 11 to 13%.
- Activated carbon sale is a stable market, with no practical substitute on the horizon.
- Activated carbon is valuable, and typically sells from $1500 to $3,000 per ton.
- High purity specialty carbons (a potential future market) can sell for $15,000 per ton.

Key Point – Activated carbon manufacturing:

- Activated carbon is a straight-forward manufacturing process using proven methods.
- Current US production levels are approximately 435 tons annually from seven major producers.
- Activated carbon manufacturing requires steam to “activate” the carbon.
- Standard activated carbon manufacturing wastes significant amounts of volatile gasses which are released from coal feed stocks.

Key Point – Why lignite coal?

- Lignite is mined locally, and produces the best activated carbon as it is already a porous feed stock.
- Costs for shipping lignite for local production of activated carbon is low.
- Costs for shipping lignite-sourced activated carbon to regional users is low.

Key Point – Why combine steam plants with activated carbon plants?

- Activated carbon plants release fuel and require steam.
- Steam plants produce steam and can use the fuel.
- Together, the two plants become much more efficient than if standing alone?

Key Point – How do the financials play out?

- Manufacturing efficiencies by combining the plant result in increased profits.
- Profits are sufficient to repay the capital investment in the carbon plant within 5 years.
- New boilers and/or steam plants can be installed and payed for in an additional 5 years.

Key Point – Win-Win

- Activated carbon is a stable market with sales generating revenue to meet the deferred maintenance needs.
- This is a model for campus self-sufficiency that reduces the need for appropriations.
- Institutions can use this model for research and education to strengthen their mission.
- This model and be replicated at other sites across North Dakota.

ACTIVATED CARBON PLANT / HEAT PLANT INTEGRATION: VCSU/UND

The need to replace the aging fleet of university and hospital district steam generating systems in North Dakota prompted a study to determine the technical and economic feasibility of a lignite-fired advanced combined heat and power system. The focus of this study, conducted by the University of North Dakota, Envergex LLC (holder of patent for the proposed process) and Burns & McDonnell (an international engineering and architecture firm), was the co-production of saleable products such as activated carbon with steam and/or electricity. Included in this study was the feasibility of utilizing the system to provide education and training opportunities for the next generation of energy experts and provide a testing platform for demonstrating emerging energy production and emissions control technologies. Other factors considered included Environmental Protection Agency (EPA) proposed new maximum achievable control technology (MACT) emission standards for industrial scale systems, pending carbon control legislation, and the desire to continue to use lignite coals as a feedstock for state-owned facilities. Results from this preliminary work showed strong potential to convert steam plant facilities within the North Dakota University System (NDUS) from a significant cost liability to a revenue generator. Study results also showed these advanced systems can be implemented with a significant reduction in the generation of air pollutants including CO_2 [10].

Valley City State University (VCSU) has become one of the first installations in the state to upgrade their steam generation facilities. A new steam plant is currently under construction. Recognizing the potential to integrate activated carbon production into the new steam plant, VCSU and the North Dakota University System (NDUS) teamed with the Institute for Energy Studies (IES) and its commercial partner, Envergex LLC to evaluate the technical and economic feasibility of integrating an activated carbon production into the new VCSU steam plant. The results presented in this pro forma statement indicate a strong investment opportunity at VCSU. If this were replicated at all 11 institutes of higher learning, the return could be over $50 million annually.

This pro forma review presents an overview of the technology and demonstrates the technical, economic and political viability of an integrated activate carbon/steam plant for VCSU. The current and future demand for activated carbon provide the market drivers for the proposed process. An overview of the process along with a breakdown of the revenues and expenses show both the technical and economic viability of the proposed project. The profitability and risk assessment provided in the report further demonstrate the high quality of this investment. Finally, the next steps required to make this project a reality, e.g. to obtain funding to build and activated carbon plant integrated with their new steam plant are presented.

Market Demand

The global activated carbon market size exceeded $3.0 billion in 2015 [14], and is expected to exceed $4.0 billion by 2019 [19], and $10.5 billion by 2024 [14]. The primary markets are in in water purification and gas cleanup. The demand, especially in the water cleanup area is global, with growth in the global market expected to grow at an even higher rate than in the US. The current suppliers in the US are a number of US producers as well as Chinese imports. The consistency of the product from China is variable.

Granular activated carbon (GAC) is used by most municipalities for water treatment. Many industries that generate significant quantities of waste water also rely on GAC as a primary treatment option. The global demand for GAC was 700,000 tons in 2014 and is expected to grow at a CAGR of 10.8% from 2014 to 2020 [14,18]. The global activated carbon market is expected to reach 2,200 thousand tons by 2022. The largest area of growth is water purification to mitigate health risks related to drinking contaminated water.

There is a developing market for powdered activated carbon (PAC). Sales of PAC are expected to reach 900 thousand tons driven in part by the EPA Mercury and Air Toxics Standards (MATS) [14, 18, 19]. PAC sorbent injection is the preferred mercury emissions control technology with 93% of the 229 coal fired units currently controlling for mercury utilizing activated carbon injection as their control strategy. Carbon produced from North Dakota lignite has superior qualities to other carbons for this market segment (see data presented in Appendix D). One coal-fired power plant is will utilize approximately 1000 tons of PAC annually. Therefore, the 6000 tons/yr produced by the proposed plant will not disrupt the market.

Calgon Carbon Corp., Cabot Corp., Haycarb PLC, MeadWestvaco, Osaka Gas Company Ltd., Kuraray Company Ltd. and Evoqua Water Technologies LLC are some of the major manufacturers of activated carbon globally. ADA Carbon Solutions LLC, Albemarle Corp., Arkema group, Carbotech AC GMBH, Indo German Carbons Ltd., Kureha Corporation, Ningxia Huahui Activated Carbon Company Ltd. and Oxbow Corporation are the other key participants in the activated carbon market.

A major user of PAC in the US, and in North Dakota in particular is Midwest Energy Emissions Corporation (ME2C). ME2C would be an ideal partner for this venture as it has several clients in North Dakota. The use of the product from VCSU would allow them to market a superior product while minimizing their transportation costs. Discussions have been initiated with Midwest Energy Emissions Corporation (ME2C) regarding the proposed process.

Proposed Technology

The proposed technology is based on the patented coproduction process developed by UND and Envergex LLC, in which a solid fuel, such as coal or biomass, is used to produce both a saleable activated carbon product and steam for heating and/or electricity production [1,2]. The proposed plant integrates two well-established and widely used processes mitigating the technology risks. The production of activated carbon integrated with steam production for use within the NDUS campuses, and VCSU in particular, with dramatically lower cost carbon production when compared to conventional activated carbon production plants. This is accomplished by the co-location of the activated carbon plant with the university heating systems. The key components of the proposed plant are summarized as follows and in Figure 1.

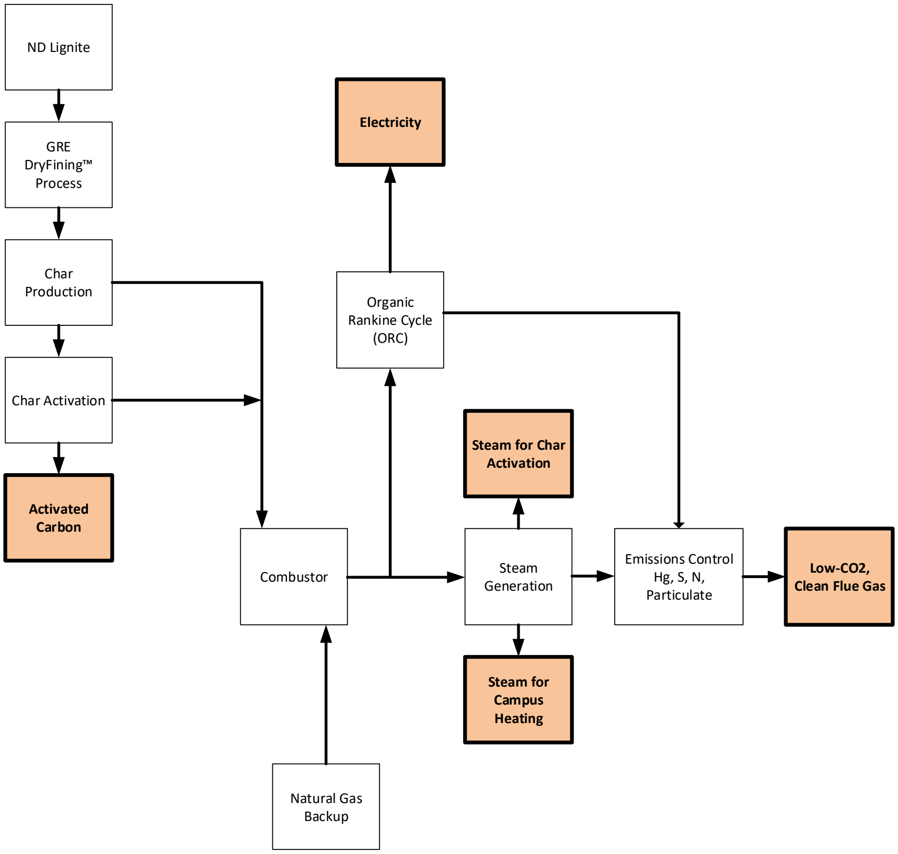


Figure 1. General schematic of proposed integrated activated carbon, steam generation, and electricity production plant.

Process Overview: Activated carbon is produced from lignite using a series of rotary kilns. Lignite is obtained from the patented GRE Dryfining^{TM} process that decreases moisture content of lignite. Dryfining^{TM} lignite at 5100 lb/hr enters the first rotary kiln to completely remove all the moisture content in the lignite before undergoing carbonization process. Carbonization also occurs in this first kiln. In this step, the volatiles are vaporized leaving behind char containing carbon and ash.

The char generated during carbonization is sent to the second rotary kiln where it undergoes activation. The char is activated using steam and occurs at 1650°F. The hot activated carbon is cooled to 200°F. The product at this stage is further sized to the specifications of the buyer of the activate carbon product. The product will be sold in bulk, so no specialized packaging is required.

The volatiles generated during the carbonization process and the syngas from the activation process are sent to the VCSU boiler. At full load, the steam boiler produces 21,000 lb/hr saturated steam. The university campus requires about 12,000 lb/hr steam for heating during its peak winter demand, and no steam during the summer. Activation of char requires about 710 lb/hr of steam. The rest of the steam produced is used to generate electricity. *The ability to use steam from the campus boilers for the activation of the carbon, and the ability of the steam boiler to use the volatiles and syngas from the activation process represents the primary synergy that makes this process more economical than stand-alone plants.*

Aspen Plus software was used to model the combined heating and activated plant. The stream and composition results generated by Aspen Plus are given in Appendix C. A detailed design of the process has been completed as a UND senior capstone project and is available upon request [11, 12].

Feedstock: ND lignite coal purchased from Great River Energy (GRE) after upgrading through their patented DryFining™ process which both dries the coal and removes impurities is proposed as the feedstock. The already upgraded coal can be trucked to the VCSU facility from the Spiritwood plant located approximately 30 miles from Valley City. The GRE process increases plant efficiency and reduces emissions. GRE has expressed their interest in the proposed plant concept. Lignite from other locations in North Dakota are also acceptable feedstocks.

Activated Carbon Production: Two general types of activated carbons are produced. With lignite as the feedstock, a char is produced through carbonization and activated with a traditional proven steam treatment method. This "standard" activated carbon can be produced as either a powdered or granular material (powdered activated carbon (PAC) or granular activated carbon (GAC)). These products can be used in many traditional applications such as mercury capture from flue gas and water treatment.

Steam/Electricity Production: The combustible product gases (volatiles, tars, syngas) from the char production and activation units are co-fired with any necessary backup fuels (i.e. natural gas) in the existing VCSU boiler to produce steam. A portion of the steam is used to heat the campus, some for standard activated carbon production, and any excess is used to produce electricity. The process is designed with back-up processes to ensure uninterrupted delivery of steam to heat the campus.

Emissions Control: The resulting flue gas from the activated carbon plant and the steam boiler is treated for particulate, mercury, sulfur and nitrogen species using methods already in commercial-scale deployment for lignite-fired power systems. The cleaned flue gas contains low CO_2 levels without the need for additional CO_2 capture because the carbon in the fuel is used for activated carbon production rather than for combustion, which stores the carbon in a permanent solid form.

Expected Impacts and Benefits

The proposed concept has many advantages compared to traditional steam generation plants currently operating within the NDUS. These are outlined in the following sections.

NDUS Heating Plants as Profit Centers: Through the proposed coproduction concept, the steam generation plant is transformed into a multi-product profit center for the university. Based on the work from this project, the coproduction concept shows the potential to not only off-set the cost of steam production for campus heating, but that the coproduction of activated carbon will result in a net annual profit for the plant.

Reduced Carbon Dioxide Emissions: The EPA's recently issued Clean Power Plan (CPP) calls for substantial reductions in CO_2 nationwide, with particularly challenging reductions requirements of 45% for the state of North Dakota. A key benefit of the proposed coproduction concept is inherently lower CO_2 emissions compared to direct firing of lignite coal. Based on the analysis of a typical ND lignite coal we can expect a total reduction in CO_2 emissions of about 40% when compared to stand-alone steam plants burning the same coal.

Abundant and Reliable Sources of Fuel: This concept takes advantage of the abundant lignite resources available in the state. The existing VCSU heating plant is severely limited by a lack of available of natural gas during the coldest months. The proposed concept includes a high degree of fuel flexibility to manage the cyclical daily and seasonal steam demands for the campus.

Opportunities for Education & Research, Development and Testing of Energy-Related Technologies: A secondary benefit of the proposed concept is to provide the opportunity to educate the next generation of energy experts. The coproduction plant can be used as a site to test new technologies and do research and development on ND lignite and biomass to enhance their value and utilization in the market. It can serve as site for testing of carbon capture and utilization technologies. The existing heating plants within the NDUS do not provide reasonable flexibility for such activities.

Revenues

Revenues are generated from the sales of activated carbon, fuel gas, and electricity. The industrial sales price of activated carbon $0.70 per pound ($1400/ton) was used as the basis. This price is reported as the current whole-sale of powdered activated carbon by local users. The current market price for activated carbon is $2400 to 3000/ton, leaving room for markup by the distributor. The process produces 1,770 lb/hr of activated carbon. Using a conservative capacity factor of 80% (plant operated only 290 days per year), 6200 tons of activated carbon will be produced per year. At a selling price of $1,400/ton, the revenue generated from the activated carbon is $8.7 million per year.

The recommended process also produces excess electricity that can be used internally to offset the purchase of electricity and/or sold back to the grid. An estimate for the price of electricity was obtained from the NDUS Facilities Management at a rate of 75% of the purchase price of electricity [3], or 6.5 cents per kWh. The process is expected to produce 3,972,500 kWh electricity annually based upon the average steam demand for campus heating during the summer and winter season. Using this selling price, the revenue generated from the sale of electricity is $260 thousand per year.

The process produces a 2,720 lb/hr of fuel gas from carbonization and activation process. The fuel gas has a total heating value of 24.9 MMBtu/hr. The revenue generated by the sale of the fuel gas was calculated using the natural gas price of $2.74/MMBtu [4] with the revenue generated from the sale of fuel gas approximating $480 thousand per year.

Table 1. Revenue streams and annual revenue generated.

Product Stream	Annual Production	Annual Revenue, $000
Activated Carbon	6,200 ton	8,700
Fuel Gas	174,300 MMBtu	480
Electricity	3,972,500 kWh	260
Total		**9,440**

Ninety-two percent of the revenue is generated from the sale of the activated carbon and represents the primary investment risk. The impact of the price received for the activated carbon on the profitability of this venture will be explored later in this report when the cash flow is presented. It will be shown that the plant will remain profitable over a wide range of activated carbon prices.

Expenses

Capital Cost

Capital costs were estimated using the widely accepted Guthrie-Ulrich cost estimating method for industrial plants. The Guthrie-Ulrich method uses the bare module cost of all the equipment to estimate the total cost for the project [5]. Vendor quotes were obtained for the most expensive piece of equipment and any other equipment within an order of magnitude of that price. Quotes were obtained for the rotary kilns, rotary dryers, rotary cooler, conveyors, and the largest compressor. Prices for all other equipment were adapted from Ulrich's "Chemical Engineering Process Design and Economics" [5] and scaled up to 2016 U.S. dollars using a ratio of the price indexes for these years. Details are presented in Appendix A. Technical specifications are being generated for a future request for proposal to the private sector for bids on constructing the plant.

The sum of all the equipment prices is equal to the total bare module cost. Contingency and fees associated with the process are estimated as 18% of the total bare module cost. The total bare module cost plus the contingency is equal to the total module cost. For a standard grass roots plant auxiliary facilities are added on at a cost of 30% of the total module cost. Adding the auxiliary facilities cost to the total module cost gives the fixed capital investment (FCI). These multipliers account for a variety of costs including shipping, installation, electrical and controls, and other costs directly associated with building an industrial plant. The working capital needed is assumed to be 10% of the FCI [6]. The working capital plus the FCI to gives the total capital investment (TCI). The total capital investment for the proposed process is $ 15.3 million with an accuracy of ± 40% at a 2016 basis date ($9.2 to $21.4 million). Table 2 presents a breakdown of the capital investment. A listing of the major pieces of equipment and their cost is given in Appendix A.

Table 2. Capital cost of the proposed concept.

Component	Annual Cost, $million
Bare Module Cost	9.08
Contingency and Fees	1.63
Total Module Cost	10.72
Auxiliary Facilities	3.21
Fixed Capital Investment	13.94
Working Capital	1.39
Total Capital Investment	**15.33**

Operating Cost

DryFined lignite coal will be purchased from Great River Energy (GRE) at a price of $38 per ton [7]. The process requires 5,200 lb/hr of as received lignite coal. At an 80% operating factor the total raw material cost is $680 thousand per year.

The current contract price of natural gas at VCSU is $2.74 per MMBtu [4]. The process has a total 6.2 MMBtu/hr heat requirement for drying, carbonization and activation process combined. The cost for the natural gas requirement is $120 thousand annually.

The operating labor was based on a 24 hours a day, 7 days a week work schedule. Four and a half shifts cover continuous operation each day [8]. The recommended process design includes 9 major unit operations and 10 minor unit operations. Based upon operational experience in similar plants, the number of operators per shift was determined to be 3 operators. One control operator per shift is included. For full time operation, the process will require 19 operators in addition to those currently operating the existing steam plant.

Operating salaries for operators at VCSU were obtained from NDUS Facilities Management. While standard operators have a salary of $35,000 per year, it was assumed a higher salary would be needed to attract workers to fill these new positions [9]. Therefore, a salary of $50,000 per year plus $21,000 for benefits for a total of $71,000 per year was used for this analysis. Control operators at VCSU have a salary of $60,000 per year with $25,500 in benefits for a total cost of $85,500 per year [9]. The cost of supervision included in the estimate is 15% of the operating labor costs. The total amount of operating labor equates to $1.6 million per year.

Since the coproduction of activated carbon and steam is a patented process, there is a patent fee that needs to be accounted for. For the activated carbon process, the patent fee is $0.025 per pound of activated carbon produced, or approximately $310 thousand.

The operating and maintenance cost for the system was estimated using industry standards. For a plant of this level of complexity, the typical O&M costs are estimated as 6% of the fixed capital investment. For the proposed plant, this amounts to $872 thousand per year. *It is critical that O&M is an on-going expense to avoid future deferred maintenance problems such as those that are currently facing the NDUS.*

The plant will utilize all of the excess steam not used to heat the campus for the activation process and to produce electricity. The value of the steam was estimated as $0.016 per lb from the existing VCSU steam plant. The annual cost for steam consumption is estimated to be $1.7 million. NOTE: If the plant is owned and operated by VCSU, this would represent an internal change of cash, and not an actual expense to the project. It was shown as a separate cost in this analysis to allow the profitability of the activated carbon plant to be assessed independent of the steam plant.

Table 3. Raw material and operating expenses

Component	Annual consumption	Annual Cost, $000
Coal	17,800 ton	680
Natural gas	43,400 MMBtu	120
Steam	4,991,000 lb	1,680
Personnel	19 operator/supervisors	1,630
O&M Cost	-	870
Royalties & Patent Fees	-	310
Total	-	**5,290**

Principal and Interest

For the purposes of this pro forma, it was assumed that the full FCI of $15.3 million will be borrowed at 4.5% interest to be paid back annually over a period of 10 years. The annual payment was estimated as $1.85 million per year.

Taxes

Calculations were done both on a tax-free (assuming 503 status) and a taxable basis (assuming operation by private entity). Taxes were calculated based on a 35% federal income tax rate and a 4.3% state tax rate for North Dakota which results in a blended tax rate of 36.4% (allows for taxes as a deductible expense). The taxable income was calculated using a 17-year MACRS tax depreciation schedule.

Profitability and Risk Assessment

The revenues were balanced against the operating costs, principal and interest payments, and income tax to project the annual cash flow from the project. Table 4 shows the analysis for the non-tax case, where the operations of the plant would be done within a 503 status, i.e. owned and operated by VCSU. In this scenario, the expected profits are approximately $2.3 million for the first ten years of the project and $4.1 million after the debt is retired. The total 20-year profit potential, neglecting the time value of money, is approximately $64 million. Net present value and DCFROR calculations have been performed and are included in Appendix B.

Table 4. Projected Annual Cash Flow for Non-Taxable Scenario ($ thousands)

	Revenue	Op Cost	P&I	Profit
Years 1 - 10	$ 9,404	$ (5,290)	($1,845)	$2,270
Years 11 - 20	$ 9,404	$(5,290)	0	$4,110
Twenty year profit potential				$63,800

Table 5 presents a similar analysis where a tax burden is realized. The annual variation in the income tax is due to the MACR depreciation schedule used. The annual cash flow under this scenario ranges from about $0.9 million to $2.7 million, with a 20-year profit potential of $37.8 million.

Table 5. Projected Annual Cash Flow Analysis for Taxable Scenario ($ thousands)

Year	Revenue	Op Cost	P&I	Gross Profit	Income Tax	Net Profit
1	$9,404	$(5,290)	($1,845)	$2,493	$ (962)	$1,307
2	$9,404	$(5,290)	($1,845)	$2,493	$ (1,031)	$1,238
3	$9,404	$(5,290)	($1,845)	$2,493	$ (1,091)	$1,178
4	$9,404	$(5,290)	($1,845)	$2,493	$ (1,146)	$1,123
5	$9,404	$(5,290)	($1,845)	$2,493	$ (1,194)	$1,075
6	$9,404	$(5,290)	($1,845)	$2,493	$ (1,237)	$1,032
7	$9,404	$(5,290)	($1,845)	$2,493	$ (1,275)	$994
8	$9,404	$(5,290)	($1,845)	$2,493	$ (1,309)	$960
9	$9,404	$(5,290)	($1,845)	$2,493	$ (1,339)	$930

Year	Revenue	Op Cost	P&I	Gross Profit	Income Tax	Net Profit
10	$9,404	$(5,290)	($1,845)	$2,493	$ (1,365)	$904
11	$9,404	$(5,290)	$0	$4,338	$ (1,365)	$2,749
12	$9,404	$(5,290)	$0	$4,338	$ (1,365)	$2,749
13	$9,404	$(5,290)	$0	$4,338	$ (1,365)	$2,749
14	$9,404	$(5,290)	$0	$4,338	$ (1,365)	$2,749
15	$9,404	$(5,290)	$0	$4,338	$ (1,365)	$2,749
16	$9,404	$(5,290)	$0	$4,338	$ (1,365)	$2,749
17	$9,404	$(5,290)	$0	$4,338	$ (1,365)	$2,749
18	$9,404	$(5,290)	$0	$4,338	$ (1,365)	$2,749
19	$9,404	$(5,290)	$0	$4,338	$ (1,579)	$2,535
20	$9,404	$(5,290)	$0	$4,338	$ (1,579)	$2,535
Twenty year profit potential						$37,803

The sensitivity of the project performance to the various input factors was examined to evaluate the potential risks to this investment. The results are summarized in Table 6. Unless otherwise noted, factors were varied by 40% of their base value in the direction that would result in reduced profitability for the plant. The results of this analysis indicate that with the exception of the sales price for activated carbon, all other factor have only a minor impact on the plant profitability (as indicated by the relatively small variation in the DCFROR and the payback time.

Table 6. Sensitivity Analysis for no-Tax Scenario	Base	New	DCFROR %	NPV (4%) $million*	Pay Back, Yrs
Base	**-**	**-**	**25.8**	**43.4**	**3.5**
AC Selling Price ($/lb)	0.7	0.55	13.8	18.1	6.2
	0.7	0.43	2.6	-2.0	15.3
	0.7	0.4	-2.7	-7.2	24.6
Capacity Factor	0.8	0.7	22.6	36.0	4.0
	0.8	0.6	19.4	28.7	4.7
Capital Cost ($million)	15.2	21.3	18.5	37.2	4.9
Labor ($million/yr)	1.63	1.97	22.5	35.8	4.0
Coal Price ($/ton)	38	53	24.2	39.8	3.8
Electricity Price ($/kwh)	0.06	0	24.3	39.9	3.77
Fuel Gas Price ($/MMBtu)	2.74	0	23.0	36.9	4.0

Table 6. Sensitivity Analysis for no-Tax Scenario	Base	New	DCFROR %	NPV (4%) $million*	Pay Back, Yrs
Base	**-**	**-**	**25.8**	**43.4**	**3.5**
Steam price, ($/lb.)	0.016	0.01	29.3	52.0	3.1
	0.016	0.022	22.1	34.8	4.1

*Net Present value calculated at a 4% hurdle rate. Payback does not consider cost of capital/interest

Table 7 show the effect of the interest rate on yearly net profit for the no-tax scenario. For a 10% interest rate, the annual benefit is reduced from $2.4 to $2.1 million for the first ten years. The annual net benefit for the remainder of the project is $4.3 million with a total benefit $64.2 million approximately for the total twenty year project life. Therefore, the interest rate is not expected to present a significant financial risk for the project.

Table 7. Sensitivity Analysis for no-Tax Scenario for interest rate.

	Yearly Net Profit, $million		Total Net Profit for 20 years, $million
Interest Rate, %	Year 1-10	Year 11-20	
4.5	$ 2.28	$ 4.11	$ 63.8
6	$ 2.16	$ 4.11	$ 62.7
8	$ 2.01	$ 4.11	$ 61.2
10	$ 1.86	$ 4.11	$ 59.7

Figures 2 and 3 show graphically the impact of activated carbon price on the payback time, DCFROR and the Net Present Value. From these calculations, the process shows a positive DCFROR at activated carbon prices greater than $0.42/lb. Net present value calculations show that even using a high hurdle rate of 12%, a positive NPV is realized when the price of activated carbon is $0.53/lb for the no-tax case, and positive when the activate carbon price is above $0.58/lb.

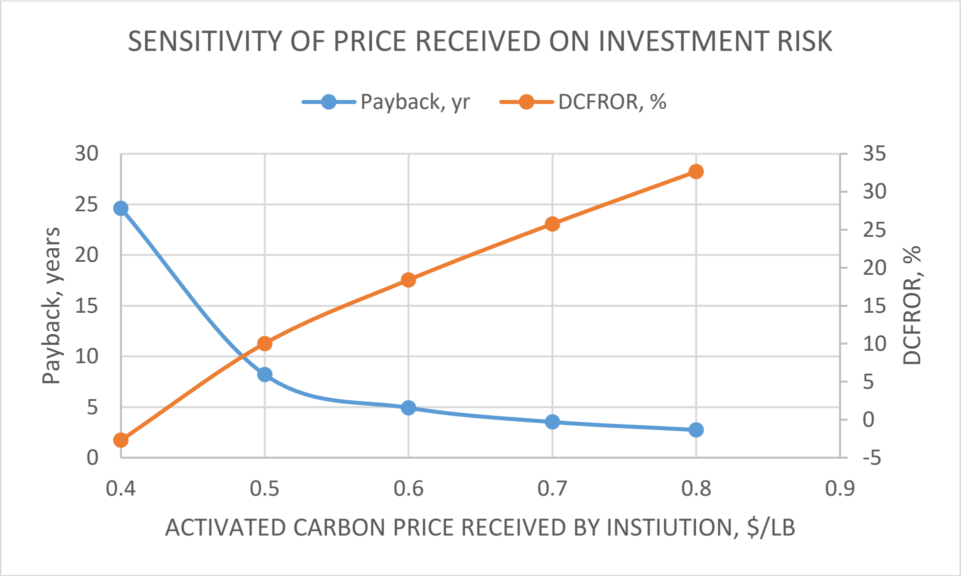


Figure 3. Sensitivity of Payback time and DCFROR on Price of Activated Carbon

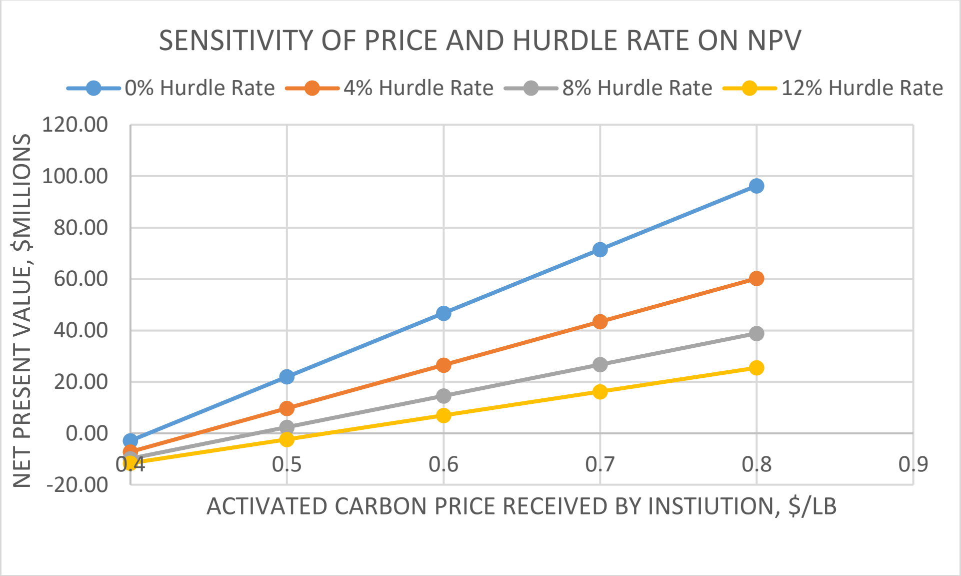


Figure 4. Sensitivity of Net Present Value on Price of Activated Carbon as a Function of Hurdle Rate

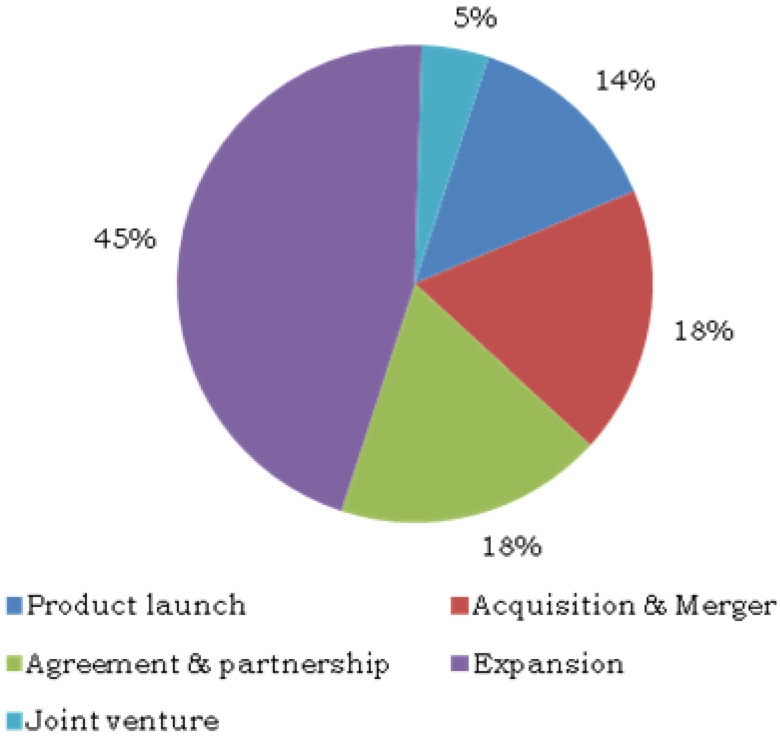
Next Steps

Results from this feasibility study indicate the building of an activated carbon plant to be operated in conjunction with the new steam plant on the Valley City State University campus represents a low risk, high return opportunity for the university. The VCSU/UND team is pursuing the next steps required to build this plant. These steps include:

- Develop a full business plan

- Performing testing at UND to obtain the final design data required to develop the detailed equipment specifications required to generate formal bid requests.
- Obtain legislative approval allowing VCSU to own and operate the proposed plant as a 503 and establish a 503 to provide the structure required for VCSU to generate and sell activated carbon.
- Develop a memorandum of understanding between VCSU and UND providing agreement on how to use revenues from the process to further the education missions at both universities.
- Obtain approval from the Bank of North Dakota to borrow the required capital OR obtain approval to sell revenue bonds to raise the required capital to fund the project.
- Solicit an A&E firm to complete the detailed design of the plant.
- Sign a contract with a company to buy the product from the plant at a guaranteed price.

Top Winning Strategies adopted by players in Activated Carbon Market



Key players largely adopt expansion as their key growth strategy. Almost 45% of the strategies that are adopted by key players of this market are business expansion. Agreements & partnerships, acquisitions & mergers, product launch and joint venture are other prominent strategies adopted by key players in order to remain competitive in the activated carbon market. These strategies have accounted for 18%, 18%, 14% and 5% of the overall key strategies, respectively.

APPENDIX E

References:

1. Srinivasachar, Srivats, et al., et al. System and method for coproduction of activated carbon and steam/electricity. 7,981,835 United States, 2011.

2. Srinivasachar, Srivats. Method of manufacturing carbon-rich product and co-products. 9,121,606 September 2015.

3. Conversation with Rick Tonder, Director of Facilities Planning for NDUS. (Received March 11th, 2016) Conversation via email.

4. Conversation with Wesley Winch, Vice President for Business Affairs, VCSU. (Recorded Dec. 3rd, 2016) Conversation via Email.

5. Ulrich, Gael D., and Palligarnai T. Vasudevan. Chemical Engineering Process Design and Economics: A Practical Guide. Durham, NH: Process (Ulrich) Publishing, 2004. Print

6. Conversation with Rick Tonder, Director of Facilities Planning for NDUS. (Recorded April 11th, 2016) Conversation via Telephone.

7. U.S. Energy Information Administration - EIA - Independent Statistics and Analysis." U.S. Energy Information Administration (EIA). Web. 2 Dec.2016. <http://www.eia.gov/coal/data.php#prices>

8. Turton R, Bailie RC, Whiting WB, Shaewitz JA, Bhattacharyya D. Analysis, Synthesis, and Design of Chemical Processes. 4th ed. Upper Saddle River: Prentice-Hall; 2012.

9. Conversation with Rick Tonder, Director of Facilities Planning for NDUS. (Recorded April 11th, 2016) Conversation via Telephone.

10. Advanced Power Systems Initiative: Lignite Feasibility Study, prepared for the North Dakota Industrial Commission by the University of North Dakota Institute for Energy Studies, Envergex LLC and Burns & McDonnell, June 2010.

11. Buehler, Jameson; Hunt, Mitchell; Oegado, Richard; Sandeen, Samatha; "Scoping Study on the Co-Production of Regular and Enhanced Activated Carbon Alongside Heating Steam for Valley City State University", prepared for Dr. Wayne Seames, May 4, 2016.

12. Buehler, Jameson; Hunt, Mitchell; Oegado, Richard; Sandeen, Samatha; "Partial Conceptual Design for the Co-Production of Regular and Enhanced Activated Carbon Alongside Heating Steam for Valley City State University", prepared for Dr. Wayne Seames, May 4, 2016.

13. Benson, Steven; et. al., "JV Task 90 – Activated Carbon Production from North Dakota Lignite" Energy and Environmental Research Center, report prepared for U.S. Department of Energy, March 2008.

14. "Activated Carbon Market Analysis By Product (Powdered Activated Carbon (PAC), Granular Activated Carbon (GAC)), By Application (Liquid Phase, Gas Phase), By End-Use (Water Treatment,

Food & Beverages, Pharmaceutical & Medical, Automotive, Air Purification) And Segment Forecasts To 2024", Grand View Research, August 2016. Data extracted from report summary available at http://www.grandviewresearch.com/industry-analysis/activated-carbon-market

15. "Activated Carbon Market by Product Type (Powdered, Granular), Application (Liquid, Gaseous) and End Use (Water Treatment, Food & Beverage Processing, Air purification) - Global Opportunity Analysis and Industry Forecast, 2014 – 2022" Allied Market Research, July 2016. Data extracted from report summary available at https://www.alliedmarketresearch.com/activated-carbon-market

16. "Chemical Profile ACTIVATED CARBON" ICIS, December 2015. Data extracted from report summary available at http://www.icis.com/resources/news/2005/12/02/544570/chemical-profile-activated-carbon/

17. "Carbon & Chemicals: The Year in Review for Graphite, Salt and Activated Carbon", LONDON, December 15, 2016 /PRNewswire. Accessed from http://www.prnewswire.com/news-releases/carbon--chemicals-the-year-in-review-for-graphite-salt-and-activated-carbon-606813116.html

18. "Global Activated Carbon Market Trends and Forecasts", aCarbons, December 2015. Accessed from http://www.acarbons.com/global-activated-carbon-market-trends-and-forecasts/

19. Sloss, L.L., "The Emerging Market for Mercury Control", IEA Clean Coal Centre, February 2015.

APPENDIX A: ASSUMPTIONS

Equipment Cost Estimate

Equipment costs were calculated using the Guthrie-Ulrich method for cost estimating. The most expensive pieces of equipment was determined from a vendor quote. Other less expensive equipment was estimated based upon standard methods in the chemical process industry. Below is an example of the cost estimation for a heat exchanger, all other estimations are performed in the same fashion. Estimated prices were all escalated to a basis date of August 2016. The bare module cost is the cost of the equipment FOB vendor. The bare module factor is a multiplier that accounts for the shipping, special material requirements, installation, piping, etc. to make the equipment functional in the plant. The value of the bare module factor is adjusted based upon experience in similar plants.

$$\mathrm{BMC} = \mathrm{C_p} \times \mathrm{F^a}_{\mathrm{BM}} \times \mathrm{n}$$

$$\mathrm{BMC} = (\$10{,}000)(2.8)(2) = \$56{,}000$$

Where:

BMC	Bare Module Cost
Cp	Purchase Cost
F^a_{BM}	Actual Bare Module Factor
n	Number of Units

$$C_{p\ basis\ date} = C_p \times \left(\frac{556.8}{400}\right)$$
$$C_{p\ basis\ date} = \$56{,}000 \times \left(\frac{556.8}{400}\right) = \$78{,}000$$

Where:

556.8	Chemical Engineering Plant Cost Index (CEPCI) for August 2016
400	CECPI for 2004

Table A1. Capital Cost Summary CAPITAL COST SUMMARY

Equipment Description	# of units	Total BMC
Lignite Coal Rotary Dryer	1	884,448
Carbonization kiln	1	1,171,893
Activation Kiln	1	906,559
Rotary Cooler Before AC Crusher	1	508,557
Activated Carbon Crusher	2	77,952
Rotary Dryer Condenser	2	32,796
Hopper	2	4,092
Air Compressor for Cooler	2	361,819
Air Compressor for N.G. Combustion	2	370,576
Air Inlet filter 1	2	122,496
Air Inlet filter 2	2	165,370
Coal Dryer Filter	2	55,123
Conveyor From Dryer to Carbonization	2	293,074
Conveyor to Activated Carbon Crusher	2	293,074
Conveyor to Activated Carbon Storage	2	293,074
Waste Water Pump	2	31,181
Organic Rankine Cycle	1	3,517,690
Total Bare Module Cost	CTBM	9,089,774
Contingency and Fee	CTBM ×0.18	1,636,159
Total Module Cost	CTM	10,725,933
Auxiliary Facilities	CTM×0.3	3,217,780
Fixed Capital Investment	FCI	13,943,713
Working Capital	FCI× 0.10	1,394,371
Total Capital Investment	**TCI**	**15,338,084**

Labor Costs

Rules of thumb were used to estimate the number of new operators required for the process. One new operator is typically required for every 5 major unit operations, and four minor unit operations are considered equal to one major unit operation. The determined number of operators were then multiplied by 4.5 shifts to cover a 24-hour work day. Operators will have a salary of $50,000 per year plus $21,000 for benefits for a total of $71,000 per year [9]. Control operators at VCSU have a salary of $60,000 per year with $25,500 in benefits for a total cost of $85,500 per year [9]. Since the plant addition is sizable, the cost of a new supervisor was included by multiplying the total operating labor cost by 15%. There are 9 major unit operations and 10 minor unit operations. The 10 minor unit operations are equivalent to 3 major operations. For a total of 12 major unit operations, 3 operators per shift will be required.

Table A2. Overview of Major and Minor Unit Operations.

Major Unit Operations	Quantity	Minor Unit Operations	Quantity
Rotary Kilns/ Dryer/Cooler	4	Heat Exchangers	1
Crusher	2	Hoppers	2
Compressor/Motor	2	Filters	3
Rankine Cycle	1	Conveyors	3
		Pumps	1
Total	**9**	**Total**	**10**

$$\text{Total major unit operations} = \text{major unit operations} + \text{ major unit operations equivalent}$$

$$\text{Total major unit operations} = \frac{10 \text{ minor unit operations}}{4} + 9 \text{ major unit operations}$$

$$\text{Total major unit operations} = 12 \text{ (rounded up)}$$

$$\text{Number of Operators} = \frac{11 \text{ major unit operations}}{5} = 3 \text{ (rounded up)}$$

$$3 \text{ operators } \times 4.5 \text{ shifts} = 14 \text{ new operators (rounded up)}$$

$$14 \text{ new operators } \times \$\,57{,}000 \text{ per year} = \$798{,}000 \text{ per year}$$

$$1 \text{ control operator } \times 4.5 \text{ shifts} = 5 \text{ new control operators}$$

$$5 \text{ new control operator } \times \$85{,}5000 \text{ per year} = \$427{,}500 \text{ per year}$$

$$\text{Total operating labor cost with a new supervisor} = (\$798{,}000 + \$427{,}500) \times 1.15$$

$$\text{Total operating labor cost} = \$1{,}409{,}325$$

Depreciation

The MACRS method was used to calculate depreciation. MACRS utilizes both double declining balance (DDB) and the straight line depreciation method. The first half of the project's lifespan is depreciated using DDB, and all remaining years are depreciated using the straight line method.

Double Declining Balance:

$$d_t = (2)\left(\frac{FCI - \sum_i^t d_i}{n}\right) = (2)\left(\frac{15{,}260{,}952 - 0}{18}\right) = \$1{,}695{,}750$$

Where:

d_t	Depreciation for date t
FCI	Fixed Capital Investment
d_i	Depreciation charges to date i
n	Lifespan of the project

Straight Line:

$$d_t = \left(\frac{FCI - d_{n/2}}{n/2}\right) = (2)\left(\frac{15{,}260{,}952 - 10{,}313{,}715}{18}\right) = \$587{,}444$$

$d_{n/2}$ depreciation charges to date n/2

Table A3. MACRS factors for the proposed process based off a 18 year useful life.

Year	MACRS Factor (% Depreciation)
1	11.1%
2	9.9%
3	8.8%
4	7.8%
5	6.9%
6	6.2%
7	5.5%
8	4.9%
9	4.3%
10	3.8%
11	3.8%
12	3.8%
13	3.8%
14	3.8%
15	3.8%
16	3.8%
17	3.8%
18	3.8%

Taxes

(100% - Effective Federal Tax Rate) × State Tax Rate = Effective State Rate

(100% - Effective State Tax Rate) × Federal Tax Rate = Effective Federal Rate

Combining:

$$\text{Effective State Tax Rate} = (100\% - (100\% - \text{Effective State Tax Rate}) \times \text{Federal Tax Rate}) \times \text{State Tax Rate}$$

North Dakota State Tax Rate = 4.31%
Federal Tax Rate = 35%
Effective State Tax Rate = 2.21%
Effective Federal Tax Rate = 34.2%
Blended Tax = Effective State Tax + Effective Federal Tax = 36.4%

APPENDIX B: DETAILED FINANCIAL CALCULATIONS AND RISK ANALYSIS

Table B.1 Breakdown of Operating Costs (thousands of dollars)

Year	Raw Materials	Personnel	O&M	Utilities	Royalties and patent fees	Yearly Total
0	$0	$0	$0	$0	$0	$0
1	$676	$1,635	$872	$1,798	$310	$5,291
2	$676	$1,635	$872	$1,798	$310	$5,291
3	$676	$1,635	$872	$1,798	$310	$5,291
4	$676	$1,635	$872	$1,798	$310	$5,291
5	$676	$1,635	$872	$1,798	$310	$5,291
6	$676	$1,635	$872	$1,798	$310	$5,291
7	$676	$1,635	$872	$1,798	$310	$5,291
8	$676	$1,635	$872	$1,798	$310	$5,291
9	$676	$1,635	$872	$1,798	$310	$5,291
10	$676	$1,635	$872	$1,798	$310	$5,291
11	$676	$1,635	$872	$1,798	$310	$5,291
12	$676	$1,635	$872	$1,798	$310	$5,291
13	$676	$1,635	$872	$1,798	$310	$5,291
14	$676	$1,635	$872	$1,798	$310	$5,291
15	$676	$1,635	$872	$1,798	$310	$5,291
16	$676	$1,635	$872	$1,798	$310	$5,291
17	$676	$1,635	$872	$1,798	$310	$5,291
18	$676	$1,635	$872	$1,798	$310	$5,291
19	$676	$1,635	$872	$1,798	$310	$5,291
20	$676	$1,635	$872	$1,798	$310	$5,291

Table B2. Economic Cash Flow with Net Present Value Calculation for taxable scenario at 4% Hurdle Rate (thousands of dollars)

ECONOMIC CASH FLOW SHEET									
Year	Revenues	Operating Costs	Gross Profit	Depreciation	Taxable Profit	Income Tax	Nontaxable Charges	Net Profit	Present Value @ HR
-1	$ -	$ -	$ -	$ -	$ -	$ -	$ (7,630)	$ (7,630)	$ (7,936)
0	$ -	$ -	$ -	$ -	$ -	$ -	$ (7,630)	$ (7,630)	$ (7,630)
1	$ 9,404	$ (5,291)	$ 4,113	$ (1,696)	$ 2,417	$ (880)	$ -	$ 3,233	$ 3,109
2	$ 9,404	$ (5,291)	$ 4,113	$ (1,507)	$ 2,606	$ (948)	$ -	$ 3,164	$ 2,926
3	$ 9,404	$ (5,291)	$ 4,113	$ (1,340)	$ 2,773	$ (1,009)	$ -	$ 3,104	$ 2,759
4	$ 9,404	$ (5,291)	$ 4,113	$ (1,191)	$ 2,922	$ (1,064)	$ -	$ 3,049	$ 2,607
5	$ 9,404	$ (5,291)	$ 4,113	$ (1,059)	$ 3,054	$ (1,112)	$ -	$ 3,001	$ 2,467
6	$ 9,404	$ (5,291)	$ 4,113	$ (941)	$ 3,172	$ (1,155)	$ -	$ 2,958	$ 2,338
7	$ 9,404	$ (5,291)	$ 4,113	$ (836)	$ 3,277	$ (1,193)	$ -	$ 2,920	$ 2,219
8	$ 9,404	$ (5,291)	$ 4,113	$ (743)	$ 3,369	$ (1,226)	$ -	$ 2,886	$ 2,109
9	$ 9,404	$ (5,291)	$ 4,113	$ (661)	$ 3,452	$ (1,257)	$ -	$ 2,856	$ 2,007
10	$ 9,404	$ (5,291)	$ 4,113	$ (587)	$ 3,525	$ (1,283)	$ -	$ 2,830	$ 1,912
11	$ 9,404	$ (5,291)	$ 4,113	$ (587)	$ 3,525	$ (1,283)	$ -	$ 2,830	$ 1,838
12	$ 9,404	$ (5,291)	$ 4,113	$ (587)	$ 3,525	$ (1,283)	$ -	$ 2,830	$ 1,767
13	$ 9,404	$ (5,291)	$ 4,113	$ (587)	$ 3,525	$ (1,283)	$ -	$ 2,830	$ 1,699
14	$ 9,404	$ (5,291)	$ 4,113	$ (587)	$ 3,525	$ (1,283)	$ -	$ 2,830	$ 1,634
15	$ 9,404	$ (5,291)	$ 4,113	$ (587)	$ 3,525	$ (1,283)	$ -	$ 2,830	$ 1,571
16	$ 9,404	$ (5,291)	$ 4,113	$ (587)	$ 3,525	$ (1,283)	$ -	$ 2,830	$ 1,511
17	$ 9,404	$ (5,291)	$ 4,113	$ (587)	$ 3,525	$ (1,283)	$ -	$ 2,830	$ 1,453
18	$ 9,404	$ (5,291)	$ 4,113	$ (587)	$ 3,525	$ (1,283)	$ -	$ 2,830	$ 1,397
19	$ 9,404	$ (5,291)	$ 4,113	$ -	$ 4,113	$ (1,497)	$ -	$ 2,616	$ 1,242
20	$ 9,404	$ (5,291)	$ 4,113	$ -	$ 4,113	$ (1,497)	$ 1,387	$ 2,616	$ 1,194
					HR =	4.00%		NPV@HR =	$ 24,191
								DCFROR =	18%

Table B3. Economic Cash Flow with Net Present Value Calculation for taxable scenario at 12% Hurdle Rate (thousands of dollars)

ECONOMIC CASH FLOW SHEET									
Year	Revenues	Operating Costs	Gross Profit	Depreciation	Taxable Profit	Income Tax	Nontaxable Charges	Net Profit	Present Value @ HR
-1	$ -	$ -	$ -	$ -	$ -	$ -	$ (7,630)	$ (7,630)	$ (8,546)
0	$ -	$ -	$ -	$ -	$ -	$ -	$ (7,630)	$ (7,630)	$ (7,630)
1	$ 9,404	$ (5,291)	$ 4,113	$ (1,696)	$ 2,417	$ (880)	$ -	$ 3,233	$ 2,887
2	$ 9,404	$ (5,291)	$ 4,113	$ (1,507)	$ 2,606	$ (948)	$ -	$ 3,164	$ 2,523
3	$ 9,404	$ (5,291)	$ 4,113	$ (1,340)	$ 2,773	$ (1,009)	$ -	$ 3,104	$ 2,209
4	$ 9,404	$ (5,291)	$ 4,113	$ (1,191)	$ 2,922	$ (1,064)	$ -	$ 3,049	$ 1,938
5	$ 9,404	$ (5,291)	$ 4,113	$ (1,059)	$ 3,054	$ (1,112)	$ -	$ 3,001	$ 1,703
6	$ 9,404	$ (5,291)	$ 4,113	$ (941)	$ 3,172	$ (1,155)	$ -	$ 2,958	$ 1,499
7	$ 9,404	$ (5,291)	$ 4,113	$ (836)	$ 3,277	$ (1,193)	$ -	$ 2,920	$ 1,321
8	$ 9,404	$ (5,291)	$ 4,113	$ (743)	$ 3,369	$ (1,226)	$ -	$ 2,886	$ 1,166
9	$ 9,404	$ (5,291)	$ 4,113	$ (661)	$ 3,452	$ (1,257)	$ -	$ 2,856	$ 1,030
10	$ 9,404	$ (5,291)	$ 4,113	$ (587)	$ 3,525	$ (1,283)	$ -	$ 2,830	$ 911
11	$ 9,404	$ (5,291)	$ 4,113	$ (587)	$ 3,525	$ (1,283)	$ -	$ 2,830	$ 813
12	$ 9,404	$ (5,291)	$ 4,113	$ (587)	$ 3,525	$ (1,283)	$ -	$ 2,830	$ 726
13	$ 9,404	$ (5,291)	$ 4,113	$ (587)	$ 3,525	$ (1,283)	$ -	$ 2,830	$ 648
14	$ 9,404	$ (5,291)	$ 4,113	$ (587)	$ 3,525	$ (1,283)	$ -	$ 2,830	$ 579
15	$ 9,404	$ (5,291)	$ 4,113	$ (587)	$ 3,525	$ (1,283)	$ -	$ 2,830	$ 517
16	$ 9,404	$ (5,291)	$ 4,113	$ (587)	$ 3,525	$ (1,283)	$ -	$ 2,830	$ 462
17	$ 9,404	$ (5,291)	$ 4,113	$ (587)	$ 3,525	$ (1,283)	$ -	$ 2,830	$ 412
18	$ 9,404	$ (5,291)	$ 4,113	$ (587)	$ 3,525	$ (1,283)	$ -	$ 2,830	$ 368
19	$ 9,404	$ (5,291)	$ 4,113	$ -	$ 4,113	$ (1,497)	$ -	$ 2,616	$ 304
20	$ 9,404	$ (5,291)	$ 4,113	$ -	$ 4,113	$ (1,497)	$ 1,387	$ 2,616	$ 271
					HR =	12.00%		NPV@HR =	$ 6,110
								DCFROR =	18%

Table B4. Economic Cash Flow with Net Present Value Calculation for non-taxable scenario at 4% Hurdle Rate (thousands of dollars)

ECONOMIC CASH FLOW SHEET WITH NO TAXES **(Thousands of dollars)**

Year	Revenues	Operating Costs	Gross Profit	Nontaxable Charges	Net Profit	Present Value @ HR
-1	$ -	$ -	$ -	$ (7,630)	$ (7,630)	$ (8,546)
0	$ -	$ -	$ -	$ (7,630)	$ (7,630)	$ (7,630)
1	$ 9,404	$ (5,291)	$ 4,113	$ -	$ 4,113	$ 3,955
2	$ 9,404	$ (5,291)	$ 4,113	$ -	$ 4,113	$ 3,803
3	$ 9,404	$ (5,291)	$ 4,113	$ -	$ 4,113	$ 3,656
4	$ 9,404	$ (5,291)	$ 4,113	$ -	$ 4,113	$ 3,516
5	$ 9,404	$ (5,291)	$ 4,113	$ -	$ 4,113	$ 3,381
6	$ 9,404	$ (5,291)	$ 4,113	$ -	$ 4,113	$ 3,251
7	$ 9,404	$ (5,291)	$ 4,113	$ -	$ 4,113	$ 3,125
8	$ 9,404	$ (5,291)	$ 4,113	$ -	$ 4,113	$ 3,005
9	$ 9,404	$ (5,291)	$ 4,113	$ -	$ 4,113	$ 2,890
10	$ 9,404	$ (5,291)	$ 4,113	$ -	$ 4,113	$ 2,779
11	$ 9,404	$ (5,291)	$ 4,113	$ -	$ 4,113	$ 2,672
12	$ 9,404	$ (5,291)	$ 4,113	$ -	$ 4,113	$ 2,569
13	$ 9,404	$ (5,291)	$ 4,113	$ -	$ 4,113	$ 2,470
14	$ 9,404	$ (5,291)	$ 4,113	$ -	$ 4,113	$ 2,375
15	$ 9,404	$ (5,291)	$ 4,113	$ -	$ 4,113	$ 2,284
16	$ 9,404	$ (5,291)	$ 4,113	$ -	$ 4,113	$ 2,196
17	$ 9,404	$ (5,291)	$ 4,113	$ -	$ 4,113	$ 2,111
18	$ 9,404	$ (5,291)	$ 4,113	$ -	$ 4,113	$ 2,030
19	$ 9,404	$ (5,291)	$ 4,113	$ -	$ 4,113	$ 1,952
20	$ 9,404	$ (5,291)	$ 4,113	$ -	$ 4,113	$ 1,877
		HR =	4.00%		NPV@HR =	$ 39,719
					DCFROR =	21%

Table B4. Economic Cash Flow with Net Present Value Calculation for non-taxable scenario at 12% Hurdle Rate

ECONOMIC CASH FLOW SHEET WITH NO TAXES **(Thousands of dollars)**

Year	Revenues	Operating Costs	Gross Profit	Nontaxable Charges	Net Profit	Present Value @ HR
-1	$ -	$ -	$ -	$ (7,630)	$ (7,630)	$ (8,546)
0	$ -	$ -	$ -	$ (7,630)	$ (7,630)	$ (7,630)
1	$ 9,404	$ (5,291)	$ 4,113	$ -	$ 4,113	$ 3,672
2	$ 9,404	$ (5,291)	$ 4,113	$ -	$ 4,113	$ 3,279
3	$ 9,404	$ (5,291)	$ 4,113	$ -	$ 4,113	$ 2,927
4	$ 9,404	$ (5,291)	$ 4,113	$ -	$ 4,113	$ 2,614
5	$ 9,404	$ (5,291)	$ 4,113	$ -	$ 4,113	$ 2,334
6	$ 9,404	$ (5,291)	$ 4,113	$ -	$ 4,113	$ 2,084
7	$ 9,404	$ (5,291)	$ 4,113	$ -	$ 4,113	$ 1,860
8	$ 9,404	$ (5,291)	$ 4,113	$ -	$ 4,113	$ 1,661
9	$ 9,404	$ (5,291)	$ 4,113	$ -	$ 4,113	$ 1,483
10	$ 9,404	$ (5,291)	$ 4,113	$ -	$ 4,113	$ 1,324
11	$ 9,404	$ (5,291)	$ 4,113	$ -	$ 4,113	$ 1,182
12	$ 9,404	$ (5,291)	$ 4,113	$ -	$ 4,113	$ 1,056
13	$ 9,404	$ (5,291)	$ 4,113	$ -	$ 4,113	$ 943
14	$ 9,404	$ (5,291)	$ 4,113	$ -	$ 4,113	$ 842
15	$ 9,404	$ (5,291)	$ 4,113	$ -	$ 4,113	$ 751
16	$ 9,404	$ (5,291)	$ 4,113	$ -	$ 4,113	$ 671
17	$ 9,404	$ (5,291)	$ 4,113	$ -	$ 4,113	$ 599
18	$ 9,404	$ (5,291)	$ 4,113	$ -	$ 4,113	$ 535
19	$ 9,404	$ (5,291)	$ 4,113	$ -	$ 4,113	$ 478
20	$ 9,404	$ (5,291)	$ 4,113	$ -	$ 4,113	$ 426
		HR =	12.00%		NPV@HR =	$ 14,545
					DCFROR =	21%

APPENDIX C: ASPEN SIMULATIONS

The technical analysis of the proposed concept was performed by performing mass and energy balance for various configuration. The results obtained from technical analysis was used to perform preliminary economic analysis. Two configurations of integrating activated carbon plant with the steam plant were studied in depth. The first configuration involved running the activated carbon plant year around at full capacity. The schematics of the year round operation of activated carbon plant is shown in Figure C1. The other alternative shown in Figure C2 is to use char slipstream to continuously match the steam demand by adjusting the carbon plant operation.

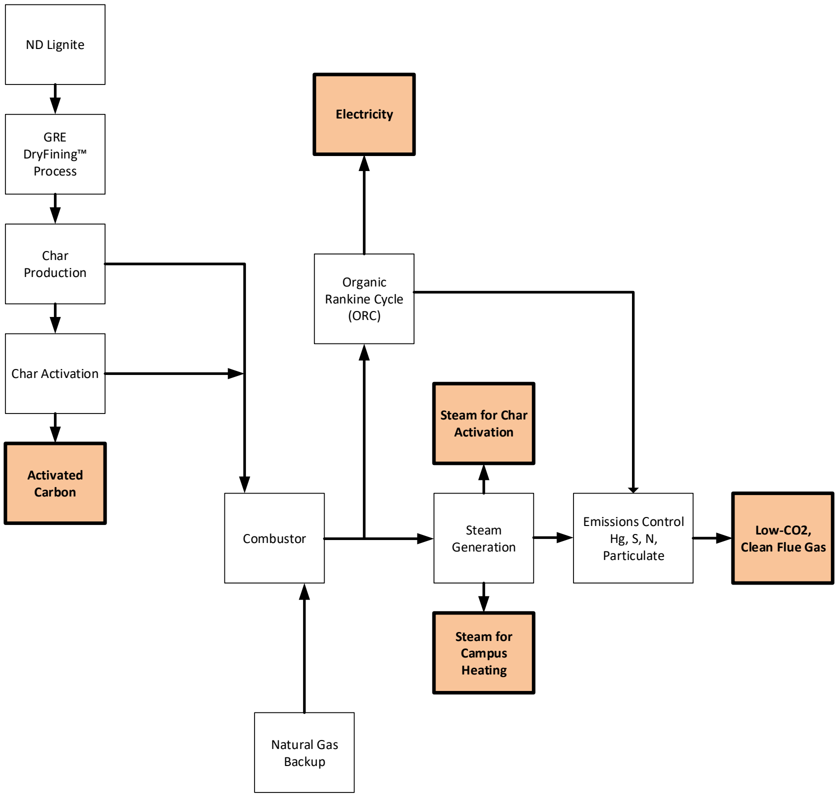


Figure C1. Schematic of the activated carbon plant with electricity generation.

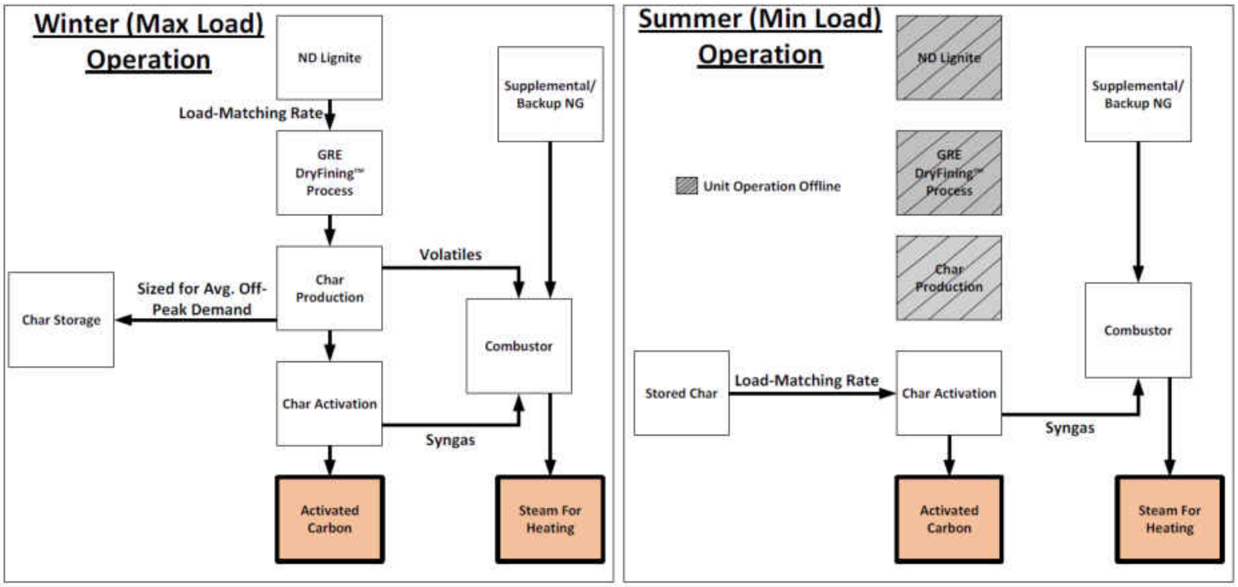


Figure C2. Schematic of the char slipstream option for seasonal variation of plant capacity.

The block diagram of the activation carbon plant producing electricity is presented in Figure C3. The results of technical analysis using Aspen Plus are listed in Table C1. Technical analysis for several other configuration of the activated carbon plant and ways to match steam demand with carbon production were also performed. The results of these analysis are available upon request.

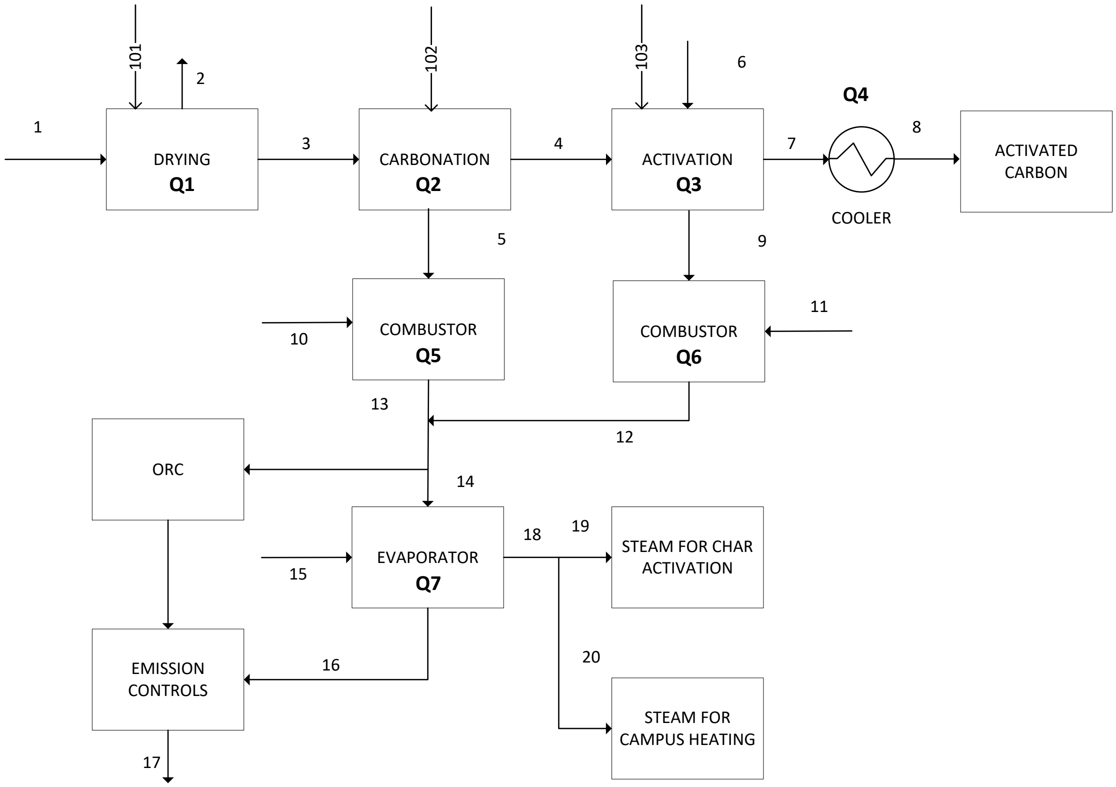


Figure C3. Block Flow Diagram for the combined activated carbon plant with heating plant.

Table C1. Process stream results using Aspen Plus.

STREAM	**1**	**101**	**3**	**2**	**102**	**4**	**5**	**6**	**103**	**9**	**7**	**8**	**10**
Mass Flow lb/hr													
O_2	0	33	0	33	42	0	42	0	31	31	0	0	2879
CO	0	0	0	0	0	0	1104	0	0	1086	0	0	0
H_2	0	0	0	0	0	0	139	0	0	77	0	0	0
CO_2	0	221	0	221	283	0	281	0	210	211	0	0	0
H_2O	0	181	0	1492	232	0	230	713	172	189	0	0	0
CH_4	0	0	0	0	0	0	0	0	0	0	0	0	0
N_2	0	1166	0	1165	1493	0	1485	0	1107	1112	0	0	9483
H_2S	0	0	0	0	0	0	27	0	0	0	0	0	0
C_2H_6	0	0	0	0	0	0	240	0	0	0	0	0	0
HCN	0	0	0	0	0	0	30	0	0	0	0	0	0
COAL	5084	0	0	0	0	0	0	0	0	0	0	0	0
DRY-COAL	0	0	3772	0	0	0	0	0	0	0	0	0	0
CHAR	0	0	0	0	0	2236	0	0	0	0	0	0	0
ACT-CARBON	0	0	0	0	0	0	0	0	0	0	1769	1769	0
Total Flow lb/hr	**5084**	**1600**	**3772**	**2912**	**2050**	**2236**	**3578**	**713**	**1520**	**2707**	**1769**	**1769**	**12362**
Mass Fraction													
O_2	0.00	0.02	0.00	0.01	0.02	0.00	0.01	0.00	0.02	0.01	0.00	0.00	0.23
CO	0.00	0.00	0.00	0.00	0.00	0.00	0.31	0.00	0.00	0.40	0.00	0.00	0.00
H_2	0.00	0.00	0.00	0.00	0.00	0.00	0.04	0.00	0.00	0.03	0.00	0.00	0.00
CO_2	0.00	0.14	0.00	0.08	0.14	0.00	0.08	0.00	0.14	0.08	0.00	0.00	0.00
H_2O	0.00	0.11	0.00	0.51	0.11	0.00	0.06	1.00	0.11	0.07	0.00	0.00	0.00
CH_4	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
N_2	0.00	0.73	0.00	0.40	0.73	0.00	0.41	0.00	0.73	0.41	0.00	0.00	0.77
H_2S	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00
C_2H_6	0.00	0.00	0.00	0.00	0.00	0.00	0.07	0.00	0.00	0.00	0.00	0.00	0.00
HCN	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00
COAL	1.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
DRY-COAL	0.00	0.00	1.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CHAR	0.00	0.00	0.00	0.00	0.00	1.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
ACT-CARBON	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.00	1.00	0.00
Total	**1**	**1**	**1**	**1**	**1**	**1**	**1**	**1**	**1**	**1**	**1**	**1**	**1**
Temperature (F)	77	3620	230	230	3620	1112	1112	345	3620	1652	1652	200	250
Pressure (psia)	14.7	15	14.7	14.7	15	14.7	14.7	125	15	14.7	14.7	14.7	14.7
Vapor Fraction	0	1	0	1	1	0	1	1	1	1	0	0	1

APPENDIX E

STREAM	**13**	**11**	**12**	**14**	**16**	**15**	**18**	**19**	**20**		**Heat Duty (MMBtu/hr)**
Mass Flow lb/hr										Q1	1.65
O_2	447	1357	155	601	601	0	0	0	0	Q2	1.6
CO	0	0	0	0	0	0	0	0	0	Q3	2.91
H_2	0	0	0	0	0	0	0	0	0	Q4	-8.41
CO_2	2830	0	1917	4747	4747	0	0	0	0	Q5	0
H_2O	1640	0	880	2521	2521	21000	21000	713	20287	Q6	0
CH_4	0	0	0	0	0	0	0	0	0	Q7	24.9
N_2	10967	4470	5582	16549	16549	0	0	0	0		
H_2S	27	0	0	27	27	0	0	0	0		
C_2H_6	0	0	0	0	0	0	0	0	0		
HCN	30	0	0	30	30	0	0	0	0		
COAL	0	0	0	0	0	0	0	0	0		
DRY-COAL	0	0	0	0	0	0	0	0	0		
CHAR	0	0	0	0	0	0	0	0	0		
ACT-CARBON	0	0	0	0	0	0	0	0	0		
Total Flow lb/hr	**15941**	**5827**	**8534**	**24475**	**24475**	**21000**	**21000**	**713**	**20287**		
Mass Fraction											
O_2	0.03	0.23	0.02	0.02	0.02	0.00	0.00	0.00	0.00		
CO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00		
H_2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00		
CO_2	0.18	0.00	0.22	0.19	0.19	0.00	0.00	0.00	0.00		
H_2O	0.10	0.00	0.10	0.10	0.10	1.00	1.00	1.00	1.00		
CH_4	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00		
N_2	0.69	0.77	0.65	0.68	0.68	0.00	0.00	0.00	0.00		
H_2S	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00		
C_2H_6	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00		
HCN	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00		
COAL	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00		
DRY-COAL	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00		
CHAR	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00		
ACT-CARBON	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00		
Total	**1**	**1**	**1**	**1**	**1**	**1**	**1**	**1**	**1**		
Temperature (F)	3745	250	4123	3877	500	128	502	502	502		
Pressure (psia)	14.7	14.7	14.7	14.7	14.7	125	125	125	125		
Vapor Fraction	1	1	1	1	1	0	1	1	1		

The key results obtained from the technical analysis using Aspen Plus are listed in Table C1. This table compares the raw material consumption, steam generated, electricity generated and throughput of activated carbon. Based on the information in table, operating the activated carbon plant year round with electricity generation has the highest potential of revenue generation.

Table C2. Comparison of key technical parameters for the two configurations

	Year round operation of AC Plant	**Slipstream Operation**
Coal Feed rate summer, lb/hr	5,084	0
Coal Feed rate winter, lb/hr		6,104
Activated Carbon summer, lb/hr	1,769	1,062
Activated Carbon winter, lb/hr		1,062
Total AC produced annually, lb	12,383,000	7,434,000
Steam generated winter, lb/hr	21,000	21,000
Steam generated summer, lb/hr	21,000	4,200
University steam demand winter, lb/hr	12,000	12,000
University steam demand summer, lb/hr	0	0
Excess steam winter, lb/hr	8282	8140
Excess steam summer, lb/hr	20282	3354
Average ORC power summer, kW	810	0
Average ORC power winter, kW	325	0
Total power produced annually, kWh	3,972,500	0

Table C3 shows the preliminary economic results for the two configurations. The results indicate that year round operation of activate carbon with electricity generation is the more economic option. Operating the activated carbon produces higher revenue compared to the slipstream operation ($5.2 million vs. $1.9 million). The payback period of slipstream operation is approximately 6 years, twice the payback period year round operation scenario.

Table C3. Preliminary economic results

	Year round Operation of AC Plant	**Slipstream Operation**
Capital Costs		
Activated Carbon Plant, $	7,473,248	7,473,248
Boilers, $	8,900,000	8,900,000
Storage Silos, $	0	1,000,000
ORC System, $	3,500,000	0
Quench system, $	0	0
Total Capital Cost, $	19,873,248	17,373,248
Contingency and Fee, $	3,577,185	3,127,185
Total Module Cost, $	23,450,432	20,500,432
Auxiliary Facilities, $	7,035,130	6,150,130
Fixed Capital Investment, $	30,485,562	26,650,562
Working Capital, $	4,572,834	3,997,584
Total Capital Investment, $	35,058,396	30,648,146
Total Capital Investment without Boiler, $	19,357,906	14,947,656
Operating Costs		
Coal, $	676,172	405,916
Boiler Feed Water, $	46,232	46,232
Natural gas, $	78,400	72,800
Waste Disposal, $	245,315	245,315
Personnel, $	1,267,425	1,267,425
O&M Cost, $	1,829,134	1,599,034
Royalties & Patent Fees, $	619,150	371,700
ORC O&M, $	39,725	0
Quench Cooling Water, $	0	14500
Calcium hydroxide, $	24,912	14,955
Annual Total, $	4,826,464	4,037,876
Revenues		
Activated Carbon, $	9,039,590	5,426,820
Electricity, $	198,625	0
Annual Total, $	9,238,215	5,426,820
Net Annual Revenue, $	5,296,018	1,955,857
Payback		
Payback with boiler, years	7.5	18.8
Payback without boiler, years	3.5	6.1

APPENDIX D: VIABILITY OF ND PRODUCED ACTIVATED CARBON

The activated carbon derived from ND Lignite show superior properties compared to the existing commercial products for various applications. The results shown here are part of the study conducted by EERC to display the viability of producing activated carbon from ND Lignite [13]. The EERC performed both bench-scale and pilot scale mercury capture tests using the ND Lignite derived activated carbon under various optimization process conditions. As detailed below, the activated carbons produced from ND lignite have greater surface area, allowing for greater capture of contaminants in comparison with competitor carbons on the market.

The iodine number for the activated carbon is a critical parameter that is used as a measure of the surface area of the product. Figure D1 compares the iodine number for ND Lignite derived activation carbon to other commercially available products. The activated carbon produced from Center Lignite show surface area in the range of 600 to 800 mg I_2/g on a pilot scale system. The product quality was superior to DARCO FGD, which has an iodine number in the range of 500 to 600 mg I2/g product, and to Rheinbraun's HOK activated coke product, which has an iodine number of around 275 mg I_2/g.

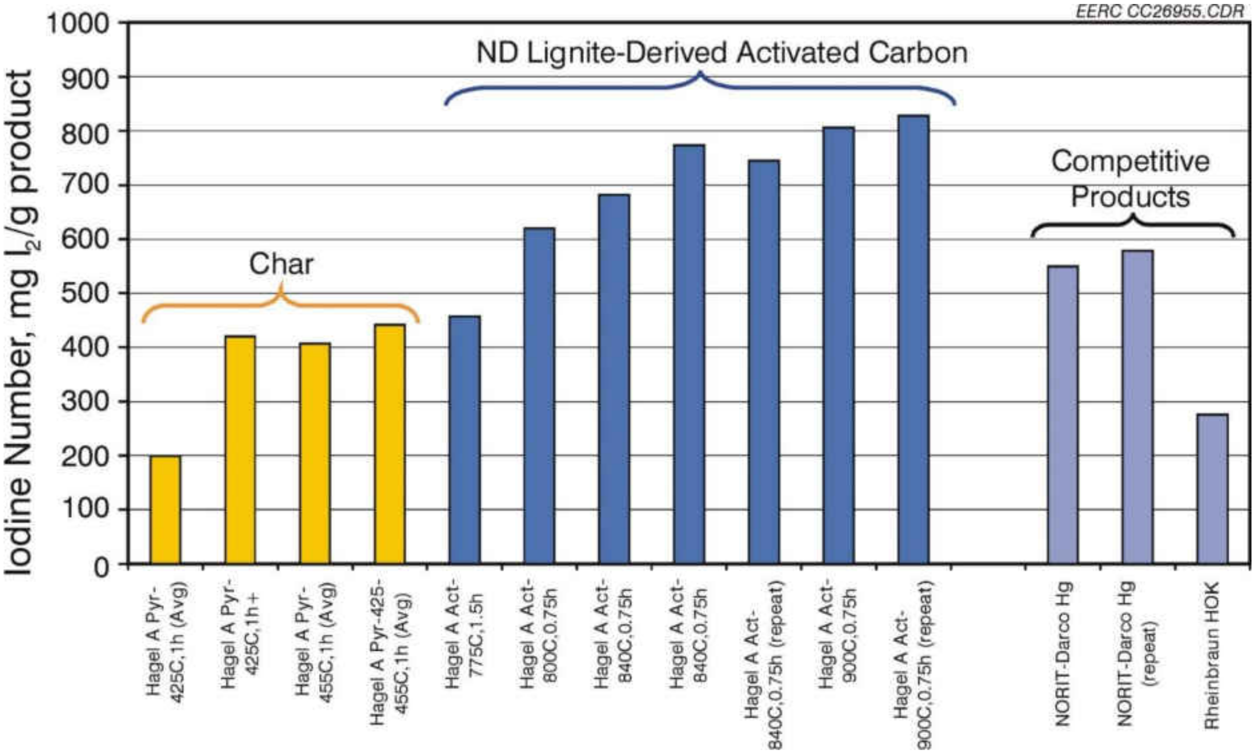


Figure D1. Comparison of ND lignite derived activated carbon to commercially available activated carbons

Figure D2 and D3 shows the mercury capture performance on pilot-scale using activated carbon under various optimization process conditions. The results indicated that the activated carbon produced from North Dakota Lignite coal is capable of removing mercury from flue gas. The tests conducted during this study showed that activated carbon with the greatest iodine number was superior to commercial DARCO FGD for mercury capture.

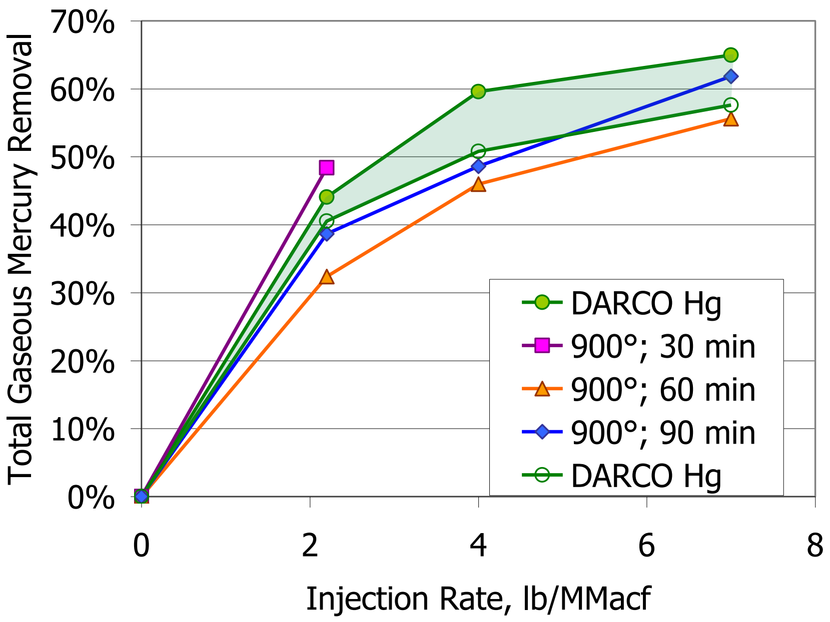


Figure D2. Performance comparison of ND lignite-derived activated carbons to commercially available carbons for mercury capture.

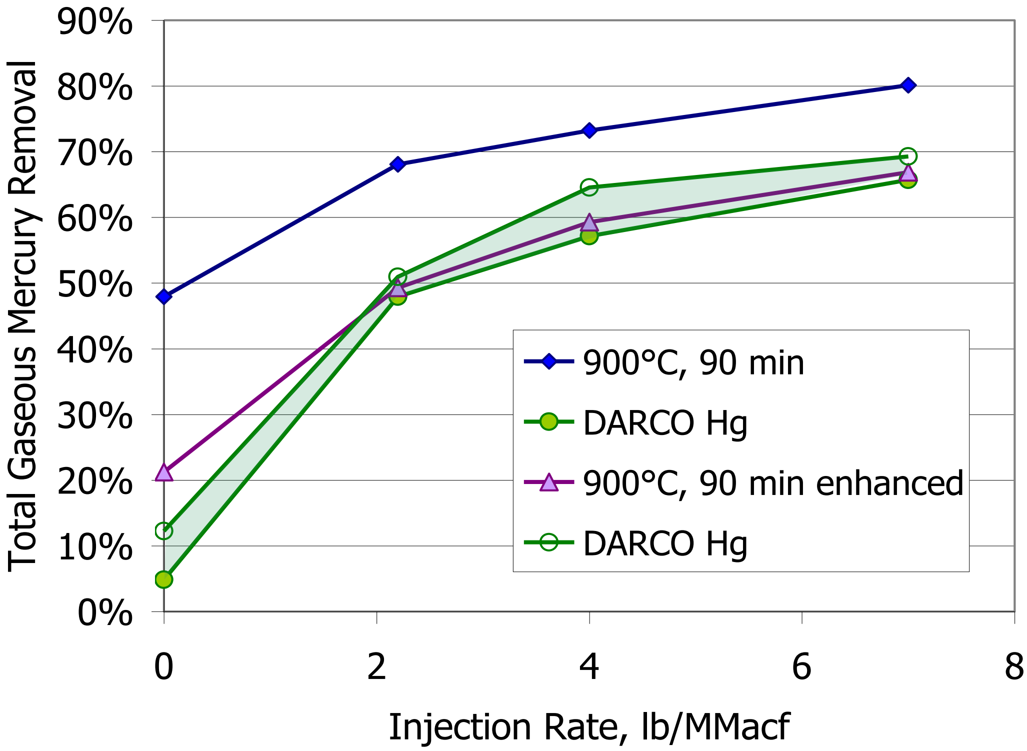


Figure D3. Performance of ND lignite-derived activated carbon showing significantly higher mercury removal than commercially available carbons.